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WASTE WATER TREATMENT WITH MAGNETIC FLUIDS

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ABSTRACT

Industrialization brought with it a huge amount of products that made life easier. The use of oil had a huge increase, due to the many possibilities it has. Production of high variety of plastics, solvents, specific chemicals and fuel uses like gasoline or diesel. An increase in the use of oil, brings also an increase in water consumption. Water is used in many stages during the oil extraction and treating processes. As expected, water after every process has a large variety of pollutants and therefore, treatment is required.

The scope of the treatment is of course to achieve low concentrations of pollutants, in accordance to the limits required by the law. The limits change according to the place. In Italy the limits are imposed by the D.Lgs. 152/06, the "Testo Unico Ambientale", a close translation would be: Unique environmental text. The purpose of these kind of regulations are associated to the preservation of the environment, the wild life, etc.

The treating procedures are several nowadays, some examples: Flotation, biological treatments, coagulation, membrane separation, and several others.

In this work, a new possibility is explored based on the use of magnetic fluids. These particular fluids are composed of nanoparticles with strong lipophilic behaviour. By exploiting the affinity between these particles and the hydrocarbons it is expected to provide a method of simple method for waste treatment and management.

Moreover, the improvement of the lipophilic characteristics of the nanoparticles is desired. By bonding a molecule with a lipophilic behaviour to the external surface of the nanoparticle, it is expected an increase in the removal efficiency. The layer composed by these lipophilic molecules is known as the coating. Different type of chemicals to formulate this coating were investigated in order to provide the most suitable nanoparticles for each waste water category.

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1 INTRODUCTION

Water is a fundamental substance for life on earth. Without water, life could not have developed nor it would be able to sustain itself. Humans not only use water for drinking purposes. Due to its characteristics it is a very versatile compound, widely used in many fields. Industrial water uses include water used for purposes such as fabricating, processing, washing, diluting, cooling, or transporting a product; incorporating water into a product; or for sanitation needs within the manufacturing facility. Some industries that use large amounts of water produce commodities such as food, paper, chemicals, refined petroleum, or primary metals.

Regarding the water which is designated for human consumption, it has to fulfill certain requirements. Most people living in the EU enjoy very good access to high quality drinking water, especially compared to some other regions in the world. This is the result of a long tradition of drinking water management in many European Member States, but is also in large measure thanks to European environmental legislation and EU funding. Since the 1980s, the EU has applied rules that require stringent water safety checks. This means that urban waste water is collected and treated, industrial emissions are safely managed, the use of chemicals is approved under strict conditions and a holistic approach is taken to managing water bodies across borders.

The initiative “Right2Water” was submitted to the European Commission in December 2013, and urged in particular that “EU institutions and Member States must be obliged to ensure that all inhabitants enjoy the right to water and sanitation” and that “the EU increase its efforts to achieve universal access to water and sanitation”. In its response, the Commission invited Member States to do everything they can to ensure everyone has

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access to a minimum water supply. This is fully in line with the Agenda 2030, in particular Sustainable Development Goal 6 and the associated target to “achieve universal and equitable access to safe and affordable drinking water for all” adopted by the United Nations in 2015.

The revision is also part of the plan to transition to a circular economy. Managing drinking water in a resource-efficient and sustainable manner, thereby helping to reduce energy use, unnecessary water loss and also helping to reduce the number of plastic bottles people use by improving confidence in tap water.

According to Eurostat (the statistical office of the European Union), Industry is one of the main water users in Europe, accounting for about 40 % of total water abstractions. Water is used in production processes (for example for cooling purposes, for cleaning/washing as well as for employees’ use) and is either provided by a public supplier or self-supplied. Furthermore, the industrial sector is a major water polluter, as only up to 60 % (value based on data from eight countries) of industrial wastewater receives treatment before being disposed of into the environment.

The data collected on water abstractions belong to four main industrial sectors: mining and quarrying, manufacturing, production of electricity, and construction and other industrial activities. The present data cover the period 2000-11.

In most countries, the main water-using industry is the “Manufacture of refined petroleum products, chemicals and chemical products”.

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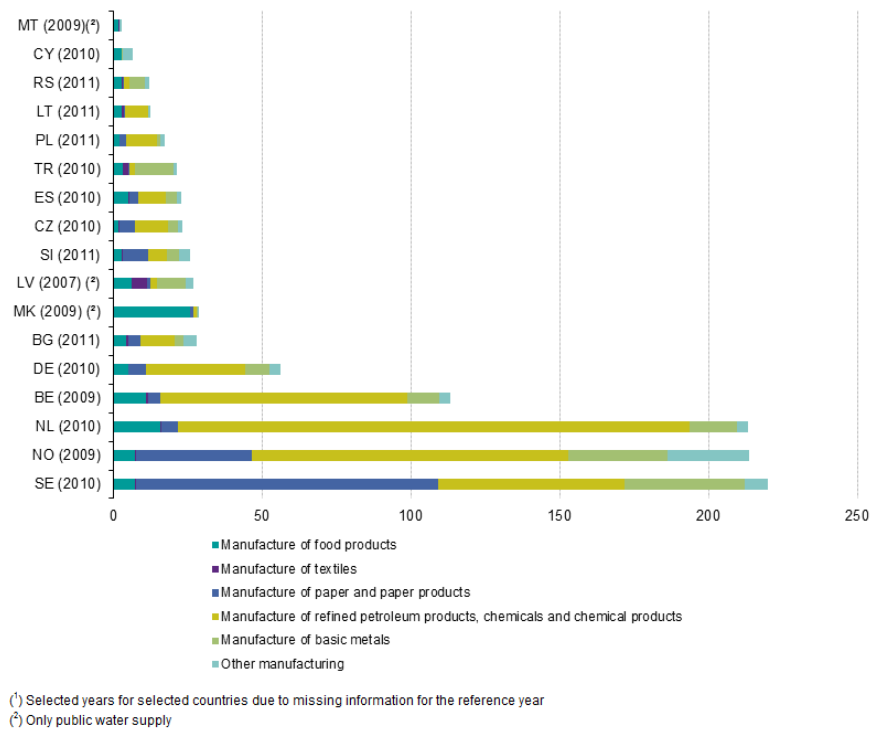


Figure 1.1: Water use in the manufacturing industry by activity, 2011 (m^3 per inhabitant).

Regarding the water involved in the oil and gas industry. The production continues to increase as exploration and production of unconventional supplies, such as gas and oil shale resources, become more prominent. Certain oil and gas recovery techniques, such as hydraulic fracturing, require large amounts of water to stimulate subsurface formations for petroleum production. Conversely, oil and gas wells also produce a significant amount of water after well development. Water that naturally exists in subsurface formations and is brought to the surface with hydrocarbon resources is termed “produced water.” Produced water is considered the largest by-product of oil and gas generation and is generally managed as a waste product (Figure 1.3). Regulatory requirements for release or disposal of water from the oil and gas industry commonly dictate water management options. The well development process, particularly for unconventional gas shale wells, results in water consumption in the geologic formation during the fracturing process.

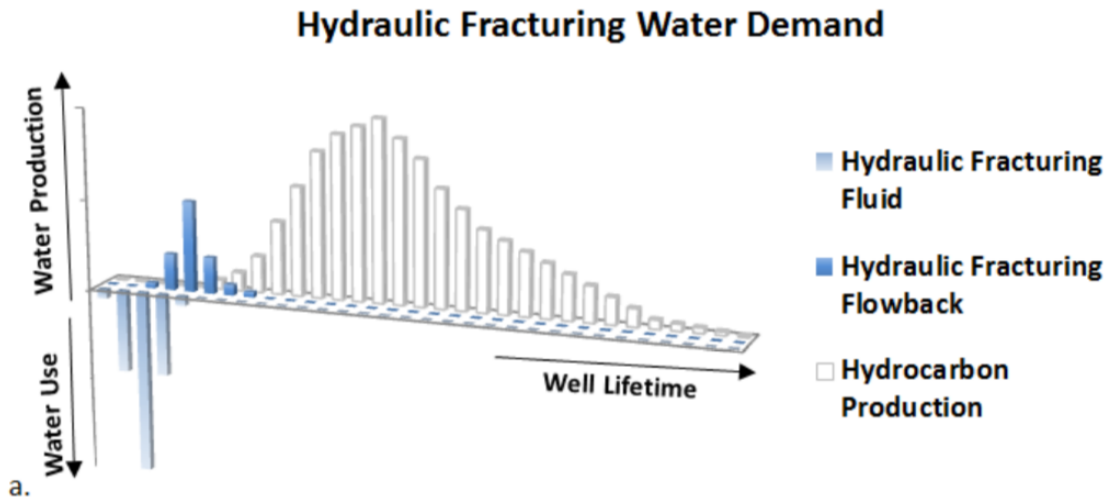


Figure 1.2: Hydraulic fracturing water demand

For the preparation of the well, first the hole is drilled in the surface of the earth in a vertical way. The drilling process is performed in stages, first drilling itself and then partially filling the hole in order to make the wall of a tube made of concrete that avoids the flow of hydrocarbons outside the hole. Once the desired deepness is reached (obtained by geological study of the field), generally between 2,000 m to 6,000 m (greatly below natural groundwater reservoirs levels), there is the possibility to continue the drilling in an horizontal way, by doing so, the efficiency of one well will be greatly improved with respect to a vertical configuration. The next stage is the well completion, perforations are made in the concrete wall with a special tool called perforating gun, connecting the well with the rock containing the oil and gas.

Pressurized water is injected at high pressure in order to fracture the rock and create paths through which the oil and gas can flow. The water contains sand, that holds the fractures open, together with other components. Hydraulic fracturing fluid consists of a mixture of water, sand, and fracturing chemicals (generally in the order of 1% of the total mixture), is injected into the formation during well development and typical return to the surface. This returning water, is called "flowback water", can range from 15 to 80 percent of injected volumes depending on the formation. Water is also consumed through management practices that dispose of flowback water in deep subsurface formations. The quantity of

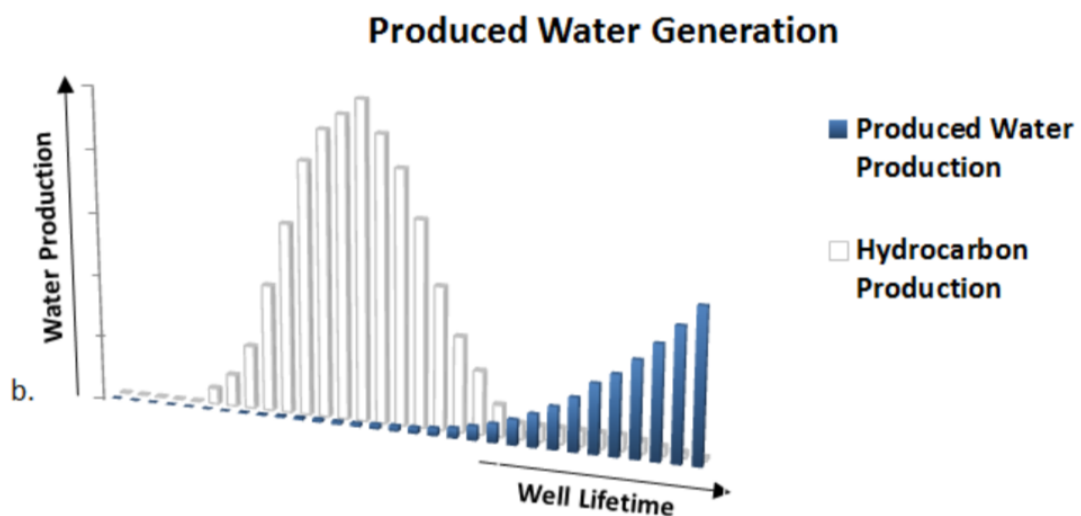
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water required is very variable, since it depends on the characteristics of the formation to be stimulated, the kind of well (horizontal or vertical) and the number of perforation stages. Nowadays, the horizontal configuration is more common, with a very large length, being able to reach 3 km in the horizontal section, with 30 to 40 perforation stages. The distance between stages ranges from 75 to 100 meters.

Since horizontal wells cover a larger area, the productivity associated is higher than single vertical wells.

Regarding the water consumption, as a general rule it is expected to use between 1000 m³ to 1200 m³ per stage. The minimum being 400 m³. Being said this, for a well with 3 km in horizontal length and 40 stages, the total expected amount of water ranges from 40,000 m³ to 48,000 m³ (an Olympic pool has a volume of 2,500 m³).

Oil and gas wells also produce a significant amount of water after the well is developed and during production. This water already introduced before as “produced water”, is the largest by-product of oil and gas generation. Produced water exists naturally in subsurface formations with hydrocarbon resources. It is brought to the surface as a byproduct during oil and gas production. Produced water is generally managed as a waste product, with most of the water disposed of through injection or evaporation. Transporting water and disposing through deep injections wells can be costly. Furthermore, in certain areas adequate disposal formations are not available for deep well injection.



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Figure 1.3: Produced water generation

Produced water cannot be simply thrown in a lake or a river. It needs to be treated in order to meet strict specifications. In other words, this by-product requires processes to make it innocuous, representing a cost to the industry in terms of purification processes.

Hydraulic fracturing requires using a fluid to apply pressure to expand natural fractures in the hydrocarbon formation, allowing oil or gas to be produced economically. Fracturing may be accomplished using a number of liquid carriers, including water or liquefied gases, such as nitrogen or carbon dioxide. Another possibility is mixing water and polymers, creating gels with higher viscosities.

The aim of this project is to reduce the pollution found in water. Focusing in the organic pollutants. As the energy requirements in the world increase, the oil demand and production increases year after year as seen in figure 1.4. Due to the oil processes of extraction and commercialization, the water requirement increases together with the oil requirement and consequently the wastewater volume (the produced water) increases.

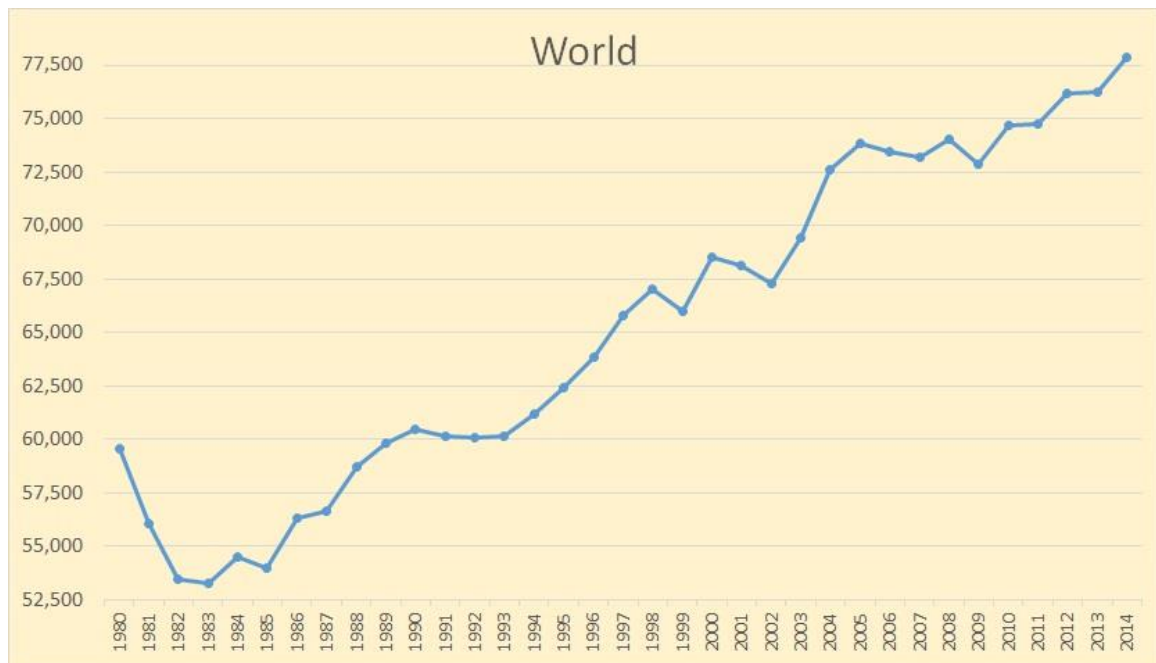


Figure 1.4: World yearly production in thousands of barrels per day.

In the graph shown above, the yearly production of oil is exhibited. Being the produced water the main by-product of oil extraction, the volumes produced are expected to be increasing as well. This stream has to be treated in order to meet the specifications dictated by the law.

There are many different parameters that indicate the pollution level in the water. The Environmental Protection Agency (EPA) provides a large list of parameters with the respective measurement methods. The list includes the regulation for several components that can be dissolved in water, such as salts, fluoride content, different metal ions contents, but also the pH and the temperature.

In this work, the Chemical Oxygen Demand (COD) was selected as the parameter of water pollution. This parameter is commonly used in industry together with the Biochemical Oxygen Demand (BOD). However, the COD measurement presents the main advantage that takes 2 hours to get the results, compared to the 5 days required for the BOC.

In this chapter, the theory aspects of these parameters will be explained.

1.1 Water purity parameters

After water is used in industrial processes, the content of different pollutants is such that direct discharge is prohibited. Treating processes must be implemented before the discharge. The limits are imposed by the jurisdiction in the specific place and also in the way the water is going to be discharged: river, ground, etc. The corresponding laws, fix the maximum allowable limits for a certain stream. Limits are associated to physical and chemical parameters.

A study of these different parameters is provided. Waste water can be characterized by means of the quantification of those parameters. Those can be divided in three different characteristics:

- Chemical parameters: those that include the concentration of different species and also water hardness.

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- Physical parameters: comprises temperature, amount of solids present in the solution, turbidity, odor, etc.
- Microbiological parameters: comprises the quantity and concentration of microorganisms.

The chemical parameters are widely used as they measure the concentration of particular species that may have a big impact in the environment. Many species can be considered, ranging from the most common ions (measurement of pH or ions normally found in tap water as Na^+ , F^- , Cl^- , etc.) to more complex species. The last ones can be subdivided into two main categories: Organics and inorganics.

Organic compounds may be present from different origins. There are those coming from the nature, decomposition of organic matter in lakes or rivers for example, and those coming from the use in industry, such as surfactants, organic solvents, additives, etc.

As the aim of this work is to remove organic compounds, parameters that allow the quantification of these kind of molecules are required. In general, the quantification of organic components is done with three parameters:

- Biochemical oxygen demand or BOC: the quantity of oxygen required to biologically oxidize the organic species in the sample.
- Chemical oxygen demand or COD: the quantity of oxygen required for complete oxidation of all the organic and inorganic components present in the sample.
- Total organic carbon or TOC: the total quantity of organic substances in the sample.

1.1.1 Biochemical oxygen demand

Measurement of BOD has long been the basic mean for determining the degree of water pollution. It is the most important measurement made in the operation of a sewage treatment plant. By comparing the BOD of incoming sewage and the BOD of the effluent water leaving the plant, the efficiency and effectiveness of sewage treatment can be judged.

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If water with a high BOD value flows into a river, the bacteria in the river will oxidize the organic matter, consuming oxygen from the river faster than it is dissolved back from the air. If this happens, fish will die due to the low oxygen concentration, a consequence known as a fish kill (Figure 1.5). Thus, sewage treatment plants must remove as much BOD as possible from the sewage water.

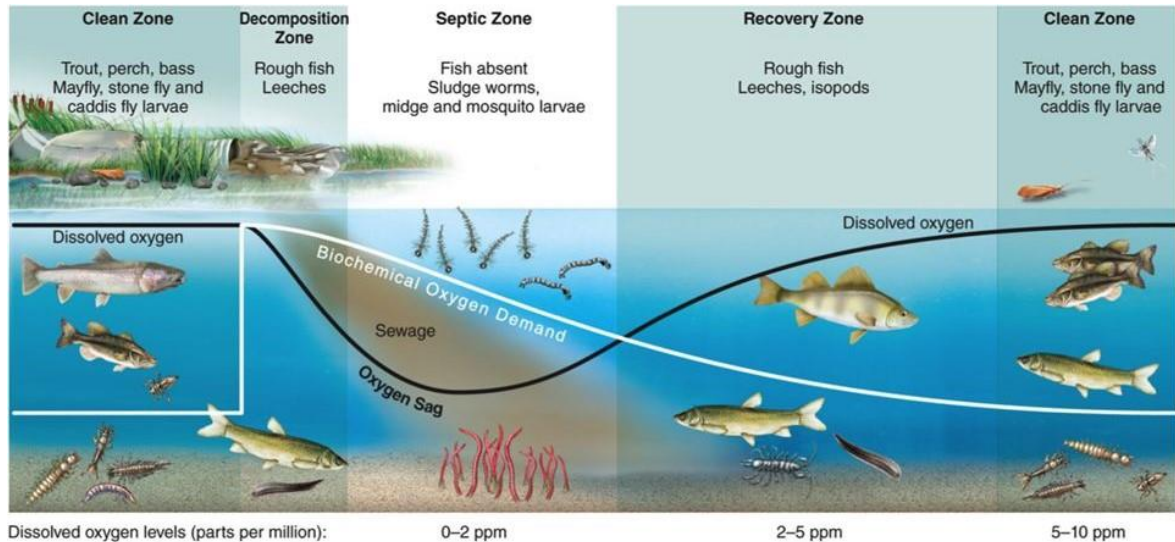


Figure 1.5: High BOD value effect 'Fish kill'

Biochemical Oxygen Demand (BOD) is the amount of oxygen, expressed in mg/L or parts per million (ppm), that bacteria take from water when they oxidize organic matter. The carbohydrates (cellulose, starch, sugars), proteins, petroleum hydrocarbons and other materials that comprise organic matter get into water from natural sources and from pollution. They may be dissolved, like sugar, or suspended as particulate matter, like solids in sewage.

Because organic matter always contains carbon and hydrogen, oxidation produces carbon dioxide (oxygen combining with carbon) and water (oxygen combining with hydrogen).

Bacteria in water live and multiply when organic matter is available for food and oxygen is available for oxidation. About one-third of the food bacteria consumed becomes the solid organic cell material of the organisms. The other two-thirds is oxidized to carbon dioxide and water by the biochemical action of the bacteria on the oxygen dissolved in the water.

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To determine BOD, the amount of oxygen the bacteria use is calculated by comparing the amount left at the end of five days with the amount known to be present at the beginning. At room temperature, the amount of oxygen dissolved in water is 8 mg/L. At the melting point, it increases to 14.6 mg/L; it also increases at high barometric pressures (low altitudes). At the boiling point, the solubility of oxygen is zero. During the five-day period of a BOD test, the bacteria oxidize mainly the soluble organic matter present in the sample. Two methods are widely used for BOD measurement. One method, the dilution method, is a standard method. The other method is the manometric method.

- 1 The dilution method: conducted by placing various incremental portions of the sample into bottles and filling the bottles with dilution water. The dilution water contains a known amount of dissolved oxygen and a portion of inorganic nutrients and a pH buffer. The bottles are completely filled, freed of air bubbles, sealed and allowed to stand for five days at a controlled temperature of 20 °C (68 °F) in the dark. During this period, bacteria oxidize the organic matter using the dissolved oxygen present in the water. At the end of the five-day period, the remaining dissolved oxygen is measured. The relationship between the oxygen that was consumed during the five days and the volume of the sample increment is then used to calculate the BOD.
- 2 Manometric method: It is easier to perform, because the oxygen consumed is measured directly rather than with chemical analysis. Since the sample is usually tested in its original state (not diluted), its behavior more closely reflects that of the waste in an actual sewage treatment plant. As the oxygen in the sample is used up, more will dissolve into the water from the air space over it. The manometer measures the drop in air pressure in the bottle. This continuous indication of the amount of oxygen uptake by the sample is an important feature of the manometric method. By graphing the results, it is possible to find the rate of oxygen uptake at any time and thereby gain considerable insight into the nature of the sample.

The BOD test measures only the oxygen taken up by wastewater during the biological

oxidation of organic matter. Therefore, a BOD test is a highly unreliable way to determine the amount of organic matter present in water. The test measures only the approximate amount of oxygen that will be required (absorbed or consumed) by a polluted water when it is exposed to air or oxygen for an extended period of time.

The growth of bacteria is highly temperamental and erratic and is affected by numerous factors, many of which are unknown or difficult to control. Also, the bacteria grow somewhat slowly, the biological oxidation is never complete. It is approximately 80 percent complete in five days at 20 °C but is not 100 percent complete even after 20 days. Many other factors also affect the tests. Toxic substances in the sample inhibit or even prevent bacterial growth, showing a lower value than the one obtained without the toxic substance.

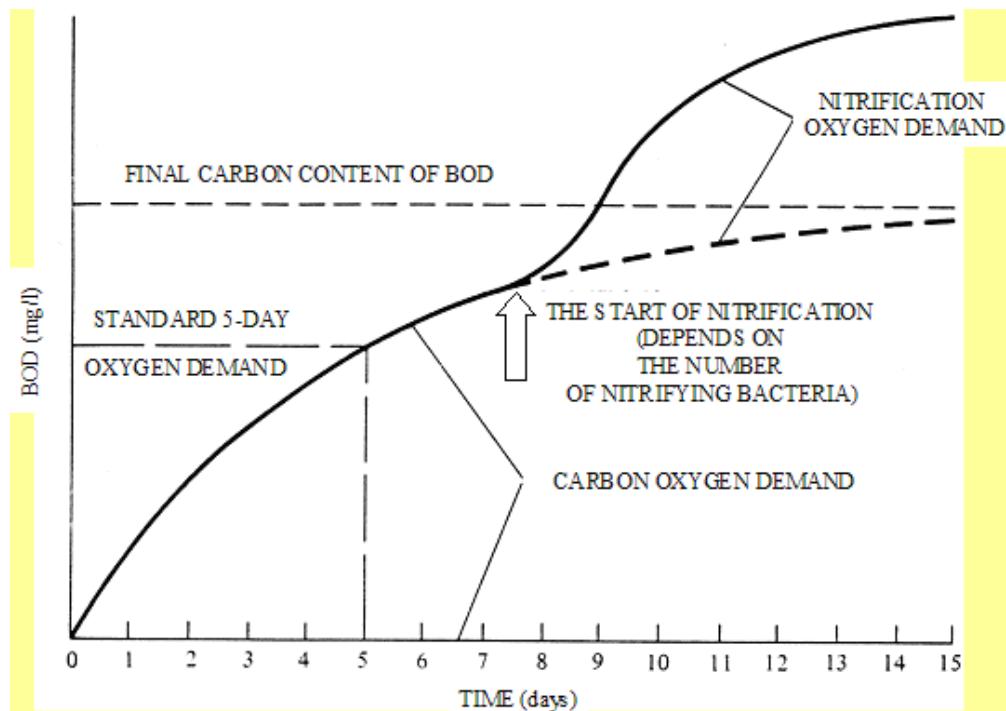


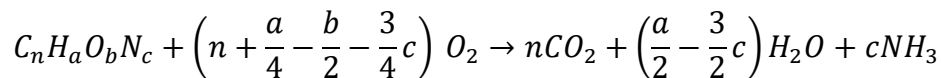
Figure 1.6: BOD evolution in time.

The anomaly shown in the solid curve after the day 7 is an example of nitrification. Biological oxidation of organic nitrogen usually occurs after five days with normal domestic waste, because it takes that long for the carbon oxidation to be near completion and the nitrogen bacteria seed to develop.

Nitrifying bacteria usually are not considered a problem in manometric BOD determinations. Because nitrification usually occurs between the fifth and seventh day of incubation, it causes only a minor error in the normal five-day BOD. However, if an abnormally high uptake of oxygen takes place due to nitrifying bacteria, Nitrification Inhibitors should be added to solve this problem.

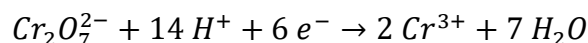
1.1.2 Chemical oxygen demand

The chemical oxygen demand (COD) is an indicative measure of the oxygen required to oxidize soluble and particulate organic matter in water. Therefore, it is an indicator of the degree of pollution in water, together with the BOD, is a common parameter for the indirect measurement of organic substances in water. Usually it is expressed as the mass of oxygen consumed over volume of the solution. In SI units mg/L.



The COD is an important water quality parameter because, similarly to the BOD, it provides an index to assess the effect discharged wastewater will have on the receiving environment. Higher COD levels mean a greater amount of oxidizable organic material in the sample. The COD test is often used as an alternative to BOD due to the significantly shorter testing time.

In order to measure the COD, it is necessary a strong oxidizing species at high temperature. Potassium dichromate in a strong acid medium is usually employed. The dichromate anion is reduced to Cr^{3+} in acid medium, according to:



Dichromate ions have an orange colour when present in solution. While the Cr^{3+} in solution have a green colour. When a sample is poured inside the dichromate solution, depending

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on the amount of compounds that can be oxidized, a proportional change in the colour of the solution should be noticed. However, if the amount of components is small and the colour change is not noticeable, special instruments can be used to quantify it.

For the strong acid medium, concentrated sulphuric acid is used. As soon as the sample is introduced in the dichromate solution, the temperature rapidly goes up due to the strong exothermicity of the reaction. So as to obtain complete homogenization, strong agitation is required for some seconds. Finally, the vial is exposed to a controlled temperature of 150°C for 2 hours to fully oxidize the sample.

For this work, vials with the dichromate solutions prepared by Hanna Instruments®. Depending on the amount of organic matter present in the sample, a different solution should be used. Hanna Instruments® provides three possibilities:

1. Low Range: COD values ranging from 0 to 150 mg O₂/L. Accuracy: 4 mg O₂/L.
2. Medium Range: COD values ranging from 0 to 1500 mg O₂/L. Accuracy: 15 mg O₂/L.
3. High Range: COD values ranging from 0 to 15000 mg O₂/L. Accuracy: 150 mg O₂/L.

The amount of oxidizable species, both organic and inorganic, is directly proportional to the quantity of dichromate consumed.

In the following images, the vials employed are shown. The picture on the left shows the original vials with the dichromate solutions before the measurement, from left to right, Low range, Medium range and High range respectively. The picture on the right, shows the medium range vials. The one on the left is a solution that has a concentration higher than 1500 mg O₂/L (above the upper limit) giving a strong green color due to the predominance of Cr³⁺ ions. In comparison with the solution of 0 mg O₂/L obtained when distilled water is used for the measurement, in other words the blank test.

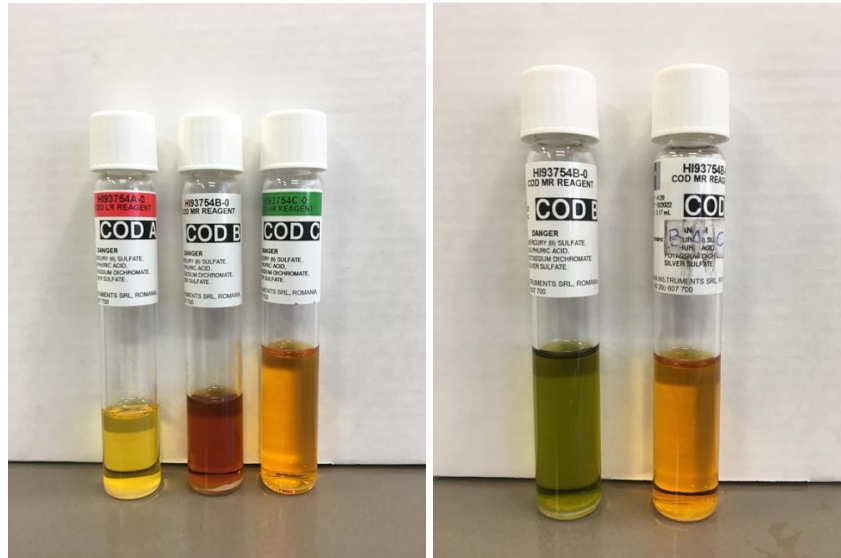


Figure 1.7: Left: Vials low, medium and high range respectively. Right: Medium range, out of range compared to the blank test.

1.1.2.1 COD interferences

Some compounds may introduce interferences to the COD value. There are some organic compounds like pyridine for example that are not oxidized by the dichromate at the conditions mentioned before.

The most significant interferences, however, are generated by halogens, particularly chloride which interacts with the catalyst; the silver sulphate.

The chloride interference becomes significant at a certain concentration, which depends on the vial range of interest:

- Low Range: 2000 mg/L.
- Medium Range: 2000 mg/L.
- High Range: 20000 mg/L.

Regular drinking water has a concentration of salts of 10 mg/L, in rivers the value may vary from 10 to 42 mg/L. Samples with a higher Cl^- concentration should be diluted first. For the

samples treated in this work, the salt content (Cl^-) was significantly lower than the limits stated above.

1.2 Conventional treatment methods

Oily wastewater is generated in many industrial processes, such as petroleum refining, petrochemical, food, leather and metal finishing. Fats, oils and greases present in these wastewater have to be removed before the water can be properly reused in a closed-loop process or discharged into the sewer system or to surface waters. These oily water streams are mainly in the form of oil-in-water (O/W) emulsions that pose a great problem in facilities attempting to stay in compliance with discharge limits.

With industrial development, there is an increase in the amount of oil used, but various technical and management developments lag behind other reasons that are not perfect and make a lot of oil into the water, forming pollution. Treating oily wastewater sources are very broad, as the oil in the oil industry, oil refining, oil storage, transportation and petrochemical industries in the production process generate lot of oily wastewater. Oily wastewater pollution is mainly manifested in the following aspects:

- (1) affecting drinking water and groundwater resources, endangering aquatic resources;
- (2) endangering human health;
- (3) atmospheric pollution;
- (4) affecting crop production;
- (5) destructing the natural landscape.

Domestic and foreign research institutions have tirelessly studied in-depth and discussed oily wastewater treatment methods, and the goal is both the removal of a large amount of oil, taking into account the removal of dissolved organic matter, suspended solids, soaps, pH, sulfide, ammonia, etc.

For oily wastewater treatment ways, each method has its specific scope, the need for different situations is studied, to determine the appropriate process. Due to the complexity of oily wastewater, using a single method is difficult to achieve national emission standards for industrial wastewater, oily wastewater deals with multi-level processing. By using a multi-stage treatment process, wastewater can be integrated into components so that wastewater treatment is able to achieve satisfactory results.

1.2.1 Flotation

Flotation consists in pouring into the water in the form of fine bubbles under pressure, the tiny air bubbles in the adhesion of oil particles suspended in the water, because the floating density of oil is less than that of water, the formation of a scum layer is separated from the water. Currently the most commonly used method is dissolved air flotation. This method is widely used in treatment of the industrial wastewater effluents from oil refineries, petrochemical and chemical plants, natural gas processing plants, general water treatment and similar facilities.

To improve flotation, flotation agents should be added, flotation agents on the one hand with breaking and sparkling role, on the other hand there are bridging adsorption, and colloidal particles can gather together while bubbles float.

Wang (2007) applied a settling tank simulation and carried out sedimentation tank, combined with the flotation process in a small pilot study, when the influent concentration of oil was 3000–14000 mg/L, the effluent quality of the oil average concentration was of 300 mg/L or less.

Dissolved air flotation showed an oil removal greater than 90% (Al-Shamrani et al. 2002) and a COD removal rate of 92.5% (Hamia et al. 2007).

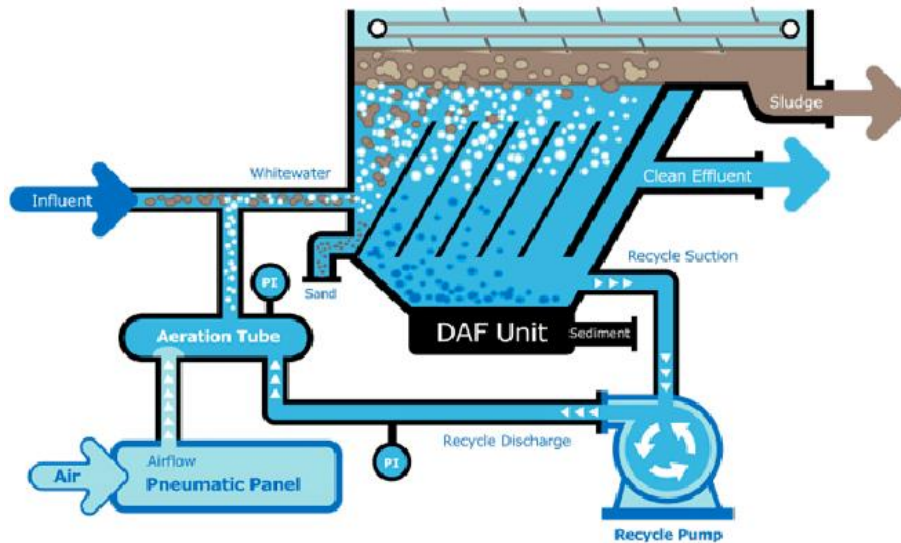


Figure 1.8. Dissolved air flotation unit

1.2.2 Coagulation

This is a process which combines small particles into larger aggregates and also adsorbs dissolved organic matter on to particulate aggregates so that these impurities can be easily removed in subsequent solid/liquid separation processes.

In a colloidal suspension, particles will settle very slowly or not at all because the colloidal particles carry surface electrical charges that mutually repel each other. A coagulant with the opposite charge is added to the water to overcome the repulsive charge and destabilize the suspension.

Metal coagulants are common choices, these are added to water and the metal ions hydrolyze quickly but in a somewhat uncontrolled way, forming a series of metal hydrolysis species. The efficiency of rapid mixing, the pH, and the coagulant dosage determine which hydrolysis species is effective for treatment. Zeng et al. (2007) using aggregation zinc silicate (PISS) and anionic polyacrylamide (A-PAM) composite flocculant oily wastewater treatment, improved oil removal efficiency up to 99%. Coagulants used for water and wastewater treatment are predominantly inorganic salts of iron and aluminum.

The main advantages of coagulation are that it reduces the time required to settle out suspended solids and is very effective in removing fine particles that are otherwise very difficult to remove. Coagulation can also be effective in removing many protozoa, bacteria and viruses.

The principal disadvantages of using coagulants for treatment of small supplies are the cost and the need for accurate dosing and frequent monitoring. Coagulants need accurate dosing equipment to function efficiently and the dose required depends on raw water quality that can vary rapidly. The efficiency of the coagulation process depends on the raw water properties, the coagulant used and operational factors including mixing conditions, coagulant dose rate and pH value. The choice of coagulant and determination of optimum operating conditions for a specific raw water have to be determined by coagulation tests.

1.2.3 Membrane separation technology

Membrane separation processes have become one of the fastest emerging technologies during the past few decades, nowadays considered as a key technology for sustainable processes and green engineering developments. Membranes used for separation purposes are typically composed of a homogeneous, polymeric composition through which some particular components are separated from the mixture. These processes operate without heating since no phase change is needed, and therefore use less energy than conventional thermal separation processes resulting in a higher energy efficiency, one of the most attractive characteristics of this process. The use of a special porous material manufactured for the interception role in the physical removal of a certain way of the trapped particle size of contaminants. The difference in pressure driven membrane separation process is generally divided into microfiltration, ultrafiltration and reverse osmosis of three kinds. The difference in pressure driven membrane separation process is generally divided into microfiltration, ultrafiltration and reverse osmosis of three kinds. The membrane separation technology is characterized by: waste oil according to the particle size membrane MWCO (Molecular Weight Cut off, the lowest molecular weight solute in which 90% of the solute is retained by the membrane) reasonable certainty, and the process in general has no phase change, a direct realization of oil–water separator; without

pharmaceutical dosing, so less pollution; reprocessing costs low, the separation process has less energy consumption; separation of water has low oil content, but good effect. It still requires the use of different materials and methods of preparing the novel and economic performance of film to improve existing treatment processes, thereby overcoming some of the technological (such as thermal stability, resistant to corrosion, film is likely to be contaminated, the process having small volume) shortcomings. In addition, a single membrane separation technology is not a good solution to the problem of oily wastewater treatment. It needs to be combined with other traditional methods.

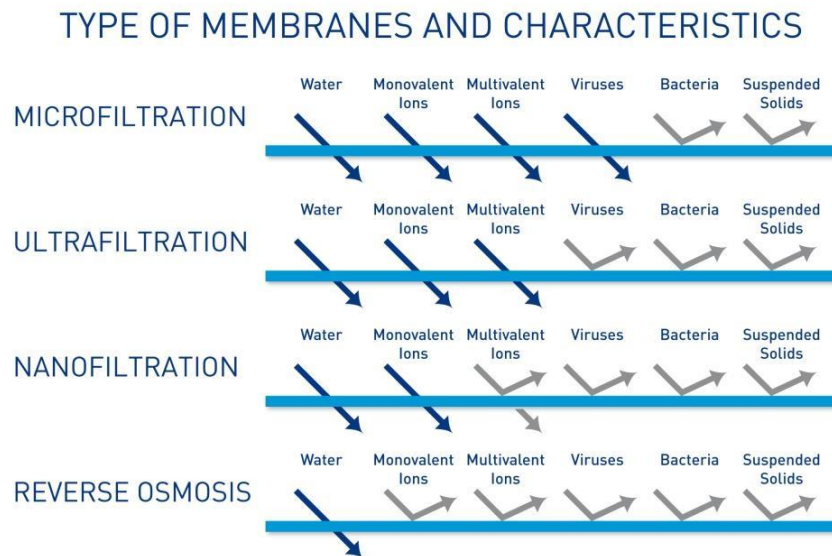


Figure 1.9: Types of membranes.

1.2.4 Biological Treatment

The use of microorganisms for oily wastewater treatment has yielded some impressive results recently. In many cases, a consortium of microbes has been used to remove hazardous pollutants in oily wastewater. Although biological treatment of oily wastewater is not well developed due to the diverse nature and behavior of microbes under different environmental conditions, recent research activities in this area have yielded notable removal percentages of contaminants from oily wastewater.

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It is an important and integral part of any wastewater treatment plant that treats wastewater from either municipality or industry having soluble organic impurities or a mix of the two types of wastewater sources.

The advantage resides in the possibility of obtaining high decontamination levels of the organic materials in a system in which the three phases, solid, liquid and gaseous coexist forming a mixture inside the reactor.

Biological treatment using aerobic Activated Sludge Process (ASP) is the most common and oldest biotreatment process. Typically, for wastewater after primary treatment, the suspended impurities removal is treated in an activated sludge process based biological treatment system comprising aeration tank followed by secondary clarifier. The aeration tank is a completely mixed or a plug flow (in some cases) bioreactor where specific concentration of biomass (measured as mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS)) is maintained along with sufficient dissolved oxygen (DO) concentration (typically 2 mg/l) to effect biodegradation of soluble organic impurities measured as biochemical oxygen demand (BOD) or chemical oxygen demand (COD).

The aerated mixed liquor from the aeration tank overflows by gravity to the secondary clarifier unit to separate out the biomass and allow clarified, treated water to the downstream filtration system for finer removal of suspended solids. The separated biomass is returned to the aeration tank by means of return activated sludge (RAS) pump. Excess biomass (produced during the biodegradation process) is wasted to the sludge handling and dewatering facility.

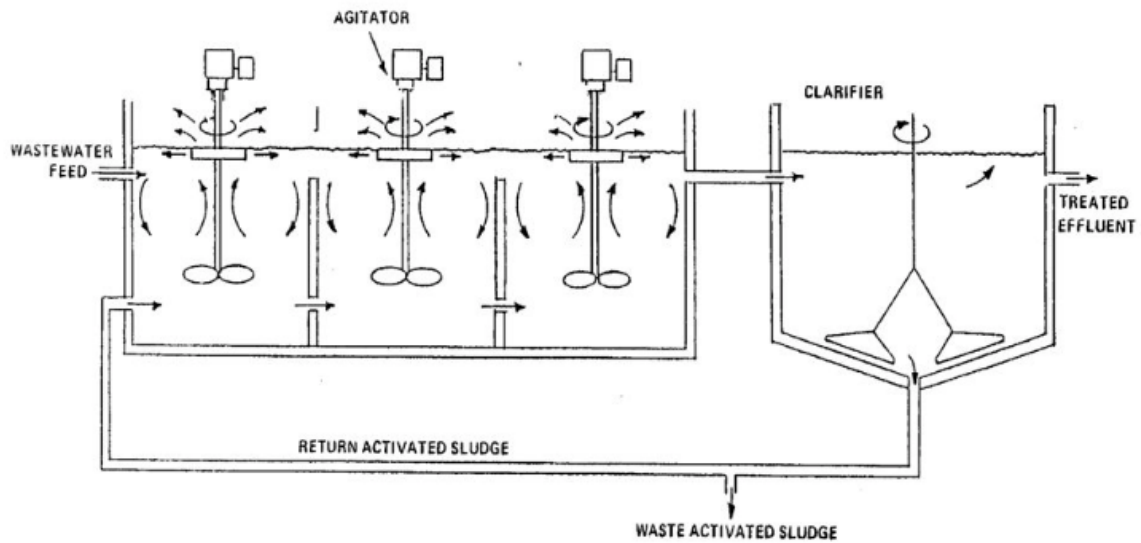


Figure 1.10: Biological treatment with activated sludge

Another possibility is the use of Membrane bioreactors. These bioreactors for wastewater treatment consist in a combination of a suspended growth biological treatment method, usually activated sludge, with membrane filtration equipment, typically low-pressure microfiltration or ultrafiltration membranes. The membranes are used to perform the critical solid-liquid separation function. In activated sludge facilities, this is traditionally accomplished using secondary and tertiary clarifiers along with tertiary filtration. The two general types of MBR systems are vacuum (or gravity-driven) and pressure-driven systems. Vacuum or gravity systems are immersed and normally employ hollow fiber or flat sheet membranes installed in either the bioreactors or a subsequent membrane tank. Pressure driven systems are in-pipe cartridge systems located externally to the bioreactor.

A membrane bioreactor system is often comprised of ten or eleven sub-systems and includes fine screening, the Membrane Zone and, in most cases, some type of post-disinfection process.

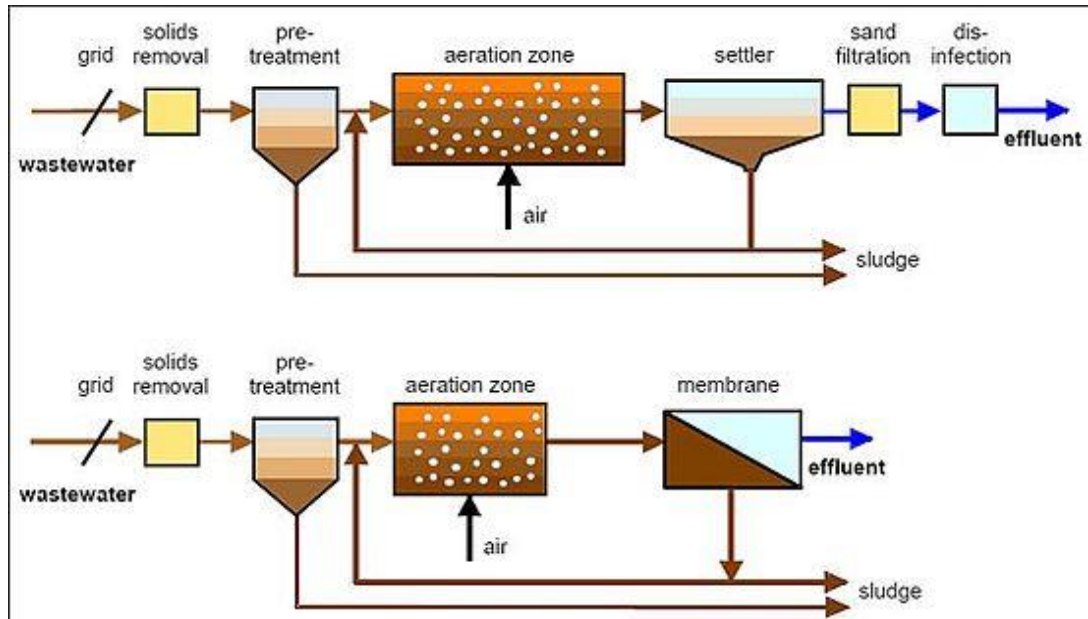


Figure 1.11. Comparison between Activated sludge process (top) and Membrane Bioreactor (bottom)

There are two possible configurations for the Membrane Bioreactor process:

- Submerged or Internal: The filtration element is installed in either the main bioreactor vessel or in a separate tank. The membranes can be flat sheet or tubular or combination of both, and can incorporate an online backwash system which reduces membrane surface fouling by pumping membrane permeate back through the membrane. Additional aeration is also required to provide air scour to reduce fouling. Where the membranes are installed in the main reactor, membrane modules are removed from the vessel and transferred to an offline cleaning tank.
- Side stream or External: The filtration elements are installed externally to the reactor, often in a plant room. The biomass is either pumped directly through a number of membrane modules in series and back to the bioreactor, or it is pumped to a bank of modules, from which a second pump circulates the biomass through the modules in series. Cleaning and soaking of the membranes can be undertaken in place with use of an installed cleaning tank, pump and pipework.

Due to the deposition of soluble and particulate materials onto and into the membrane, attributed to the interactions between activated sludge components and the membrane, the filtration performance inevitably decreases with filtration time.

In membrane separation processes, fouling is the most serious problem affecting the system performance. This problem leads to a significant increase in hydraulic resistance. In systems where flux is maintained constant, the energy required to achieve filtration increases with time. Therefore, frequent membrane cleaning is required, increasing significantly the operating costs as a result of cleaning agents and production downtime. More frequent membrane replacement is also expected.

1.3 Regulations

As for the regulations, Italy was chosen for the analysis. In this country, the legislations concerning the urban, industrial and agricultural discharges are regulated by the legislative decree 152/06, the so called "Testo Unico Ambientale" a close translation for this is: Unique environmental text. This decree establish the main current regulations regarding water pollution, regulating the quality and conditions of the streams and imposing the limits for the emission according to the type of water receptor.

The obligations related to the discharge and the necessary requirements for sewage networks, connections and purification stations make the "Testo Unico Ambientale", as defined in art. 100-108, the "Qualitative protection of the resource: discipline of the discharges".

1.3.1 Legislative decree 152/06

This is the national reference measure for environmental management: in fact, it regulates in detail all aspects of environmental impact assessment, in particular the defense of the

soil, the protection of water, the management of waste, reduction of air pollution and compensation for environmental damage.

The “Testo Unico Ambientale”, which came into force on 29 April 2006, has replaced, as regards the qualitative and quantitative assessment of water, the previous regulatory source, Legislative Decree No. 152 of 11/05/1999.

The Legislative Decree 152/06 was originally composed of 318 articles divided into 6 sections. From its date of entry into force to this day, however, has undergone various changes and additions by successive measures that have redesigned the content.

For this work, the most interest section is the third part of the decree, which contains the list of the norms that are directly related to our purposes: from the articles 53 to 176 the quantitative and qualitative protection of the water resource with the relative planning, the discipline of the discharges and the integrated water service, as well as sanctions and compensation criteria are addressed in detail.

1.3.2 Objectives and definitions

The provisions of section II "Tutela delle acque dall'inquinamento" which means Protection of water from pollution, define the general framework for the protection of surface, marine and underground waters with the main objectives of:

- 1) to prevent and reduce pollution and to rehabilitate polluted water bodies;
- 2) to achieve the improvement of the state of the water and adequate protection of those destined to particular uses;
- 3) to pursue sustainable and durable uses of water resources, with priority for drinking water;
- 4) maintain the natural self-purification capacity of water bodies, as well as the ability to support large and well-diversified animal and plant communities.

As stated in article 73, the achievement of the stated purposes is accomplished through the following tools:

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- a) the identification of environmental quality objectives and specific destination of water bodies;
- b) the integrated protection of the qualitative and quantitative aspects within each hydrographic region and an adequate system of controls and sanctions;
- c) compliance with the limit values for discharges established by the state, as well as the definition of limit values in relation to the quality objectives of the receptor body;
- d) the adaptation of sewerage systems, collecting and purification of water discharges, within the integrated water service;
- e) the identification of measures to prevent and reduce pollution in vulnerable areas and sensitive areas;
- f) the identification of measures aimed at the conservation, saving, reuse and recycling of water resources;
- g) the adoption of measures for the gradual reduction of discharges, emissions and any other source of widespread pollution containing hazardous substances or for the gradual elimination of them when having priority hazardous substances, contributing to reach concentrations close to the values of natural environment for substances present in nature and close to zero for anthropogenic synthetic substances;
- h) the adoption of measures to control discharges and emissions into surface waters according to a combined approach.

Article 74 of the Consolidated Environmental Text defines as pollution "the direct or indirect introduction, as a result of human activity, of substances or heat in the air, water or soil that may harm human health or the quality of aquatic ecosystems or terrestrial ecosystems that depend directly on aquatic ecosystems, disrupting, disfiguring or impairing recreational values or other legitimate uses of the environment".

The water pollution that is of interest for this work, is caused by improper discharges, where it is considered as a discharge "any intake of waste water into surface water, on the

ground, in the subsoil and in the sewage system, regardless of their polluting nature, even subjected to preventive treatment of purification", Art. 44 paragraph 1, letter ff.

In this paragraph there is also the classification of the different types of discharges based on their origin; as a consequence, the waste water is subdivided as follows:

- A. domestic waste water: wastewater from residential and service establishments and deriving mainly from human metabolism and domestic activities;
- B. industrial waste water: any type of waste water from buildings or installations where commercial activities or production of goods take place, different in quality from domestic wastewater and from run-off, meaning those in contact with substances or materials, including pollutants, not connected with the activities carried out in the plant, the characteristics of such wastewater are variable according to the type of industrial activity;
- C. urban waste water: the mixture of domestic waste water, industrial wastewater, and/or so-called runoff conveyed into sewage systems, even if separated, and coming from agglomeration; runoff water contains various micro-pollutants, such as hydrocarbons, pesticides, detergents, rubber debris.

1.3.3 Quantitative protection of water and water saving

The article 95 states that: "The quantitative protection of the resource contributes to the achievement of quality objectives through a planning of the use of water aimed at avoiding repercussions on the quality of the same and to allow a sustainable water consumption".

Therefore, it is not permitted to dilute the discharge water with cooling or washing water, before their treatment to adapt them to the specified limits.

1.3.4 Qualitative water protection and discharge regulations

All the discharges are regulated according to the compliance with the quality objectives of the water bodies and must in any case comply with the limit values set out in Annex 5 to the third part of this decree.

According to the Art. 74, paragraph 1 letter oo, the emission limit value is defined as the "limit of acceptability of a pollutant contained in a discharge, measured in concentration, or in mass per unit of product or raw material worked, or in mass per unit of time".

The sampling of the waste water must guarantee a characterization of the same by comparison with the reference values of both physical (temperature, color, odor) and chemical parameters (pH, concentration of particular chemical species, COD, BOD).

Industrial waste water can be differentiated into hazardous and non-hazardous wastewater, taking into account the toxicity, persistence and bioaccumulation of the considered substance in the environment where the waste is discharged.

The arrangements concerning discharges of dangerous substances apply to establishments where activities involving the production, processing or use of the substances referred to in Tables 3/A and 5 of Annex 5 to the third part of the Decree are carried out, and in those discharges in which the presence of these substances is found in quantities or concentrations exceeding the limits of detection allowed by the detection methods in place.

For both types of industrial wastewater, there are limits depending on the discharge receiving body and not on the specific pollutant load in question. There will therefore be distinctions according to discharge into surface water, sewage and soil.

In particular, for industrial waste water it is possible to identify the following cases (described in Art. 101-108):

- for the discharge of significant superficial water volumes of industrial and non-hazardous wastewater, the values shown in Table 3 attached to the "Parte Terza" or Third Part of D.Lgs 152 / 06 and in Table 3 / A attached to the third part of D.Lgs 152 / 06;

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- for discharge into non-significant surface water volumes, therefore when there is the presence of running water for less than 120 days a year, non-hazardous industrial waste water must be respected the limits listed in Table 4 attached to the Third Part D.Lgs 152 / 06;
- the discharge of hazardous industrial wastewater into non-significant surface water volumes of hazardous industrial wastewater is prohibited by law;
- for the discharge to the ground of non-hazardous industrial wastewater, the limits are shown in Table 4 attached to the Third Part D.Lgs 152/06;
- the discharge of hazardous industrial waste water to the ground is prohibited by law;
- for sewage discharge there is no longer any distinction between hazardous and non-industrial wastewater, the values shown in Table 3 attached to the third part of Legislative Decree 152/06 second column are followed.

As can be seen in Table 5 of Annex 5 to Part Three of the Testo Unico Ambientale (Table 1.1), the family of pollutants treated in this work, that of hydrocarbons of oil origin, belongs to substances that identify industrial wastewater as dangerous.

1	Arsenic
2	Cadmium
3	Total Chromium
4	Hexavalent Chromium
5	Mercury
6	Nickel
7	Lead
8	Copper
9	Selenium
10	Zinc
11	Phenols
12	Persistent mineral oils and hydrocarbons of oil origin

13	Aromatic organic solvent
14	Nitrogenated organic solvents
15	Halogenated organic compounds (including chlorinated pesticides)
16	Phosphoric pesticides
17	Organic compounds containing Tin
18	Substances of which, according to the indications of the International Agency for Research on Cancer(IARC), the carcinogenic power is confirmed

Table 1.1 - Substances for which limits less restrictive than those indicated in Table 3 cannot be adopted, for draining in surface water (1) and for draining into the sewer system (2), or in Table 4 for discharge to the ground. Legislative Decree 152/06 (Part Three, Annex 5, Table 5.)

1.3.5 Attachments and emission limit values

The Annex 5 of the third part of the Testo Unico Ambientale provides the maximum tabulated values of contamination threshold levels of industrial waste water for the various receiving bodies.

The discharges of industrial waste water into surface water must comply with the emission limits indicated in the following table 3 of the regulation or with the relative regulations decided by the Regions.

The emission limit values which the discharges concerned must not exceed are expressed, in principle, as a concentration.

The analytical determinations for the control of compliance of industrial wastewater discharges are normally referred to an average sample taken within three hours.

The limits established for discharge into the sewage system are mandatory in the absence of limits established by the competent authority or in the absence of a final treatment plant capable of respecting the final discharge emission limits.

Table 1.2 provides the list of emission limits, according to the parameter of interest with the relative unit of measurement, for the discharge into surface waters (column a) and in

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the drainage system (column b). Table 1.3, on the other hand, outlines the emission limits for the discharge of urban and industrial wastewater into the soil.

The legal limits for the emission of industrial waste water polluted by hydrocarbon substances provide maximum values of the COD parameter of 100, 160 and 500 mg O₂ / L, depending on the discharge respectively on the soil, in surface water and in sewage system.

Parameter number	Parameter	Unit of measurement	Discharge in surface water	Discharge in sewage system
1	pH	-	5.5 – 9.5	
2	Temperature	°C	/	/
3	Color	/	Imperceptible after 1:20 dilution	Imperceptible after 1:40 dilution
4	Odor	/	Must not produce discomfort	Must not produce discomfort
5	Coarse materials	/	Absent	Absent
6	Total solids	mg/L	≤80	≤200
7	BOD5	mg O ₂ /L	≤40	≤250
8	COD	mg O ₂ /L	≤160	≤500
9	Aluminum	mg/L	≤1	≤2
10	Arsenic	mg/L	≤0.5	≤0.5
11	Barium	mg/L	≤20	/
12	Boron	mg/L	≤2	≤4
13	Cadmium	mg/L	≤0.02	≤0.02
14	Total chromium	mg/L	≤2	≤4
15	Chromium VI	mg/L	≤0.2	≤0.2
16	Iron	mg/L	≤2	≤4

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17	Manganese	mg/L	≤2	≤4
18	Mercury	mg/L	≤0.005	≤0.005
19	Nickel	mg/L	≤2	≤4
20	Lead	mg/L	≤0.2	≤0.3
21	Copper	mg/L	≤0.1	≤0.4
22	Selenium	mg/L	≤0.03	≤0.03
23	Tin	mg/L	≤10	≤
24	Zinc	mg/L	≤0.5	≤1
25	Total cyanides	mg/L	≤0.5	≤1
26	Free active chlorine	mg/L	≤0.2	≤0.3
27	Sulfides	mg H ₂ S/L	≤1	≤2
28	Sulfites	mg SO ₃ /L	≤1	≤2
29	Sulphates	mg SO ₄ /L	≤1000	≤1000
30	Chloride	mg/L	≤1200	≤1200
31	Fluoride	mg/L	≤6	≤12
32	Total phosphorus	mg P/L	≤10	≤10
33	Ammoniacal nitrogen	mg NH ₄ /L	≤15	≤30
34	Nitrous nitrogen	mg/L	≤0.6	≤0.6
35	Nitric nitrogen	mg/L	≤20	≤30
36	Animal / vegetable fats and oils	mg/L	≤20	≤40
37	Total hydrocarbons	mg/L	≤5	≤10
38	Phenols	mg/L	≤0,5	≤1
39	Aldehydes	mg/L	≤1	≤2
40	Aromatic organic solvents	mg/L	≤0,2	≤0,4
41	Nitrogenated organic solvents	mg/L	≤0,1	≤0,2

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42	Total surfactants	mg/L	≤ 2	≤ 4
43	Phosphorated pesticides	mg/L	$\leq 0,10$	$\leq 0,10$
44	Total pesticides (excluding phosphorated ones)	mg/L	$\leq 0,05$	$\leq 0,05$

Table 1.2 – Limit values for discharge in surface water and sewage (D. Lgs 152/06)

<i>Parameter number</i>	Parameter	Unit of measurement	Maximum concentration in the discharge
1	pH	-	6 – 8
2	SAR	/	10
3	Coarse materials	-	Absent
4	Total suspended solids	mg/L	25
5	BOD5	mg O ₂ /L	20
6	COD	mg O ₂ /L	100
7	Total nitrogen	mg N ₂ /L	15
8	Ammoniacal nitrogen	mg NH ₄ /L	5
9	Total phosphorus	mg P/L	2
10	Total surfactants	mg/L	0.5
11	Aluminum	mg/L	1
12	Beryllium	mg/L	0.1
13	Arsenic	mg/L	0.05
14	Barium	mg/L	10
15	Boron	mg/L	0.5
16	Total chromium	mg/L	1
17	Chromium IV	mg/L	0.05
18	Iron	mg/L	2

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19	Manganese	mg/L	0.2
20	Nickel	mg/L	0.2
21	Lead	mg/L	0.1
22	Copper	mg/L	0.1
23	Selenium	mg/L	0.002
24	Tin	mg/L	3
25	Vanadium	mg/L	0.1
26	Zinc	mg/L	0.5
27	Sulfides	mg H ₂ S/L	0.5
28	Sulfites	mg SO ₃ /L	0.5
29	Sulphates	mg SO ₄ /L	500
30	Active chlorine	mg/L	0.2
31	Chlorides	mg Cl/L	100
32	Fluorides	mg F/L	1

Table 1.3 –Limit values for urban and industrial waste water which are delivered to the soil

2 FERROMAGNETIC NANOPARTICLES

The main goal of this work is the water treatment, ultimately reflected in the COD value. The desired final COD value is a parameter fixed by the law. The violation of this fixed values may result in fines (economical loses) for the industry and it will surely have an undesired impact in the ecosystem, affecting the water leading to contamination in plants and both the aquatic life and animals who drink the water, but it will also affect humans that use that water. It is therefore imperative that this limits are below the maximum level.

The COD value after the treatment will depend in several factors, the initial value of COD of the tested water, the time of contact between the sample and the magnetic particles, the amount of nanoparticles employed, but also in the interactions between the nanoparticles and the pollutant components in the sample.

The magnetic fluid is composed of the solvent, in all cases water, and of course of the magnetic agent. This agent is composed of magnetic nanoparticles of Fe_3O_4 . In order to increase the cleaning efficiency of this nanoparticles, a good idea is to increase the lipophilic character of this particles.

It is possible to chemically attach molecules to the surface of the nanoparticles. In other words, the magnetic core can be coated with a suitable molecule. However, certain requirements for this molecules are required:

1. Presence of a group that can link to the nanoparticles. The formation of bonds between the magnetic core and the molecule is desired. This bond can be formed for example, if the molecule contains a carboxyl group inside its structure.
2. The molecule has to contain group/s that enhance the interactions between the nanoparticles and the pollutants. Since the pollutants contain usually components

of organic nature; substances with hydrocarbon chains. The addition of lipophilic group is recommended.

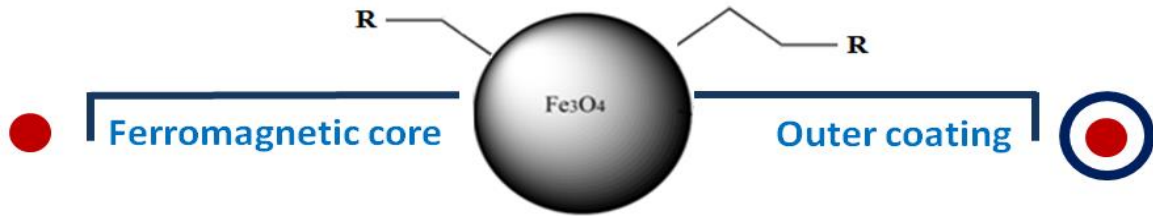


Figure 2.1: Structure of the coated nanoparticle.

By taking into account these considerations, a molecule with a long hydrocarbon chain and carboxyl group is a good candidate. Therefore, oleic acid was chosen. Not only because it properly fulfills the conditions but also because it is economically cheaper than other options.

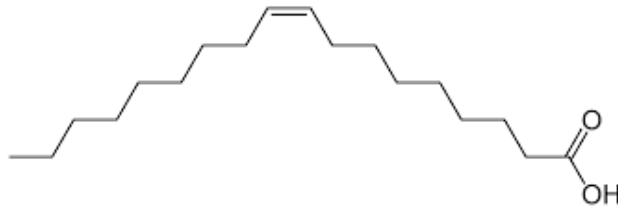


Figure 2.2: Oleic acid, unsaturated fatty acid. Present in animal and vegetable fats and oils.

The tests were run in a batch like process. A water sample was selected and pretreated. This pretreating is simply agitation for 10 minutes and in some cases a sonication stage for some minutes, in order to obtain a high amount of pollutants in a homogenous phase. The sonication is a method in which energy is applied to the sample in the form of sound waves. By applying this sonication stage, the COD value obtained is higher than without making use of it. In fact, in industrial processes a sonication stage is not only complex to implement but also undesired since it promotes the dissolution of pollutants. However, for this work this effect was desired, because by amplifying the COD values, the quantification of the

differences is higher (from the initial value of COD to the final one). In other words the precision is higher.

After the sonication stage, samples were taken and the nanoparticles were used in a certain dose. The agitation was performed with a magnetic agitator during a desired time. Finally, the COD measurement is performed using the proper reagents and the heating stage that is required by this process.

Different water samples were tested:

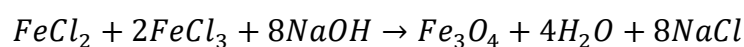
- Water 575 ppm 2-methyl propanol.
- Water 410 ppm Toluene.
- Water 770 ppm Diethyl ether.
- Water with 5000 ppm of commercial lubricant oil (lab prepared).
- Sample water obtained from a farm who produces lubricants (mostly linear compounds).
- Sample water obtained from a farm who produces lubricants (mostly aromatic compounds).

Firstly, in order to obtain a better knowledge of the particles interaction with a particular class of chemical, the tests were performed by using single pollutant samples: toluene or diethyl ether in water.

Different polluted industrial water samples were tested. Those samples contained a rather big diversity of hydrocarbon molecules used in industry, for example the lubricants commonly employed in industry contain components such as polyolefins, esters, fluorocarbons, aromatic compounds and detergents among others.

2.1 Synthesis

The synthesis of the nanoparticles is due to the following reaction:



Chapter 2: Ferromagnetic Nanoparticles

The product Fe_3O_4 is known as iron(II) iron(III) oxide according to IUPAC or, more commonly as magnetite. This compound exhibits permanent magnetic characteristics and as a powder it exhibits a black opaque color. It has a Curie temperature of 850 K or 577°C.

The chosen method used to produce the nanoparticles was co-precipitation, a very common method. For this reaction it is needed the presence of ions Fe^{2+} and also Fe^{3+} in strong basic medium.

According to the surface characteristics of the functionalized NPs, small molecules or surfactants functionalized iron oxide NPs can be simply divided into three types: oil-soluble, water-soluble, and amphiphilic. Oil-soluble type refers to the surface of functionalized iron oxide NPs containing molecules which have weak attraction for the solvent environment, it is generally hydrophobic group, such as the fatty acid, alkyl phenol ($n = 6-10$, linear or branched). Conversely, water-soluble type refers to the surface of functionalized iron oxide NPs containing chemical groups which have a strong attraction for the solvent environment, it is generally hydrophilic groups, such as the ammonium salt, polyol, lysine. Amphiphilic type refers to the surface of functionalized iron oxide NPs containing both hydrophilic and hydrophobic chemical groups.

Oil-soluble type functionalization used to prevent or decrease the agglomeration of iron oxide NPs and increase the stability give rise to the monodispersity, for instance, iron oxide NPs frequently dispersed in long-chain substance of hexadecane, the classic example being oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$), which has a C18 tail with a cis-double-bond in the middle, forming a kink. Such kinks have been postulated as necessary for effective stabilization, and indeed stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$) with no double-bond in its C18 tail, cannot stabilize the iron oxide NPs. Also, Oleic acid is widely used in ferrite nanoparticle synthesis because it can form a dense protective monolayer, thereby producing highly uniform and monodisperse particles. However, relative to the naked iron oxide NPs, the average diameter of functionalized NPs will increase in the range of 0–5 nm, and its saturation magnetization (M_s) almost unchanged.

Taking into account the factors stated above, the compound chosen for the coating was the oleic acid in different proportions.

2.1.1 Procedure

Three solutions were prepared:

- A. Solutions containing the iron Salts: FeCl_2 and FeCl_3 .
- B. Solution of Sodium hydroxide in excess. In order to guarantee a 100% conversion of the iron salts to Fe_3O_4 , a 10% sodium hydroxide excess was employed.
- C. Coating: The oleic acid. Amount of coating depending on the final coating concentration that is desired.

Since oleic acid has a strong hydrophilic behavior, when it is directly poured into the sodium hydroxide solution the neutralization of the carboxylic acid takes place and also it forms agglomerates that are difficult to break. In order to completely dissolve it two different strategies were adopted:

1. Oleic acid was poured in the sodium hydroxide solution. The formation of agglomerates was immediate. In order to separate them, ethanol was employed together with a strong agitation.
2. Oleic acid was first dissolved in ethanol. The new solution was poured in the sodium hydroxide.

The second approach gave better results since much smaller volumes of ethanol were needed. Obtaining immediately a homogenous solution that was employed for the following steps. It is important to mention that ethanol excess is undesired since it is a compound that can be oxidized, it will result in an undesired positive deviation in the COD value. However, the use of ethanol is necessary and for this reason, it is desired to remove the ethanol after the synthesis.

Once the iron salts solution and the sodium hydroxide with the coating were prepared, and then loaded into syringes. The next picture shows the configuration employed.

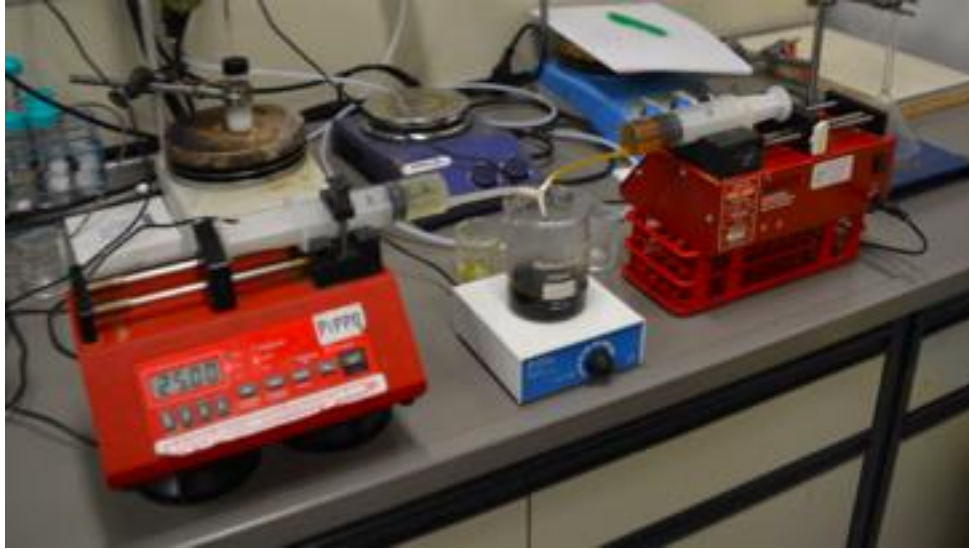


Figure 2.3: Synthesis of ferromagnetic nanoparticles.

The pumps velocities were configured according to the respective volumes of the solutions. The goal was to have the same discharge time for both solutions. The configuration involved introducing the diameters for the syringes and also the rates in the pump set up. The rates were determined with the following equation:

$$t_{discharge} = \frac{V_1}{r_1} = \frac{V_2}{r_2}$$

Mixing with a magnetic stirrer was used during the synthesis. Once the syringes fully delivered their respective volumes, the stirring was left for 30 minutes.

As mentioned before, the ethanol has to be removed due to its interference effect in the COD value. Different approaches were employed:

1. Simple distillation: After the synthesis, the solution was weighted and then distillation was performed. The heating was performed in oil bath for approximately 20 minutes. The distillation ended when the difference between the remaining mass and the initial mass was equivalent to the amount of ethanol that was initially added. It is important to add that this process is feasible since the most volatile species is indeed the ethanol with a boiling temperature of 78 °C. The mixture began

to boil when the temperature of the bath was 100.2 °C and continuously raised as the distillation was performed, reaching a final value of 110 °C. The COD was measured for some synthesis, immediately after the synthesis and after distillation, effectively showing the decrease in the COD value.

2. The second method consisted in heating the solution after the synthesis, until the evaporated mass (the difference between initial and final mass) was equal to the added ethanol. The COD value also decreased after this stage was performed.

In the beginning, distillation was chosen because the verification of the distillate is possible. The distillate presented a strong ethanol odor, and it was colorless. Additionally, a small quantity of it was mixed with pure oleic acid, in order to verify its organic nature, the mixture formed an homogeneous solution.

Finally, the solution was washed multiple times with tap water and also with diluted acid in order to obtain neutrality.

2.2 Coating verification

According to the literature, the coating molecules attachment to the nanoparticles surface happens thanks to the presence of carbonyl groups in the first ones. By knowing this, a requirement for the molecules to attach is to have this groups. In this work oleic and benzoic acid were employed.

However, a method of verification of the correct attachment of the coating – nanoparticles couple has to be provided. Two methods were employed and will be further explained.

2.2.1 Coating verification: Iodine value

This procedure was employed with the nanoparticles containing 5% and 20% of oleic acid coating. In both cases the syntheses were performed with the regular solution of iron chlorides (FeCl_2 and FeCl_3) first and then diluting this solution in order to obtain a concentration of salts 10% weight in volume. Summarizing, 4 syntheses were performed:

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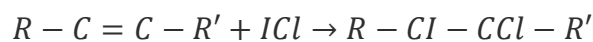
nanoparticles with 5% oleic acid coating concentrated and diluted and nanoparticles with 20% oleic acid coating concentrated and diluted.

The iodine value is a measure of the relative degree of unsaturation in oil components, as determined by the uptake of halogen atoms in the double bonds. The greater the iodine value, the more unsaturation and the higher the susceptibility to oxidation. More accurately, it is defined as the mass of iodine that is consumed by 100 grams of chemical substance.

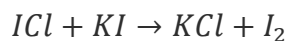
Frequently this method is used to quantify the unsaturation level in oil mixtures. For this work instead, it was employed knowing that oleic acid has a double bond into its structure, so it is possible to check if there is free oleic acid in the supernatant after the synthesis and in an affirmative case, to quantify it.

The iodine value was determined following the Wijs method. For this method, the so called Wijs solution was used: a solution of Iodine monochloride (0.1 M) in acetic acid. After the synthesis of the coated nanoparticles is completed, it is centrifuged at 5000 rpm for 5 minutes, making sure that most of nanoparticles precipitated. The phases are separated, the liquid phase or supernatant will be further employed for the quantification of the iodine value while the precipitate will proceed to the washing procedure.

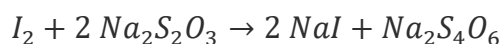
The supernatant was weighted and then mixed with a 25 ml of Wijs solution. Then, the mixture is left for 2 hours in the dark in order to obtain complete reaction:



The fatty acid is the limiting reactant. After the 2 hours, potassium iodide KI is introduced in the mixture. The unreacted iodine monochloride will react to give molecular iodine:



Finally, the molecular iodine is titrated with a standard solution 0.1 N of sodium thiosulfate:



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The titration was performed both with the supernatants and just water. The volumes of sodium thiosulfate employed were:

Sample	Water	5% Conc	5% Dil	Water	20% Conc	20% Dil
<i>Initial mass (g)</i>	12.2	12.1	12.2	20	20	20.02
<i>Volume (ml)</i>	43.3	43.2	43.2	42.9	43	42.9
<i>Iodine Value</i>	-	0.01	0.01	-	0.063	0.063

Table 2.1

The iodine values were obtained thanks to the formula provided by the method:

$$\text{iodine value} = \frac{12.69 * (B - S) * M_{Na_2S_2O_3}}{\text{weigh of the sample}}$$

In the determination of the iodine value for the 20% case, a bigger mass was chosen because of two reasons: the available mass was higher and also because a higher mass results in a higher precision.

By remembering the definition of the iodine value, it was possible to estimate the amount of oleic acid in the supernatants. However, it is noticeable the very small difference between the volumes in the titration of the blanks and the respective samples. For this reason, the difference could be assigned to a respective amount of oleic acid in the supernatants or, to the precision obtained with the burette (maximum error: 0.1 ml). Being said this, the results are expressed in the maximum possible quantity of oleic acid in the supernatants as a percentage:

Sample	5% Conc	5% Dil	20% Conc	20% Dil
<i>Max oleic acid (%)</i>	2.57	5.03	0.367	0.67

Table 2.2

According to the values obtained, it is possible to state that the amount of oleic acid in the supernatants was negligible. Being the only other possibility, for them to be attached to the nanoparticles.

2.2.2 Coating verification: IR spectroscopy

Infrared spectroscopy involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. It can be used to identify and study chemicals. Solid, liquid, or gas samples can be analyzed.

Infrared spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions occur at resonant frequencies; the frequency of the absorbed radiation matches the vibrational frequency.

The range of frequencies employed comprises wavelengths from 4000 cm^{-1} to 400 cm^{-1} (2500 nm to 25000 nm), referred as mid-infrared.

As mentioned before, the absorption of a certain frequency indicates a certain characteristic on the structure. By knowing specifically how the bond between the nanoparticles and the coating is, certain frequencies are expected to be adsorbed. These bonds happen between the oxygen atoms and the iron oxide.



Figure 2.4: Iron oxide coated nanoparticle

Oleic acid has the carbon-oxygen double bond of the carbonyl group; this group has a strong absorption between 1680 cm^{-1} to 1710 cm^{-1} . When the iron particle bonds with the acid, there is a delocalization of the electrons that originally formed the double bond with the carbon atom. Now, those electrons belong to the group of atoms composed by the carbon and the two oxygen atoms. For this reason, it is expected not to observe the peak corresponding to the carbonyl group in the IR analysis of the coated nanoparticles.

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On the other hand, inorganic compounds do not absorb frequencies in the region 4000-600 cm^{-1} , which for many years was the region covered by the commercial spectrometers. Instead, these compounds absorb frequencies lower than 600 cm^{-1} .

Particularly for the case of magnetite, according to the literature, this compound shows two broad bands at approximately 570 cm^{-1} and 400 cm^{-1} .

The iron nanoparticles were dried at 40°C for 12 hours. The infrared analysis was performed with the nanoparticles without coating, nanoparticles with 5% and 20% coating. Additionally, the IR analysis of the oleic acid was performed.

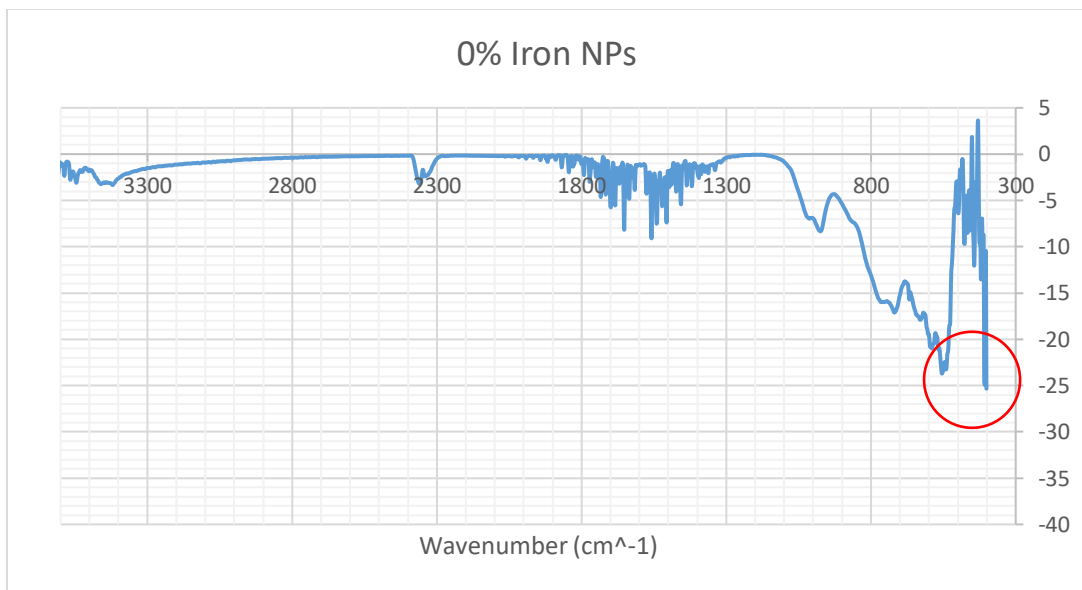


Figure 2.5: IR spectra 0% coating

The absorbance in the range of frequencies higher than 3300 cm^{-1} can be explained by traces of water in the sample. The peak at 550 cm^{-1} can be assigned to the Fe–O stretching mode of the tetrahedral and octahedral sites and the Fe–O stretching mode of the octahedral sites for the band at 400 cm^{-1} .

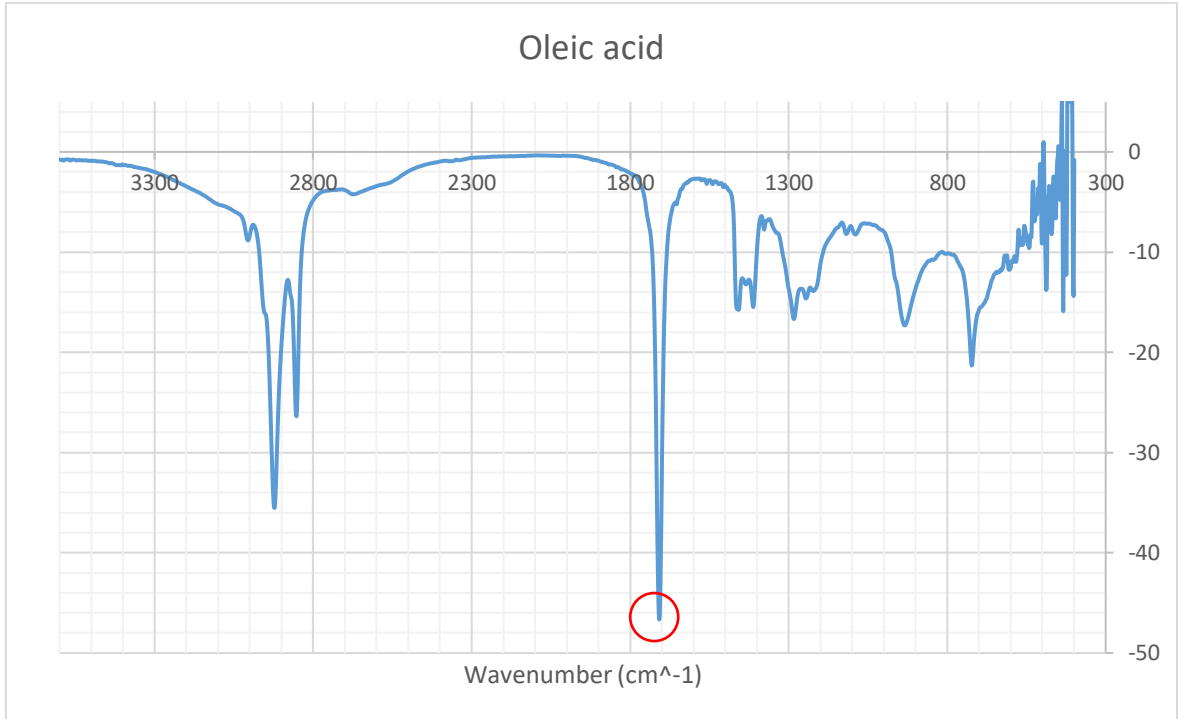


Figure 2.6: IR spectra oleic acid

In the oleic acid spectra two sharp bands at 2920 and 2850 cm^{-1} were attributed to the asymmetric CH₂ stretch and the symmetric CH₂ stretch, respectively. The intense peak at 1700 cm^{-1} (inside the red circle) was derived from the existence of the C=O stretch, and the band at 1290 cm^{-1} exhibited the presence of the C–O stretch. The O–H in-plane and out-of-plane bands appeared at 1462 and 937 cm^{-1} , respectively.

The spectra for the coated nanoparticles are:

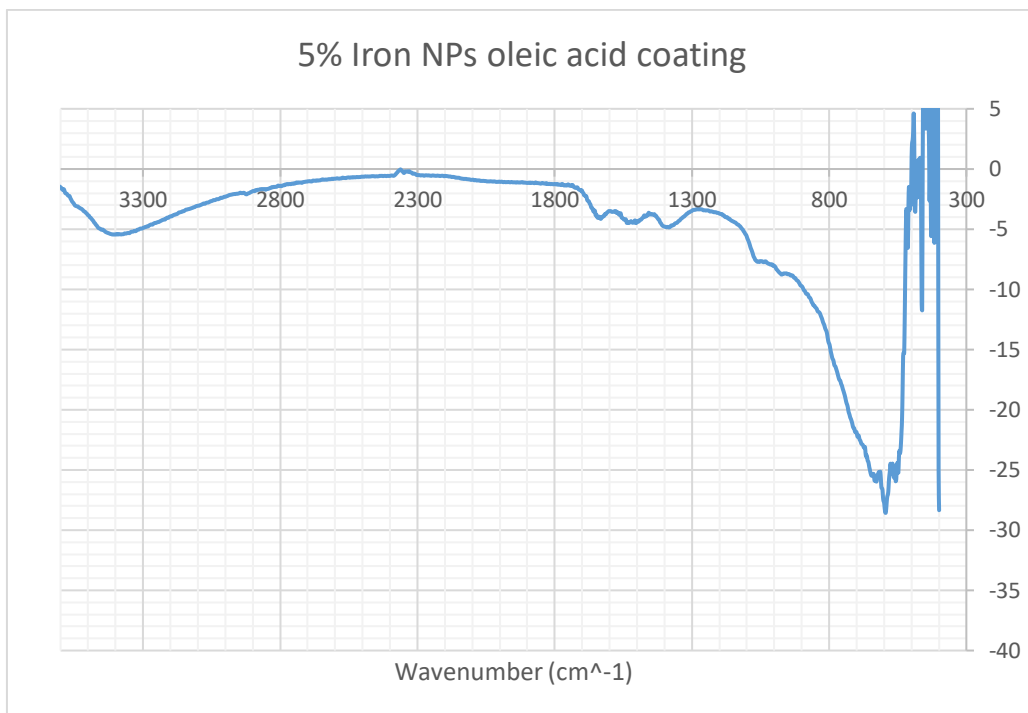


Figure 2.7: IR spectra 5% coating

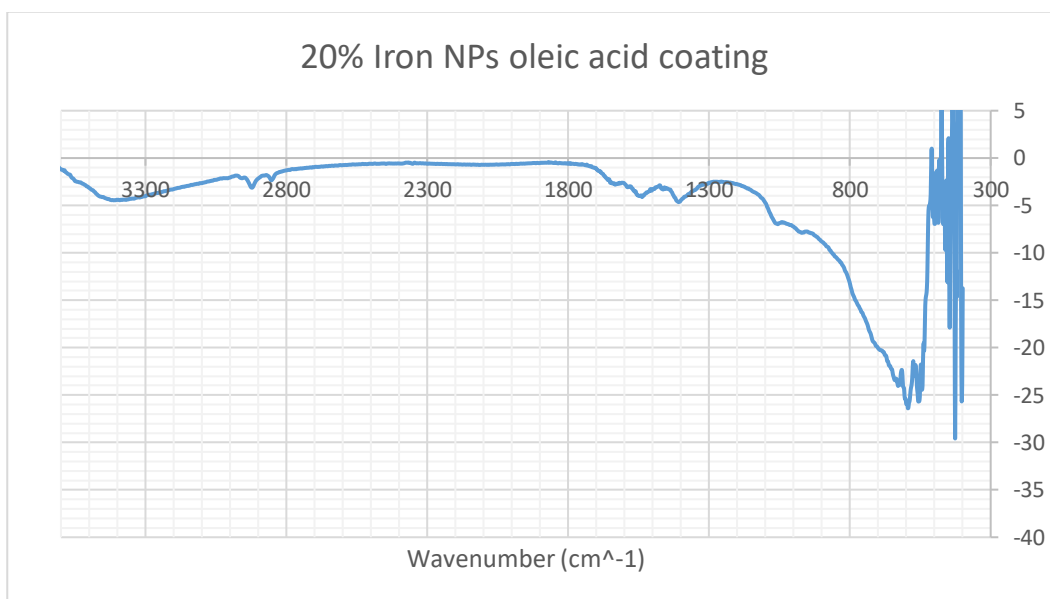


Figure 2.8: IR spectra 20% coating

In both cases, it can be seen that the peaks at 600 and 400 cm^{-1} still appear. The asymmetric CH_2 stretch and the symmetric CH_2 show small peaks at approximately 2920 and 2850 cm^{-1} , respectively. Two bands at 1550 and 1650 cm^{-1} , which were characteristic of the asymmetric COO^- and the symmetric COO^- stretch, instead. A strong adsorption at

1050 cm^{-1} arises from C-O single bond stretching. As expected, the peak at 1700 cm^{-1} disappeared for the coated nanoparticles. It is worth mentioning also some characteristics concerning the carbon carbon double bond present in the oleic acid. Weak small peaks are expected between 1700-1680 cm^{-1} due to the C=C stretching. Also a stronger peak is expected between 980-960 cm^{-1} corresponding to the C=C bending. Both of these features appear more noticeable in the 5% spectra.

2.2.3 Coating verification: Conclusion

According to the results obtained in the first test, the iodine value, the presence of oleic acid in the supernatant was negligible in all cases. It is clear that the absence of oleic acid in the supernatant can only mean that it is present together with the iron oxide nanoparticles.

The second analysis, the IR verification, allowed the verification of the nature of the interaction between the nanoparticles and the oleic acid. If the oleic was merely adsorbed in the solid surface, the characteristic peak of the carbonyl group would have been easily noticeable. The nonappearance of that peak, together with other characteristics, indicate that the oleic acid is covalently bonded to the surface of the nanoparticles.

2.3 Magnetic fluids

The magnetic fluids employed included different kinds of oleic acid coating in the particles surface as it was seen before and one that contained benzoic acid. The particles were synthesized and washed to remove the sodium hydroxide excess. Finally, water was added to obtain 10% solutions (weight in volume).

- 0%: This represent the uncoated nanoparticles, without any presence of oleic acid. This solution was the darkest one and it has a higher surface tension than the other ones (When it was dropped into a flat surface it formed droplets with smaller

amount with respect to the coated nanoparticles, and also this fluid did not wet the plastic container);

- 1% oleic acid;
- 3% oleic acid;
- 5% oleic acid;
- 20% oleic acid;
- 10% Benzoic acid.

The magnetic fluids that were coated, presented some physical differences that were noticeable with respect to the uncoated one. As mentioned before, the surface tension of the uncoated one was higher, when a strong agitation of the fluid was induced, the walls of the plastic container turned black for a small amount of time. On the other hand, for the coated ones, under the same disturbance, the walls remained black for very long periods of time. Also, the 0% magnetic fluid remained as a homogenous solution even when it was undisturbed for days. The coated ones, after a long period of time, tend to precipitate on the bottom of the container forming two phases. It actually makes sense since the cohesive interactions between the water and the nanoparticles are smaller when an organic wall is introduced between these two.

After the magnetic fluid was introduced into the water to be treated, the nanoparticles interacted with the pollutants thanks to the lipophilic interactions between those two. This interaction promotes the agglomeration of the pollutants, covering the surface of the magnetic nanoparticles. After a designated interval of time, the separation of the phases was needed. However, the nanoparticles are of course too small, and the force of gravity is not effective for the precipitation. The Brownian motions associated to these particles are quite important due to their small sizes. For this reason, it is necessary the introduction of a force field that can effectively separate the phases. Taking advantage of the magnetic properties of the nanoparticles, an external magnetic field is chosen via a magnet. By making use of this last one, the separation can be done in matter of tens of seconds to some minutes.

The effectiveness was promoted by favouring the contact between the particles and the sample via agitation, increasing the kinetic energy of the fluid has a significant effect. A magnetic stirrer was employed to fulfil this requirement.

2.4 Operative conditions

The conditions in which the process is run have a significant effect in the amount of pollutants that are extracted from the sample. The conditions that have to be taken into account are:

1. Quantity of nanoparticles employed. This is expressed in the concentration of particles per volume of sample. In other words, grams of particles divided liters of solution.
2. pH of the solution. It is important to have a neutral to basic condition.
3. Contact time. In industry it is desired to have the smallest contact time possible, this will save costs in terms of the sizes of the units.
4. Agitation.

2.4.1 pH influence

When the synthesis of the nanoparticles is performed, a large excess of sodium hydroxide is used in order to guarantee the complete consumption of the other reagents. This situation leaves a final high concentration of the unreacted OH⁻ ions.

The pH is the cologarithm in base 10 of the concentration of ions H⁺. The concentration of H⁺ and OH⁻ is linked through the dissociation of water.



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A neutral situation has a concentration of H^+ of 10^{-7} mol/L, or $[H^+]=10^{-7}$ mol/L. The same concentration value for ions OH^- in accordance with the equilibrium constant. This situation has a $pH=7$.

A basic pH is higher than 7, and an acid one is lower than 7.

As it was said before, an excess of sodium hydroxide was employed. After the synthesis the pH was measured with a pH indicator, giving strong basic medium.

The pH has a very important effect when it comes to the nanoparticles stability.

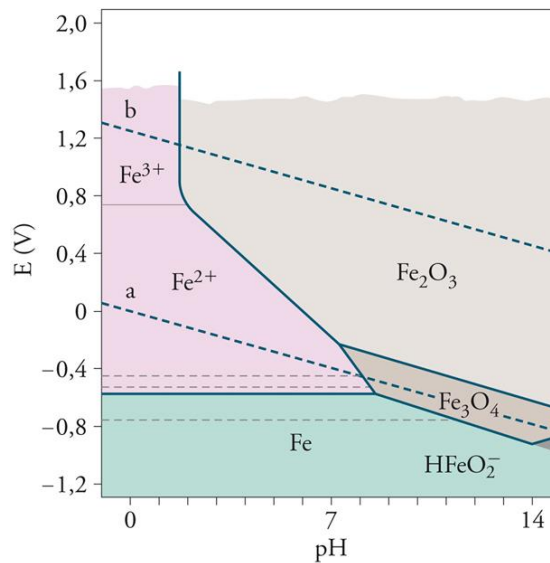


Figure 2.9: Pourbaix diagram for iron.

The picture above is the Pourbaix diagram, in which it is represented the possible forms iron can exist. The stability of those forms depend on the pH of the medium. The one that is desired for the purpose of this work is the one in the bottom left (Fe_3O_4).

An acid pH is unfavorable for our purposes (a pH bellow 7). For example, when a strong acid is added to the nanoparticles, they will dissolve in the solution forming ions Fe^{3+} and Fe^{2+} making them completely useless when it comes to the water treatment.

2.4.2 Contact time and agitation influence

When the particles are in contact with the polluted sample, the adsorption process starts. Due to the nature of the nanoparticles, the adsorption process is thermodynamically

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favoured, however it is needed time in order to reach the equilibrium. This process follows a kinetic mechanism in which the magnetic nanoparticles are in continuous motion and they impact with water molecules but also with the different lipophilic pollutants, these last ones can be adsorbed into the surface of the nanoparticles.

The importance of the agitation comes from the relative velocity of the nanoparticles. When this velocity is increased the probability of collision is increased significantly, this effect was noticed in the results of this work.

There is also a compromise situation between contact time and concentration of nanoparticles. When a small contact time is required, for example a small volume for the mixing, the concentration of the nanoparticles should be increased in order to obtain the same effects. Conversely, if the amount of nanoparticles wants to be minimized, the contact time should be increased.

3 MATERIALS AND METHODS

In this chapter, a brief description about the materials and methods that were employed during both synthesis and analysis of the nanoparticles purification characteristics.

3.1 Sonicator

Due to the different nature of the molecular interactions intrinsic to water and oil molecules, these particles experience repulsion from each other. The result is large agglomerations of water molecules on one side and oil or organic molecules on the other side. In other words the final solution is not homogeneous, it separates in organic and polar phase. Nevertheless a small amount of water is dissolved in the organic phase and similarly a small amount of oil is dissolved in water.

The presence of certain functional groups in the hydrocarbon mixture can greatly improve the solubility of the oil phase, in some cases making it completely soluble. For example, ethanol or acetic acid, 2 carbons present in the molecule structure, are completely soluble in water due to the possibility of hydrogen bonds with water.

However, oils usually treated with water in different processes have larger carbon chains, increasing the organic nature of the overall interaction, therefore, reducing the solubility in water.

As the efficiency of the nanoparticles needs to be tested, then an appreciable quantity of organic molecules needs to be dissolved in the polar phase.

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Sounds is a wave of alternating high and low pressure. The frequency of a sound wave is how often the particles of a substance vibrate when the sound wave passes through it. Sonication typically uses ultrasound waves with frequencies of 20 kHz (20.000 cycles per second) or higher. These frequencies are above what human can perceive, even though ear protection is still recommended during sonication because the process generates loud screeching noises. The greater the frequency, the stronger the agitation of the particles. During sonication, cycles of pressure form thousands of microscopic vacuum bubbles in the solution in a process known as cavitation. This causes powerful waves of vibration that release an enormous energy force in the cavitation field, which disrupts molecular interactions such as interactions between molecules of water, separates clumps of particles, and facilitates mixing.

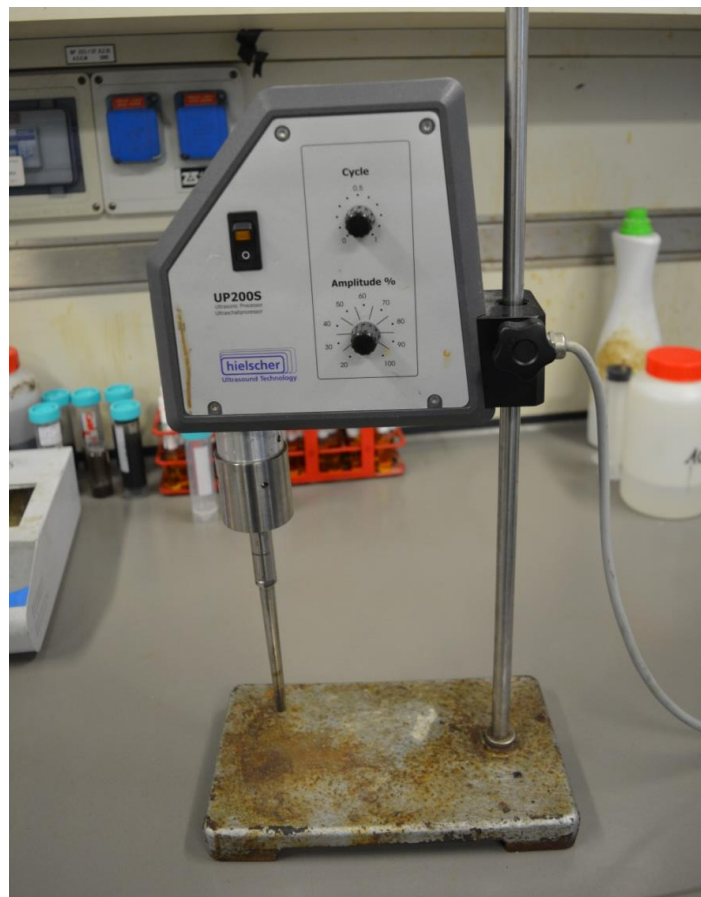


Figure 3.1: Sonicator employed

The sonicator that was employed is shown above. The interest sample was first agitated with a magnetic stirrer for some minutes and then the sonicator was employed together with the mixing during a time varying from 10 to 15 minutes. Once finished, the samples were collected in vials with a capacity of 20 ml.

3.2 Magnetic stirrer

It is a device that employs a rotating magnetic field to cause a stir bar immersed in a liquid to spin, thus stirring it. The rotating field may be created either by a rotating magnet or a set of stationary electromagnets, placed beneath the vessel with the liquid.

The efficiency of the mixing directly depends on the frequency of the rotating field and of the size and shape of the stir bar. A bigger bar generates higher liquid velocities for the same rotating frequency of the magnetic field.

The magnetic stirrer was frequently used for this work. It was used in the pretreatment of the samples, with or without the sonicator, and also during the mixing of the sample water with the selected nanoparticles. Also it was used during the synthesis of the nanoparticles; during the preparation of the reagents and also to guarantee homogenization during the synthesis itself.

Indeed, during the treatment of the sample with the nanoparticles, the mixing plays a major role in the efficiency. A good mixing will guarantee an optimal contact between the nanoparticles and the pollutants. Another important consideration to take into account is to provide the same stir bars for every vial during the treatment, this together with the same frequency of rotation and contact time, gives the same mixing conditions for every test during a particular analysis. This last factor mentioned is not minor, indeed this reduces the fluctuations and uncertainties.

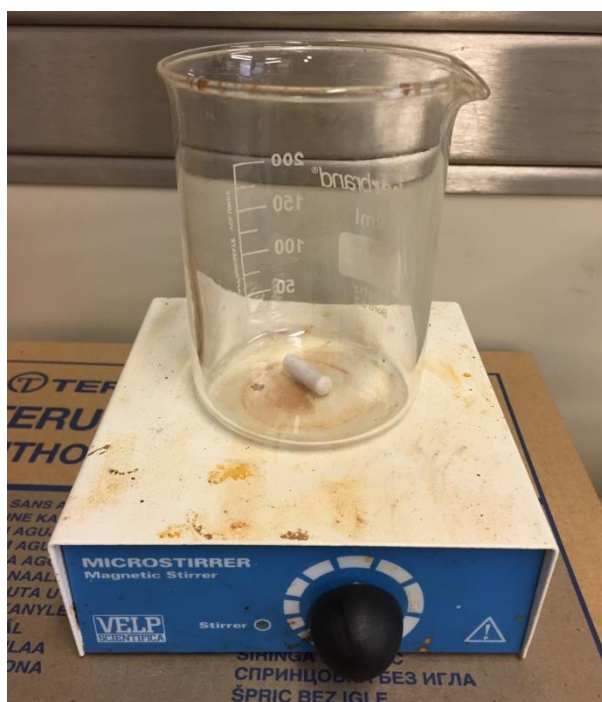


Figure 3.2: Magnetic stirrer with beaker and stir bar.

3.3 Dry bath

The COD measurement takes place thanks to the oxidation reaction that was described before and it requires high temperatures for a relative long period time: 150°C for 2 hours. This conditions are sustained thanks to a dry bath with 12 holes designed to hold the tubes in position, achieving a total contact between the tube wall and the metal surface.

The dry bath used for this work was a FB15103 by Fisher Scientific.



Figure 3.3: Dry bath used.

3.4 Multiparameter spectrophotometer with COD

Spectrophotometry is a quantitative analysis of molecules depending on how much light is absorbed by colored compounds. Spectrophotometers measure a light beam's intensity as a function of its wavelength. The basic principle is that each compound absorbs or transmits light over a certain range of wavelength. This measurement can also be used to measure the amount of a known chemical substance.

The process of measurement is usually done first with a calibration curve, samples with a known concentrations are used in order to obtain values of the Absorbance, where:

$$A = \text{Absorbance} = -\log(\text{Transmittance}) = -\log\left(\frac{I}{I_0}\right)$$

And according to the Beer-Lambert Law:

$$A = -\log\left(\frac{I}{I_0}\right) = \epsilon Lc$$

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Where:

- ϵ = is the molar extinction coefficient, it is a measurement of how strongly a chemical species attenuates light at a given wavelength. It is an intrinsic property of the species.
- L = the path length.
- I_0 = the intensity of the incident beam.
- I = intensity of the beam after the absorption.
- c = is the concentration of the interest species.

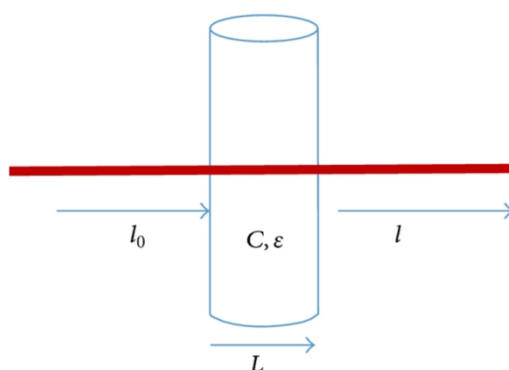


Figure 3.4: Beer-Lambert Law.

As mentioned in the previous chapter, the vials prepared by Hanna Instruments® were used. With them it was possible to skip the step involving the calibration curve. Instead a blank test is required, the volume required for each vial containing the dichromate is filled with distilled water.

Once the oxidation process is completed, in other words after the 2 hours at 150°C the vials, the vials are inserted into the spectrophotometer shown below.



Figure 3.5: Spectrophotometer with COD HI83399.

This device uses a tungsten lamp, controlled by a microprocessor, emits a beam that is As a final remark it is worth mentioning that the vials surface was carefully cleaned before each run. If the surface of the wall is dirty or scratched the results may significantly change.

3.5 Magnets

As it is expected, the external magnetic field is essential as its interaction with the nanoparticles will result in the driving force that produce a rapid sedimentation. The magnets used contained iron and neodymium coated with nickel. Neodymium magnets are very strong magnets. However, pure neodymium has a extremely low Curie temperature of 19 K, above this temperature the magnetic behavior disappears. It is for this reason that neodymium magnets contain a mixture of neodymium and transition metals, for example iron.

Another important factor is the coating, as neodymium tends to be oxidized by oxygen if it is untreated. For this reason it is coated with a protective layer of nickel.



Figure 3.6: Neodymium magnet.

4 RESULTS

The tests were run in a Batch way. The sample water was pretreated as it was mentioned before and then 20 ml were taken and a determined volume of nanoparticles was injected. Subsequently, the agitation step was performed during a determined amount of time. In the end the external magnetic field was applied to properly separate the phases, and the COD measurement was performed.

All the fluids employed had a concentration of 10% weight in volume. In all cases they are micro-sponges aggregated in nanoparticles with a magnetic core.

<i>Name of the magnetic fluid</i>	Description
0%	No oleic acid employed, pure iron nanoparticles.
1%	1% in weight oleic acid (coating). 99% iron oxide.
3%	3% in weight oleic acid (coating). 97% iron oxide.
5%	5% in weight oleic acid (coating). 95% iron oxide.
10%	10% in weight oleic acid (coating). 90% iron oxide.
20%	20% in weight oleic acid (coating). 88% iron oxide.
R	10% in weight benzoic acid (coating). 90% iron oxide

Table 4.1. Description of the magnetic fluids employed.

In some cases, additional treatments were employed for the nanoparticles. Such as distillation to remove any traces of ethanol employed during the synthesis (ethanol can be oxidized, meaning that it can potentially increase the COD value) as it was explained before.

Chapter 4: Results

As it was previously mentioned, the removal efficiency of a specific fluid can be quantified by the difference between the COD value pretreatment and the COD value after the treatment with the magnetic particles.

The removal efficiency will be measured as a percentage, according to the following formula:

$$\varepsilon = \frac{COD_i - COD_f}{COD_i}$$

This value ranges between 0 and 1. When is equal to 1, a complete removal of the pollutants was achieved. A value equal to 0 means that it was completely inefficient, the nanoparticles did not adsorb any pollutants.

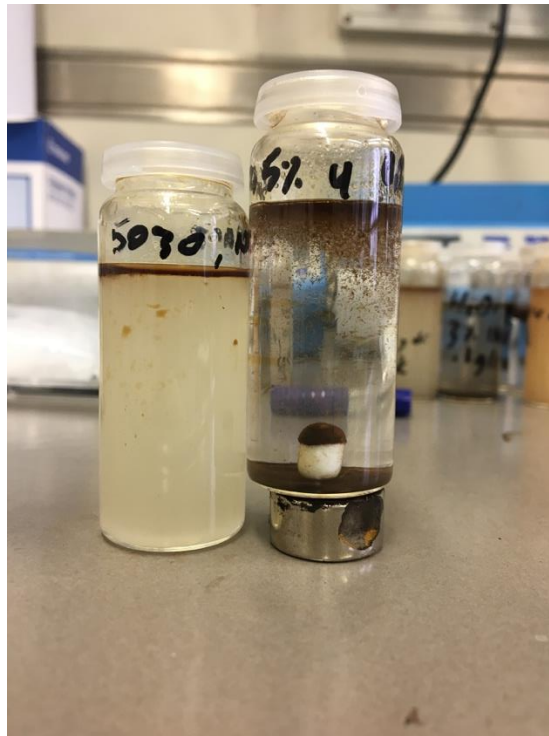


Figure 4.1: Sample water vs treated water.

In the picture shown above, it is evident the cleaning due to the nanoparticles. In this case the initial sample was 5000 ppm wastewater after sonication stage. The other one was treated with 0.5 g/L nanoparticles with 5% oleic acid coating for 20 minutes. This coating showed the best results, even though the other ones exhibited low COD values as well.

The volume of magnetic fluid required is obtained with the following formula:

$$C_{req} = \frac{C_{np} V_{np}}{V_{sample} + V_{np}}$$

Where C_{req} is referred the final required concentration of the nanoparticles in the sample. C_{np} is the concentration of the nanoparticles in the magnetic fluid (always 10% weight in volume, 100 g/L). V_{sample} is the volume of the sample, always 20 ml. And finally, V_{np} is the volume that has to be added to the sample of interest.

With the proper mathematical derivation, the volume needed is:

$$V_{np} = \frac{V_{sample}}{\frac{C_{np}}{C_{req}} - 1}$$

It can also be assumed that the volume of the nanoparticles solution (always below 0.3 ml) is negligible with respect to the volume of the sample (20ml), a very reasonable hypothesis. By doing so, the formula obtained is:

$$V_{np} = \frac{C_{req}}{C_{np}} V_{sample}$$

For a concentration of 1g/L, a volume of: 0.202 ml is required with the formula without the simplification, 0,200 ml with the simplification.

4.1 Controlled samples

In order to better understand the efficiency of different type of particles in removing chemicals of various nature, samples containing hydrocarbons with a specific nature were prepared. By doing so, the results obtained are expected to show more clearly how the nanoparticles interact with the different groups.

For the choosing procedure, some considerations were taken into account.

For this tests, the medium range COD vials were used. Therefore, it was necessary to choose an amount of sample that would not be give a COD higher than the upper limit (1500 mg O₂/L) but also a sufficiently high value in order to facilitate the comparison of removal efficiency.

By using the formula of the COD value for a sample in which the molecular formula is known, it is possible to obtain an expression that indicates the amount of sample that

should be provided for a desired value of COD. The expression used was obtained from the definition of COD and reorganizing the expression.

For a compound with a generical chemical formula $C_nH_aO_bN_c$, the mass of the chosen hydrocarbon is:

$$m_{HC} = \frac{COD_{req} Mr_{HC}}{\left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right) Mr_{O_2}}$$

4.1.1 Controlled samples: Diethyl ether

Diethyl ether was chosen because it is a slightly polar compound due to the oxygen present in the structure, however it is not as polar as an alcohol, because it cannot form hydrogen bonds. In other words, it has certain polarity which simplifies the dissolution in water, but it has also a strong organic behavior (diethyl ether is commonly used as solvent for waxes, fats, oils, etc.).

Effectively, the solubility in water is 60 g/L. Therefore, very high COD values are possible.

In saturation condition, the COD value is higher than $1.5 \cdot 10^5$ mg O₂/L.

A COD value target of 1300 mg O₂/L was desired; this value corresponds to a concentration of diethyl ether of 0.5 g/L. The obtained value of COD was 1160 mg O₂/L. This smaller value is assigned to the partial evaporation of the diethyl ether in the pretreating stage. When the sample was being prepared, the characteristic smell of diethyl ether was easily distinguished.

The test was run for 30 minutes with small magnets, the particle concentration was 1 g/L and different kinds of coatings were used. The following values were obtained:

	Test 1	Test 2	Test 3	Average (mg O ₂ /L)	Std. Dev.	Efficiency (%)
0%	736	740	741	739	2,6	36,29
5%	440	438	434	437	3,1	62,30

20%	573	571	567	570	3,1	50,83
R	340	338	341	340	1,5	70,72

Table 4.2. Controlled sample: water-diethyl

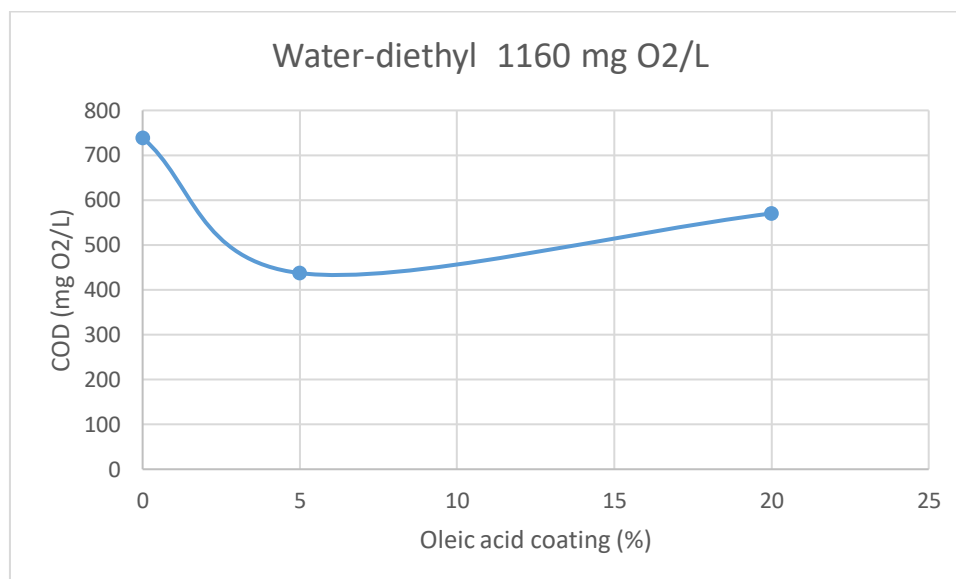


Figure 4.2: Nanoparticles in water-diethyl ether.

The polarity of the ether gives a better interaction with the aromatic rings present in the coating, compared to the coatings that only have the lipophilic chains of oleic acid.

4.1.2 Controlled samples: 2-methyl-1-pentanol

An alcohol was tested as well. However, it was desired an alcohol with a relatively long lipophilic chain, consequently this alcohol was selected. This is a carbon 6 branched alcohol. The solubility in water of this compound is 6 g/L. At the saturation condition, the COD value is higher than 16,000 mg O₂/L. So, with the proper dilution, it is possible to use this solution. For this case, individually, it was chosen to use a more concentrated solution of alcohol with respect to the one that would give 1300 mg O₂/L. A solution of 1800 mg O₂/L was desired and for this case.

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The test was run for 30 minutes with small magnets, the particle concentration was 1 g/L and different kinds of coatings were used. The following values were obtained:

	Test 1	Test 2	Test 3	Average (mg O ₂ /L)	Std. Dev.	Efficiency (%)
0%	1081	1081	1075	1079	3,46	37,27
5%	712	719	717	716	3,61	58,37
20%	890	896	882	889	7,02	48,29
R	954	949	951	951	2,52	44,69

Table 4.3. Control sample alcohol

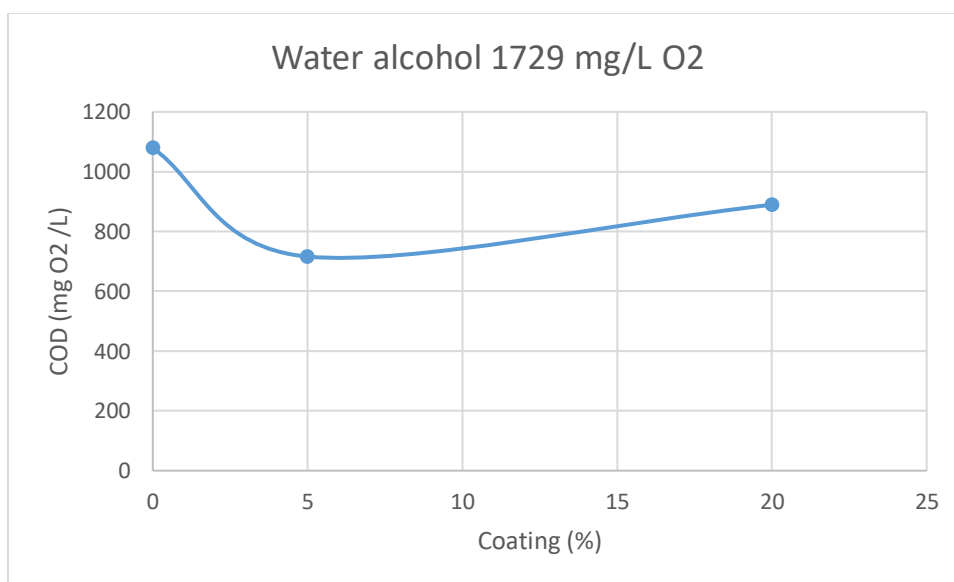


Figure 4.3: Nanoparticles in water-alcohol.

For this case, the oleic coating did a better job showing that the interactions between the relatively long hydrocarbon chain of the alcohol and the oleic acid was higher than the one of benzoic acid and the alcohol. The efficiency was higher with the 5% oleic acid coating.

4.1.3 Controlled samples: Toluene

Toluene was chosen because it is a very popular and simple aromatic component. It has been used for many applications, for example it is widely used as a solvent.

Due to the electrons present in the aromatic ring, aromatics have a greater interaction with water molecules compared to the saturated hydrocarbons with water. The solubility of toluene in water at 20°C is 0.52 g/L, on the other hand methylcyclohexane (same structure but saturated) has a solubility much smaller than this value: 0.014 g/L at 15°C.

If the later was used to measure the efficiency, a technical problem would arise. The COD value in the saturation condition is still too low. Applying the formula, a theoretical maximum COD value of 48 mg O₂/L would be obtained. For toluene, however, the maximum value that can be obtained is: 1627 mg O₂/L. Therefore, it is physically easier to check the efficiency using an aromatic compound. Additionally, as aromatics are widely present in many applications, it is interesting to analyze this case and not the one of the cyclic saturated compound.

By using the formula described before, the value of COD chosen is 1300 mg O₂/L, this value corresponds to a concentration of toluene of 0.415 g/L. The obtained value of COD was 1292 mg O₂/L.

The test was run for 30 minutes with small magnets, particle concentration was 1 g/L and different kinds of coatings were employed. the following values were obtained:

	Test 1	Test 2	Test 3	Average (mg O ₂ /L)	Std. Dev.	Efficiency (%)
0%	840	838	835	838	2,5	35,17
5%	634	631	628	631	3,0	51,16
20%	703	701	707	704	3,1	45,54
R	486	479	480	482	3,8	62,72

Table 4.4. Controlled sample: Toluene

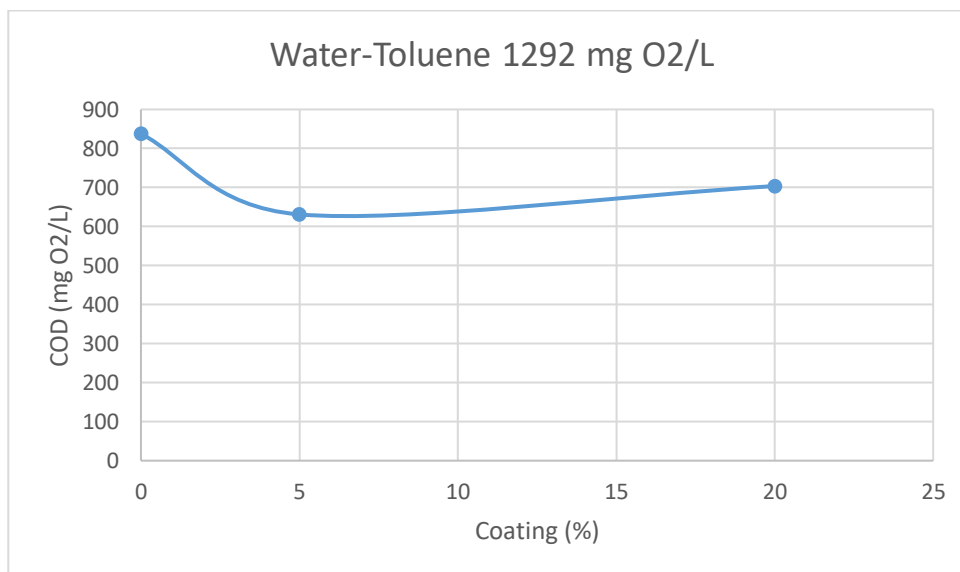


Figure 4.4: Nanoparticles in water-toluene

The nanoparticles coated with benzoic acid showed a better performance with respect to the oleic acid coated ones and the one without coating. The COD value obtained was 482 mg O₂/L with the highest efficiency 62.7%.

According to those results, an expectable situation was obtained. The coating with similar nature to the impurity (toluene) had a better performance than the other ones.

4.2 Sample: Waste water 5000 ppm.

This sample was prepared with a common lubricating oil and tap water in a concentration of 5000 mg/L. After several minutes of strong agitation and performing the sonication treatment. The sample was ready to be tested with the different magnetic fluids.

In this tests, the treatment was performed with the oleic acid magnetic fluids: 0%, 1%, 3% and 5%.

The results obtained with these series of tests, were very important and allowed to understand the big importance the agitation has when the treatment is taking place.

For the first test, the parameters were:

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- Concentration of nanoparticles: 0,25 g/L
- Contact time: 20 minutes.

The COD value of the solution without treating was 4944 mg O₂/L.

	Test 1	Test 2	Test 3	Average (mg O ₂ /L)	Std. Dev.	Efficiency (%)
0%	1136	1142	1162	1147	13,61	76.9
1%	2798	2798	2777	2791	12,12	43.5
3%	1070	1048	1062	1060	11,14	78.5
5%	1760	1793	1766	1773	17,58	64.4

Table 4.5. Sample water 5000 ppm

The COD values obtained after the treatment are plotted in the following graph:

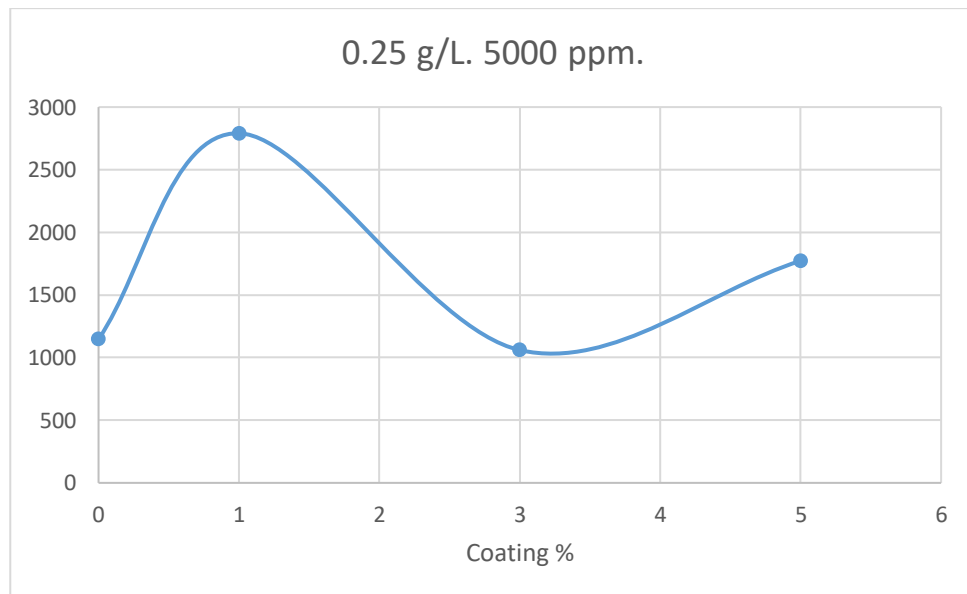


Figure 4.5: Waste water 5000 ppm treating with different magnetic fluids.

The next day the same exam was performed with the same conditions of concentration and contact time. The only parameter that was changed was the size of the magnetic

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stirrers employed. Big magnetic stirrers were used that allowed the formation of a bigger vortex, in other words, a better mixing.

	Test 1	Test 2	Test 3	Average (mg O ₂ /L)	Std. Dev.	Efficiency (%)
0%	0	0	0	0	0	100
1%	109	109	116	111,3	4,04	97.7
3%	0	0	0	0	0	100
5%	64	64	55	61	5,2	98.7

Table 4.6. Sample water 5000 ppm, good mixing

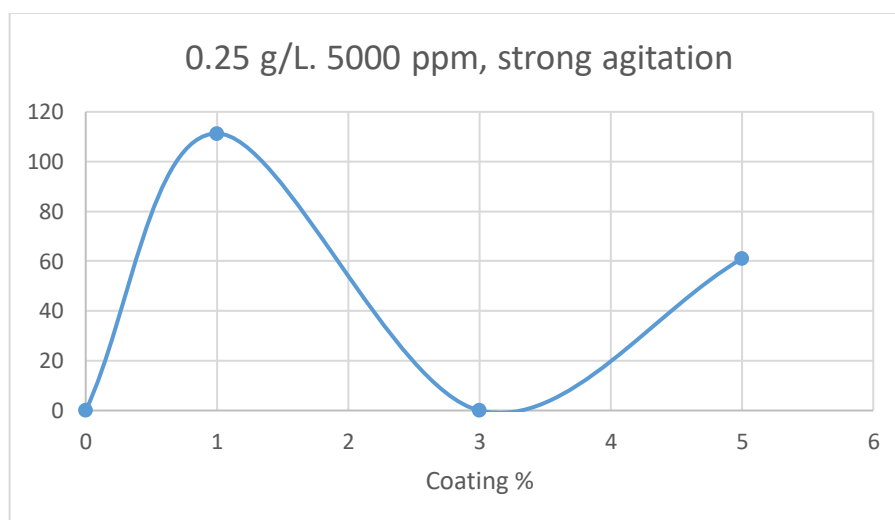


Figure 4.6: Waste water 5000 ppm treating with different magnetic fluids. Strong agitation.

The difference is significant and it had an important effect in the way the subsequent analysis were run. After this results were obtained, the agitation conditions were carefully controlled, paying special attention that every single vial would have the same conditions (revolutions per minute and size of magnetic stirrer).

4.3 Sample: Industrial wastewater.

After understanding the behavior of different type of magnetic particles in relationship with the nature of the waste, some industrial wastewater were treated according the nature of their pollutants. The waste water samples were purchased from a plant who produces heavy oil lubricants. In this experimental part the relationship between the amount of particles used and contact time against the treatment efficiency was investigated. In all cases the linear coating was the oleic acid at 5% and the aromatic one was benzoic acid at 10%.

4.3.1 Industrial wastewater: linear pollutants

This waste water contains mainly linear compounds, so according the previous results magnetic particles coated with oleic acid were used for the treatment. For comparison, a series of tests using particles without coating and the aromatic coating were done. The value of COD of the un-treated sample is 3500 mg O₂ / L.

<i>Wastewater with linear pollutants</i>						
COD START : 3500 mg O₂ / L						
Dosage : 250 ppm						
Contact time [min]	COD after treatment mg O₂ / L				Average COD mg O₂ / L	Efficiency (%)
10	1078	1065	1098	1091	1083	69
20	655	625	644	635	639.7	81.7
30	218	220	225	209	218	93.8
Dosage : 500 ppm						
10	609	604	615	622	612.5	82.5
20	401	399	408	415	405.8	88.4
30	184	189	171	182	181.5	94.8
Dosage : 1000 ppm						
10	415	421	408	402	411.5	88.2
20	351	362	349	355	354.3	89.9
30	103	109	118	111	110.3	96.9

Table 4.7. Industrial wastewater linear pollutants

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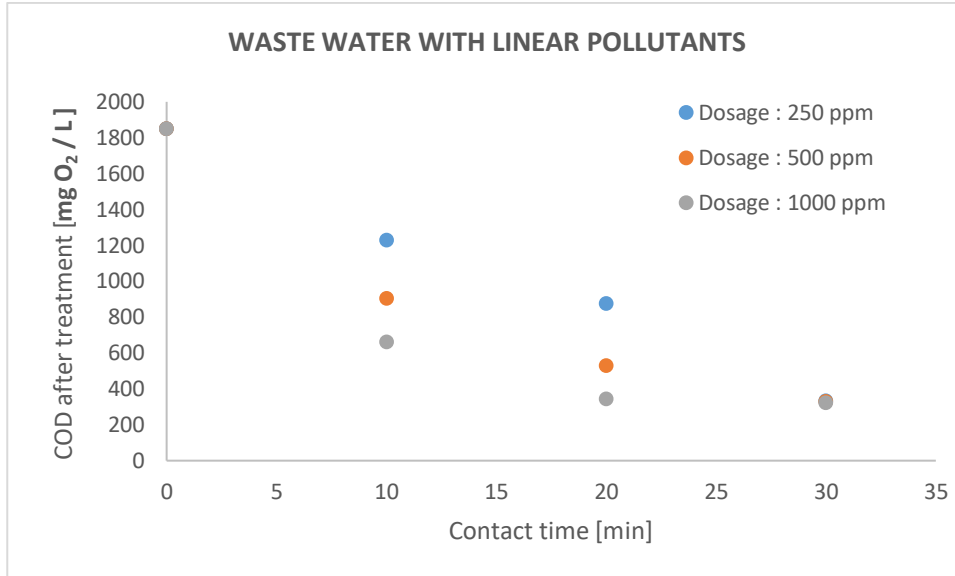


Figure 4.7: Waste water with linear pollutants and nanoparticles

Treatment test by using non coated particles and particles coated with an aromatic compounds were done only using the higher dosage and contact time. The COD values obtained after treatment were respectively 1254 mg O₂ / L (efficiency 64.2%) and 654 mg O₂ / L (efficiency 81.3%).

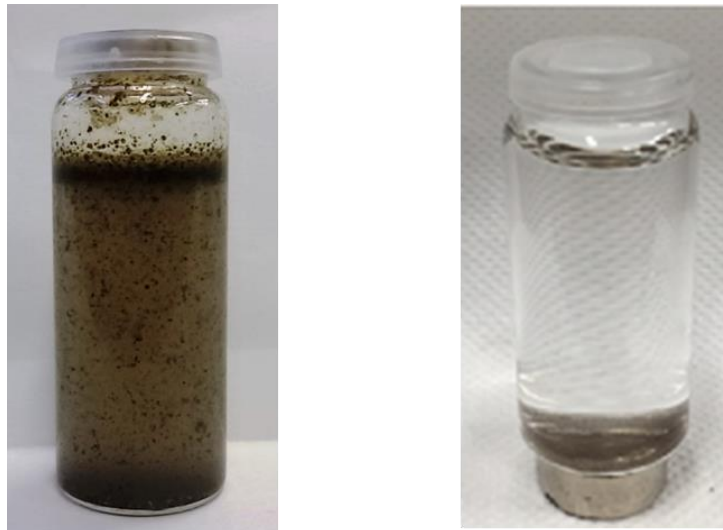


Figure 4.8: Treatment performed with the nanoparticles coated with oleic acid

The bare nanoparticles and aromatic coated ones performed certain cleaning but not as good as the oleic acid coated ones. The better results were obtained when the oleic acid

was employed, obtaining an efficiency of almost 97% for the same conditions of time and concentration, in accordance to the similar nature (linear compounds) of the coating and pollutant that was described in the first section 4.1.

The time effect is clearly seen in the figure 4.6 showing the negative trend of the COD values as it was expected.

4.3.2 Industrial wastewater: aromatic pollutants

This waste water contains mainly aromatic compounds, so according the previous results magnetic particles coated with benzoic acid were used for the treatment. For comparison a test using particles without coating and a linear coating were performed. The value of COD of the un-treated sample is 1850 mg O₂ / L.

<i>Wastewater with aromatic pollutants</i>						
<i>COD START : 1850 mg O₂ / L</i>						
Dosage : 250 ppm						
<i>Contact time [min]</i>	COD after treatment mg O₂ / L				Average COD mg O₂ / L	Efficiency (%)
<i>10</i>	1212	1235	1248	1234	1232.3	33.4
<i>20</i>	888	874	869	881	878	52.5
<i>30</i>	351	318	334	341	336	81.8
Dosage : 500 ppm						
<i>10</i>	912	899	904	908	905.8	51
<i>20</i>	541	534	518	527	530	71.4
<i>30</i>	318	341	333	339	332.8	82
Dosage : 1000 ppm						
<i>10</i>	598	584	581	891	663.5	64.1
<i>20</i>	355	352	328	354	347.3	81.2
<i>30</i>	309	325	321	336	322.8	82.6

Table 4.8. Industrial wastewater: aromatic pollutants

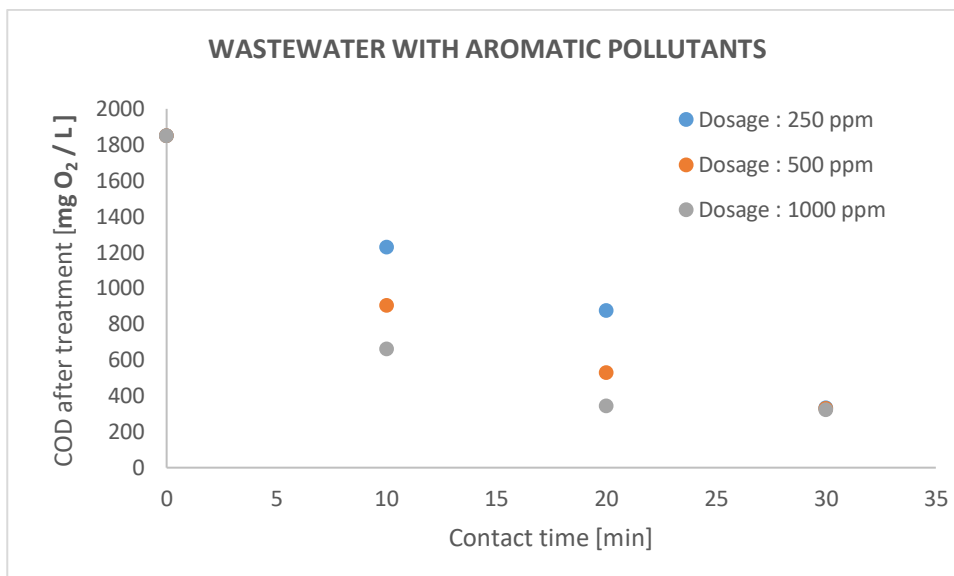


Figure 4.9: Waste water with aromatic pollutants and nanoparticles

Treatment test by using non coated particles and particles coated with a linear compound were done only using the higher dosage and contact time. The COD values obtained after treatment were respectively 1098 mg O₂ / L (efficiency 40.6%) and 810 mg O₂ / L (efficiency 56.2%).

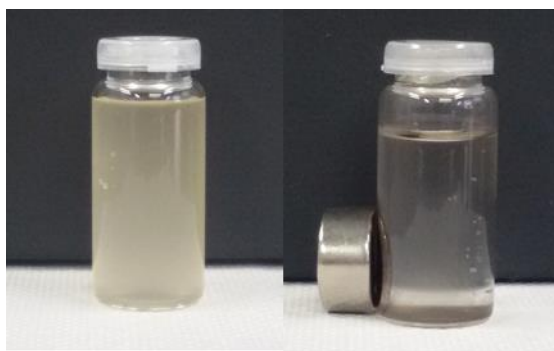


Figure 4.10: Treatment performed with the nanoparticles coated with benzoic acid

Similarly as in section 4.3.1, the better results were obtained when the particles with similar nature were employed (the aromatic coating) obtaining an efficiency value of 82.6%, significantly higher than the uncoated nanoparticles and the ones containing the

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oleic acid. Again, the effect of time was clearly noticeable with the same trend as in section 4.3.1 as it was expected.

5 CONCLUSIONS

The aim of this work was to verify the behavior of different coating percentages and types when exposed to water polluted with hydrocarbons of different nature.

After the synthesis different techniques were employed, aimed to the purification of the recently synthesized nanoparticles. Techniques such as heating or distillation, in which the evaporation of the most volatile species was exploited, showed positive results reducing the value of the COD associated with the nanoparticles.

Another important point that was needed to corroborate was the presence of the coating in the nanoparticle surface, by the presence of a covalent bond between these two.

The first method based on the use of the Iodine Value, was meant to answer the question: Is the coating substance present in the supernatant? If yes, on which amount? The result of this test was highly positive, showing that the coating was not in the supernatant, demonstrating that it was attached to the nanoparticles.

As for the second method, the question that was meant to answer, was related to the previous one: Is the coating species attached to the nanoparticle due to a chemical bond? If the species has an interaction of a physic origin with the nanoparticles surface, it will not be effective as a coating. The chemical bond is wanted in order to form the nanoparticle structure that was shown before (Figure 2.1). The method used in this case was the IR spectroscopy. As exposed in the analysis of the graphs in section 2.2, it is possible to confirm that the coating species is effectively attached by a coordinate covalent bond as desired.

Chapter 5: Conclusions

Following to the experimental tests, different samples were employed and certain variables were changed which allowed to obtain some conclusions. The performance of the nanoparticles greatly depends on:

- The concentration of the nanoparticles;
- The contact time;
- The agitation;
- Nature of the coating

With the controlled samples tests (section 4.1), it was quite noticeable the fact that a coating that shared a similar nature to that of the pollutant would have a better, and therefore, stronger interaction. Ultimately reflected in the better performance for one kind of coated nanoparticles than other. Also it is important to mention that the nanoparticles with 5% coating showed better results than the other ones, being this one the optimal coating found for this sample.

However useful the previous test was, in industry a situation where the effluent has only one component as a pollutant is not a realistic. It was, therefore, interesting to analyze the case of industrial wastewater (section 4.3), where the sample contained a mixture of different components. In this case, certain knowledge regarding the composition of the sample was available. In one case the sample was richer in aromatics and in the other one in linear hydrocarbons. The results with the nanoparticles treatment were similar to those obtained for the controlled samples, in other words, coatings with similar nature to the pollutants showed a greater affinity towards them.

Another important remark about the test involving the industrial wastewater, is that the role of both the contact time and the concentration of the particles can be graphically noticed (section 4.3). By increasing the concentration of nanoparticles, the treatment process is faster, which in industry would mean a reduction of the sizes of the units involved but paying the prize for the greater amount of nanoparticles. On the other hand, increasing the sizes of the units mean a greater contact time, that is also positive in the efficiency point of view.

Chapter 5: Conclusions

In conclusion the treatment works in general and it has the potential to be implemented on a big scale in the future as a small amount of nanoparticles can remove a big amount of pollutants due to its big surface area. Optimization is always possible by taking into account the variables mentioned before. Knowing the chemical nature of the waste water has very high importance, as this will allow selecting the most suitable coating for the specific treatment reducing the quantity of nanoparticles needed for the process. As for the quantity and the size of the units, in other words concentration and contact time, there is a compromise situation as this two variables are closely related.

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