Ana Rita Lino Oliveira

Heavy metal ions removal from aqueous solutions by Multiwalled Carbon Nanotubes

Master's thesis in the scientific area of Chemical Engineering, supervised by *Professor Doctor Maria da Graça Bontempo Vaz Rasteiro* and *Professor Doctor António Alberto Santos Correia* and submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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UNIVERSIDADE DE COIMBRA

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Supervisors

Professor Doctor Maria da Graça Bontempo Vaz Rasteiro

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Only when you drink from the river silence shall you indeed sing.

And when you have reached the mountain top, then you shall begin to climb.

And when the earth shall claim your limbs, then shall you truly dance. – Kahlil Gibran

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Life is made of cycles and depends on us to have courage to start and to end them. However, the biggest challenge is to find that courage. In the end of my academic cycle, I would like to write some heartfelt words to all persons and institutions that gave me that courage and made this journey possible.

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For last, but with a special emotion, I thank to my family for the eternal support and dedication, for trusting me in every decisions, for their love, values, patience and force, even when life seemed to be darker. I thank to my guardian angels for the infinite light.

Thank you to all that help me to believe that I can be everything I want to be.
Thank you.

Abstract

Nowadays, water crisis is taking a special care by UN (Union Nations), governments and scientific community since the population growth is leading to a consequent water demand almost impossible to control. On the other hand, factors as pollution, especially by heavy metals, will difficult that water management.

Carbon nanotubes are one of the most studied nanoparticles, reaching innumerous scientific areas due to their physical, chemical and electronic properties. However, avoiding MWCNTs (Multiwalled Carbon Nanotubes) aggregates is one of the main difficulties and an issue that will influences the performance of these nanoparticles.

In this work, three types of surfactants, SDBS (anionic), Pluronic F-127 (non-ionic) and polyDADMAC MMW (cationic), were applied in order to study not only their efficiency on MWCNTs dispersions but also their influence in heavy metal ions removal, presenting in high amounts in Portugal, such as Pb (II), Cu (II), Ni (II) and Zn (II). The concentration of MWCNTs applied were 0.01% (w/w) and 0.05% (w/w). The conditions of mechanical treatment applied in MWCNTs dispersion – sonication– were optimized as well, but applying Glycerox as surfactant. The optimum reached was when it was applied 75% of sonication energy, during 15 minutes.

In terms of quality of MWCNTs dispersion, SDBS was the surfactant with better results, once it was possible to disaggregate both concentrations of MWCNTs with a surfactant concentration of 0.03% (w/w). Pluronic F-127 showed to be efficient in the same concentration, but only for 0.01% (w/w) of MWCNTs. When the concentration of MWCNTs was increased, it was necessary to increase the surfactant concentration as well. In this case, the optimum result was for 1% (w/w) of Pluronic F-127. On the other hand, polyDADMAC MMW was not efficient for none of the MWCNTs concentrations, what means that higher concentrations of surfactants were applied (0.05% (w/w), 1% (w/w) and 2% (w/w)). The results for these three concentrations were worse than when applied the initial concentration of 0.03% (w/w). In this way, this concentration were considered the optimal and it was chosen to perform the adsorption tests.

Adsorption tests were developed with the optimal concentrations of surfactants, during 7 days under stirring conditions (100 rpm) and taking samples at 4h, 18h, 24h and after 7 days. The influence of MWCNTs concentration were studied, where it was concluded that there is no significant influence in increasing the concentration to 0.05% (w/w).

During the tests, Pb (II) was the metal with higher removal, possibly due to its high electronegativity and smaller size, and Ni (II) the one less removed. On the other hand, since Ni (II) showed to be released by the complex surfactant-MWCNTs, a test with no stirring was performed. In fact, the percentage of Ni (II) removed stabilized at 18h, what means that the hydrodynamic forces during the adsorption might be the cause for Ni (II) releasing.

Besides individual heavy metal ions adsorption tests, the comparison between all cations was also studied throw a competitive adsorption test, where the general result of percentage adsorbed were Pb (II) > Cu (II) > Zn (II) > Ni (II).

All surfactants showed to have a good behavior in metal ions adsorption, even when polyDADMAC MMW was applied as surfactant. SDBS worked as a kind of trap for cations, due its negative zeta potential, but comparing with Pluronic F-127, this last showed to be more efficient possibly due to its smaller size, promoting, in this way, a higher surface area and consequently more available active adsorption sites. Since, SDBS and Pluronic F-127 showed to reach good results in terms of MWCNTs dispersion and metal ions removal, a test with their mixture were applied. It was possible to reach a higher metal ion removal when the concentration of MWCNTs was equal to 0.05% (w/w). This result might be explained by the fact that a better dispersion of MWCNTs was reached, promoting the increase of surface area of these nanoparticles.

The objectives of this work could be reached, not only in terms of heavy metal ions removal but also and in terms of MWCNTs dispersions with Pluronic F-127 and SDBS as surfactants. However, in some adsorption tests, the limits required by National Legislation were lower than the detection limit of Atomic Absorption Spectrometry equipment, what means that it was not possible to conclude for sure if the targets were truly reached or not.

Key words: carbon nanotubes; heavy metals; surfactants; dispersion; aqueous solutions; adsorption.

Resumo

Atualmente, a crise da água tem-se vindo a mostrar um problema que requer especial atenção por parte da ONU (Organização Nações Unidas), governos e comunidade científica. Isto acontece, uma vez que o crescimento populacional está a conduzir as sociedades para um desenvolvimento não sustentável no que diz respeito à procura de água. Por outro lado, fatores como a poluição, especialmente poluição associada a metais pesados, vem dificultar a gestão deste recurso.

Os nanotubos de carbono são das nanopartículas mais estudadas na atualidade, conseguindo abranger, através das suas propriedades físicas, químicas e elétricas, inúmeras áreas científicas. No entanto, atingir um elevado grau de dispersão destas nanopartículas, livre de agregados, é uma das principais dificuldades, tornando-se também um problema em termos da eficácia dos nanotubos de carbono para com os objetivos definidos.

Neste trabalho, três tipos de surfactantes foram estudados - SDBS (aniónico), Pluronic F-127 (não iónico) e polyDADMAC MMW (catiónico) – no sentido de concluir não só em termos da sua eficácia na dispersão dos MWCNTs mas também em termos da remoção de metais pesados, encontrados em abundância em Portugal, tais como Pb (II), Cu (II), Ni (II) e Zn (II). A concentração de MWCNTs aplicada foi de 0.01 % (w/w) e 0.05% (w/w). As condições do tratamento mecânico aplicado na estabilização das suspensões, nomeadamente dispersão por energia ultrassónica, foi também otimizada mas aplicando Glycerox como surfactante. O melhor resultado conseguido nestas dispersões foi 75% de intensidade da energia do equipamento de ultrassons, durante 15 minutos.

Em termos da qualidade das dispersões de MWCNTs, o SDBS foi o surfactante com melhores resultados obtidos, uma vez que foi possível estabilizar ambas as suspensões de MWCNTs com uma concentração de surfactante igual a 0.03% (w/w). Para esta mesma concentração, o Pluronic F-127 foi eficiente apenas na suspensão de 0.01% (w/w) de MWCNTs, sendo que com o aumento da concentração da suspensão para 0.05% (w/w), houve também a necessidade de aumentar a concentração de Pluronic F-127 para 1% (w/w). Por outro lado, para 0.03% (w/w) de concentração do surfactante catiónico polyDADMAC MMW, este não foi totalmente eficaz, sendo que para ambas as concentrações foram visíveis a “olho nu” agregados de nanotubos de carbono. Desta forma, foram estudadas as concentrações de 0.05% (w/w), 1% (w/w) e

ainda 2% (w/w), cujos resultados não foram melhores que no caso inicial de 0.03% (w/w). Assim sendo, nos testes de adsorção, a concentração aplicada para o polyDADMAC MMW foi a concentração de partida.

Os testes de adsorção foram desenvolvidos com base nas concentrações ótimas de dispersão dos surfactantes, durante 7 dias sob o efeito de agitação de 100 rpm, e amostras foram recolhidas às 4h, 18h, 24h e depois de 7 dias de adsorção. Nestes ensaios, a influência da concentração de nanotubos foi estudada, sendo que a concentração mais elevada de 0.05% (w/w) não foi significativamente melhor que a de 0.01% (w/w).

Ao longo dos ensaios, o Pb (II) foi o metal com maior remoção, possivelmente devido à sua elevada eletronegatividade e reduzido raio atómico, enquanto que o Ni (II) foi o que apresentou menores percentagens de remoção. Por outro lado, nos testes de remoção do Ni (II), este metal foi libertado pelo complexo surfactante-MWCNTs. Desta forma, um teste sem agitação foi desenvolvido. De facto, a percentagem de remoção deste metal estabilizou às 18h, sendo que as forças hidrodinâmicas poderão estar na causa da libertação subsequente, durante os ensaios de agitação.

Além dos ensaios de adsorção individual dos metais, a comparação entre a remoção dos metais pesados das soluções aquosas foi também estudada, através de uma mistura de todos os metais numa só solução. De uma modo geral, o resultado foi semelhante aos testes individuais, sendo que o Pb (II) mostrou maior adsorção, seguido do Cu (II) e Zn (II) e por fim o Ni (II).

Todos os surfactantes se mostraram eficazes na remoção dos metais, mesmo no caso da polyDADMAC MMW. O SDBS desempenhou uma espécie de armadilha para os catiões, dado o seu negativo potencial zeta. No entanto, comparando este com o Pluronic F-127, este último mostrou-se ser mais eficaz, sendo que o seu tamanho reduzido, poderá ter conduzido a uma maior dispersão das suspensões de MWCNTs e uma maior disponibilidade de sítios de adsorção. Desta forma, uma mistura de SDBS e Pluronic F-127 foi estudada, tendo sido possível concluir que uma maior remoção de metais pesados foi atingida quando aplicada uma maior concentração de MWCNTs. Este resultado poderá ser explicado pela melhor dispersão de MWCNTs conseguida, o que promove o aumento da área de superfície disponível para reter os iões.

Os objetivos deste trabalho foram alcançados, não só em termos de remoção de metais pesados como também em termos da dispersão dos MWCNTs, quando aplicados SDBS e Pluronic F-127. No entanto, em alguns ensaios de adsorção, o limite

estabelecido pela Legislação Nacional é inferior ao limite de deteção do equipamento de espectrometria de absorção atómica, o que significa que em alguns casos não foi possível concluir se os objetivos de remoção foram atingidos ou não.

Palavras-chave: nanotubos de carbono; metais pesados; surfactantes; dispersões; soluções aquosas; adsorção.

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Nomenclature and Symbols

Nomenclature

AAS	Atomic Absorption Spectrometry
C-SWCNTs	Carboxylated Single Walled Carbon Nanotubes
CMC	Critical Micelle Concentration
CNTs	Carbon Nanotubes
DLS	Dynamic Light Scattering
DWCNTs	Double Walled Carbon Nanotubes
ELS	Electrophoretic Light Scattering
ERSAR	Entidade Reguladora dos Serviços de Águas e Resíduos
FCTUC	Faculdade de Ciências e Tecnologias da Universidade de Coimbra
H-SWCNTs	Hydroxylated Single Walled Carbon Nanotubes
IARC	International Agency for Research on Cancer
LDV	Laser Doppler Velocimetry
MMW	Medium Molecular Weight
MWCNTs	Multiwalled Carbon Nanotubes
PRESGRI	Plano Estratégico de Gestão de Resíduos Industriais
RI	Refractive Index
SLS	Static Light Scattering
SWCNTs	Single Walled Carbon Nanotubes
UN	United Nations
UK	United Kingdom
ZSN	Zetasizer Nano

Symbols

A_2	Virial coefficient
A_{HD}	Average hydrodynamic diameter
C	Concentration;
$C_{max,NL}$	Maximum concentration of metals defined by National Legislation
COOH	Carboxilic Acid
Cu	Copper
$CuCl_2 \cdot 2 H_2O$	Copper chloride (II) dehydrate

$\frac{dn}{dc}$	Differential refractive index increment
D_z	Intensity weighted harmonic mean size of the hydrodynamic diameter distribution
E	Sonication Energy
ε	Dielectric constant;
f(ka)	Henry’s function
HCl	Cloridric Acid
HNO_3	Nitric Acid
H_2SO_4	Sulfuric Acid
K	Optical constant
λ_o	Laser wavelength
M	Molecular weight;
N_A	Avogadro’s Number
Ni	Nickel
$Ni(SO_4) \cdot 6\ H_2O$	Nickel sulfate (II)
n_o	Solvent refractive index
η	Viscosity;
P	Power of sonication
Pb	Lead
$Pb(NO_3)_2$	Lead nitrate (II)
$P(\theta)$	Angular dependence of the sample scattering intensity.
q_e	Capacity of Ni (II) sorption by CNTs
R_θ	Rayleigh ration
SO_3H	Sulfonic Acid
t	Time of sonication
U_E	Electrophoretic Mobility;
V	Volume of suspension
z	Zeta potential;
Zn	Zinc
$Zn\ SO_4 \cdot 7\ H_2O$	Zinc Sulfate

1 Introduction

Among numerous 21^{st} century crises, water, besides fossil fuels, has proven to be one of the most important issues. A universal truth is that water plays a pivotal role in three main pillars of sustainable development: economic, social and environmental. After years of bad management and serious pollution of water resources, it is essential that world organizations and governments make a stand against this crisis.

According to UN, in 1800, the global population was around 1 billion, when nowadays it has been estimated at around 7 billion. With this growth rate, it is expected that in 2050 the Planet Earth will have 9.3 billion inhabitants [1]. One of the problems when we talk about water crisis is that in 2050 water demand will grow by 55% [2], not only due to domestic use but also because of industries and thermal electricity generation. The unsustainability comes when this competition between sources will stop the expansion of some sectors as energy, food and health, carrying with it conflicts among nations, contributing to social inequality and environmental imbalance.

The key to control and slow down this problem is to pay attention not only to minimizing risks (Prevention) but also to maximizing benefits (Reutilization). To this end, norms and legislation have been changed and scientific and technological knowledge have been improved in order to ensure that countries contribute to sustainable water consumption, and consequently to a sustainable world.

For a long time, scientists have been studying many techniques to eliminate pollution from water resources based on coagulation, flocculation, filtration and disinfection. However, with the industrialization and urbanization growth, pollution levels have a consequent increase, turning these conventional techniques less efficient, even more, when we talk about drinking water [3]. In this case, it is necessary to pay special attention once there are pathogen agents or certain compounds that are extremely difficult to remove or neutralize. For instance, advanced membrane filtration (e.g microfiltration, ultrafiltration, nanofiltration or reverse osmosis) can reach efficacy of around 99.46%, but it becomes a costly process when it is necessary to conjugate it with other treatment techniques, for example, pretreatments to prevent fouling problems or membrane degradation [4] .

One of the cost-effective solutions may come in the form of carbon nanotubes (CNTs) due to their remarkable properties. Once these new materials have a porous and hollow structure, high specific surface area and low density, it is possible to hold inside their structure toxic substances such as organic contaminants or metal ions [5]. On the other hand, when we talk about bacteria and viruses, CNTs have an inherent cytotoxic power that will assure the inactivity of these pathogen agents [6].

One concern about CNTs is their effect on human and environmental exposure. There is not a lot of information about this exposure, but it is known that the quantities applied in water system treatment will be less than other adsorbents. Furthermore, CNTs have an extreme tendency to form aggregates, which leads to the need of using surfactants to disperse the suspensions [5].

As consequence of urbanization and industrialization growth, water sources have been polluted by several types of substances, such as organic and inorganic pollutants, heavy metals, residues from fertilizers and pesticides, among others. These compounds will change equilibrium in ecosystems, changing physical, chemical and biological state of water [7].

Among the aforementioned substances, heavy metals have raised scientific interest and strong public concern. These compounds are characterized by their consequent accumulation in organisms, which in turn affects different living beings in high levels. Eventually, heavy metals such as zinc, arsenic, lead, nickel, and others will reach human beings and cause serious diseases, such as cancer and mutagenic problems.

The objectives of this work, in line with the concerns stated above, are to study:

1- the efficacy of two different concentrations of CNTs (0,01% (w/w) and 0,05% (w/w)) in the removal of heavy metal ions (Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+});
2- the effect of three types of surfactants (nonionic, anionic and cationic) in CNTs dispersions;
3- the efficiency of these three types of surfactants in heavy metal ions adsorption;
4- the characterization of the surfactants selected (hydrodynamic diameter, zeta potential and molecular weight);
5- the optimization of the conditions used in the tests (time and magnitude of ultrasounds used in the CNTs dispersions, pH, temperature and surfactant concentration).

The work presented here is structured in five chapters:

- Chapter 1: introduction and presentation of main objectives;
- Chapter 2: state of art where the principal fundaments are explained and other works are mentioned;

- Chapter 3: presentation of materials and techniques employed and description of the experimental procedure;
- Chapter 4: presentation and discussion of results from CNTs dispersions and metal ions adsorption;
- Chapter 5: conclusions and future works proposals.

2 State of Art

2.1 Carbon Nanotubes

2.1.1 Background

The first time scientific community heard about carbon nanotubes dates back to 1991, when Sumio Iijima found an extremely “thin needle-like material” while studying carbon materials. During his post-doctoral research at Arizona State University, Dr. Iijima developed a high-resolution electron microscope that allowed them to study individual metal atoms. Around 1990, Prof. Iijima was encouraged by Prof. H. Kroto to apply his high-resolution electron microscope to carbon materials, due to the remarkable results got at that time with fullerene. In June of the next year, Sumio Iijima saw some elongated filaments for which he could conclude they were carbon nanotubes [8]. However, around 1985, scientific community discovered a new class of carbon molecules – fullerenes, a spherical pure carbon structure – and later, in 1990, Dr. Richard Smalley recognized that this structure could be tubular [9].

Nowadays, there are four methods to produce CNTs: *arc discharge, laser ablation, chemical vapor deposition* and *flame synthesis.* These techniques are relatively expensive due to their high temperature reactions, although, in some cases, it is possible to have an industrial CNTs production [10]. Another issue is that evaporation methods lead to highly entangled forms mixed with unwanted forms of carbon, decreasing the purity of CNTs and consequently their performance [11]. This problem can be solved by annealing, for example, reducing structural defects and removing catalytic metals used in synthesis. On the other hand, *functionalization* (adding of specific groups to CNTs network) can be applied in order to increase the dispersity in aqueous solutions [12].

Due to their electrical, electrochemical and optical properties, carbon nanotubes have been applied in several areas like electronics and communications as conductors, in medicine as drug deliverers, or as probe needles for scanning probe microscopes [8]. However, one of the most important development area is environment and green technologies like wastewater treatment. Since CNTs have a high surface area and a controlled pore size distribution, it is possible to remove the principal contaminants present in waters such as metal ions, dioxins, bacteria or viruses [13]. Concerning bacteria and viruses, due to their cytotoxic power, CNTs can reduce their pathogen activity, ensuring that even after the treatment, bacteria and viruses cannot colonize [6]. However, Kang et al [12] concluded that some modifications of CNTs structure can alter this cytotoxicity power and turn them less efficient in terms of bacteria and viruses activity.

2.1.2 Characterization of CNTs

Chemistry of Carbon is a large area where we can find different classes of carbon molecules. Molecular configurations of pure carbon are called “allotropes”, such as amorphous carbon, diamond, graphite, fullerenes, and CNTs – **Figure 1**.

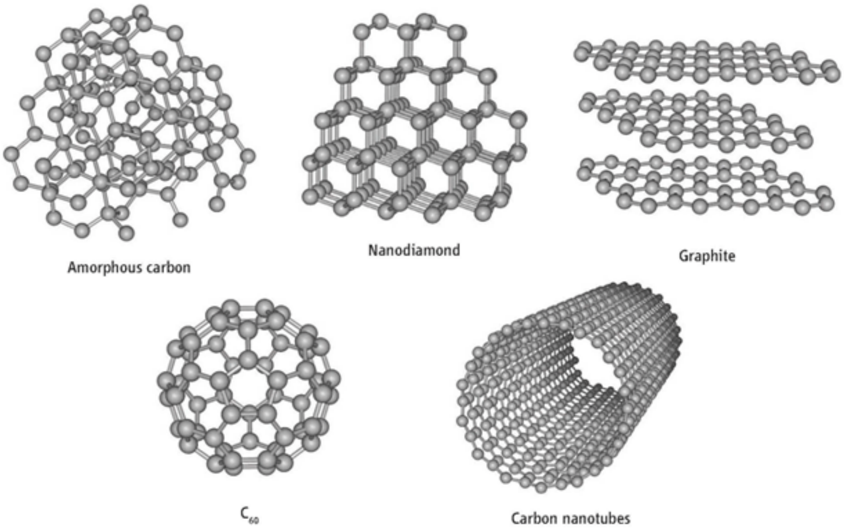

Figure 1 *Allotropes of Carbon, where fullerene represented is a C60 and the CNTs a single walled structure. (adapted from Ehrenfreund 2010)* [65]

As the name indicates, carbon nanotubes are tubular structures of carbon atoms, with only one layer (Single Walled Carbon Nanotubes, SWCNTs), two layers (Double Walled Carbon Nanotubes, DWCNTs) or multiple layers (Multiwalled Carbon Nanotubes, MWCNTs), positioned at nano scale (1-1000×10^{-9}nm) and with several micrometers in length [14]. Typically, SWCNTs are 0.4-5 nm in diameter and MWCNTs are up to 100 nm in diameter. On the other hand, it is possible to distinguish between CNTs structures depending on the sheet direction in which

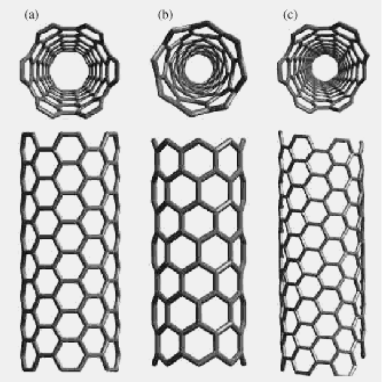

Figure 2 *Structures of SWCNTs according to carbon atoms disposal: (a) armchair, (b) zig-zag and (c) chiral.* [66]

the graphite sheet is rolled. According to carbon atoms disposal, these structures can be classified as armchair, zig-zag or chiral structure - **Figure 2**. This chirality determines the band gap of the structure and then the electrical properties. For example, an *armchair* structure has a straight edge of the hexagonal matrix perpendicular to the tube axis, and consequently a small band gap thus typically metallic. In the case of *zig-zag* SWCNTs structures, they have a straight edge of the hexagonal matrix parallel to the tube axis, which means that we can have metallic or semiconductor structures. SWCNTs can be semiconducting or metallic but MWCNTs are almost always metallic [15].

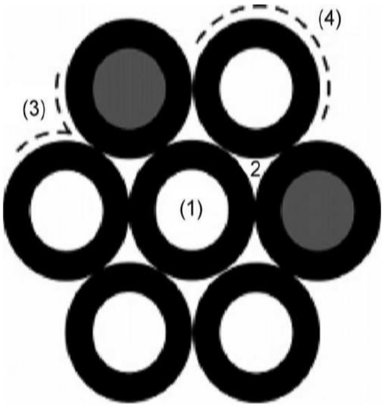

Figure 3 *Adsorption sites on a homogeneous bundle of SWCNTs. (1) internal, (2) interstitial channel, (3) external groove site and (4) external surface.* [67]

Finally, paying attention to adsorption sites in CNTs structure, there are four possible sites where it can occur: at hollow interiors of nanotubes, at interstitial pore spaces between the tube bundles, at groves present at the boundary of nanotube bundles or on the external surface of the outermost CNTs [5] - **Figure 3**. However, since these materials are extremely hydrophobic, their tendency to aggregate is huge, therefore it is necessary to use techniques, such as addiction of surfactants, to prevent those effects. Therefore, in adsorption tests it is necessary to take into account the influence of surfactant application on sites of adsorption.

2.1.3 Properties of CNTs

CNTs are the strongest and stiffest materials known to scientific community. As it has already been mentioned, the different properties of CNTs will change according to their degree of graphitization, chirality and type (single or multiwalled), depending on their growth process [16], which means that CNTs have a special capacity of changing their physical properties according to different axes of the matrix. This phenomenon is called “anisotropy” [10].

Carbon atoms in CNTs form strong covalent bonds in the hexagonal sp^2 hybridization state, making these materials stronger than diamond (sp^3 bonds) and extremely hydrophobic [17]. In the same way, the high surface area combined with Van der Waals bonds will contribute to the aggregation of CNTs, making their dispersion in aqueous solutions extremely difficult and consequently affecting the adsorption processes. The application of a surfactant is a solution to this problem and, eventually, can also change the properties of CNTs [16]. Another common solution is the *functionalization*, i.e. adding functional groups to the CNTs structure with the purpose of conferring a specific function to CNTs, which also changes their properties. The only problem with this approach is that in the case of SWCNTs some carbon-carbon bonds are destroyed, which affects the mechanical properties of the structure.

It has been difficult to reach a consensus on the exact mechanical properties of CNTs, however some studies show a Young's modulus in order of TPa and a tensile strength in order of GPa. A perfect match for this high stiffness is its low density compared to other tough materials, around 1800 kg/m^3, one-fifth of the density of steel. In terms of electrical properties, CNTs can range their electrical conductivity between 10^2 and 10^6 S/cm and reach thermal conductivities of 6000 W/mK, in the case of SWCNTs [17,18].

It is easy to conclude that CNTs can reach innumerous goals due to the versatile nature of their physical, electrical and chemical properties.

2.1.4 Stabilization of Carbon Nanotubes

CNTs stabilization is closely related to the achievement of high performance of these nanoparticles. Nanocomposites are seen as the new face of Material Engineering due to their remarkable properties, and nowadays, it is possible to improve characteristics of materials with the coupling of two or more different materials. CNTs are one of such materials.

On the other hand, it is known that the nanoscale dimensions of CNTs are a challenge when talking about dispersion in aqueous solutions. If there is a decrease in particle dimensions, there will be a consequent growth of superficial area and, eventually, an increase of attractive forces between these particles. This means that in order to reach an equilibrium, these particles will have a strong tendency to form aggregates [16].

In order to reach the goals on properties improvement of this kind of nanocomposites, the aggregation of CNTs must be overcome and a good alignment is required. Two general routes for achieving a good CNTs dispersion are through chemical and mechanical methods. In some cases, a combination of both methods is applied to guarantee a better dispersion.

Chemical Methods

Chemical methods of changing particle surface are defined by the modification of surface energy and can be generally categorized as covalent or noncovalent. Basically, these methods use surface functionalization to improve their chemical compatibility with the target medium [16].

Covalent methods involve the addition of functional groups which establish bonds with CNTs. Normally, this functionalization, as it is known, is based on oxidative formation of specific functional groups (carboxyl or alcohol groups) on CNTs surface, followed by the grafting of organic moieties on the surface. Unfortunately, covalent functionalization disrupts parts of the electronic structure of CNTs, compromising their inherent properties, such as electrical, mechanical and optical properties [19].

Acid treatment is one of the most common techniques reported in literature. It applies acids as HNO_3, H_2SO_4 and HCl. The addition of these functional groups will increase the removal of heavy metals by different mechanisms, especially by electrostatic interactions. Although Stafiej and Pyrzynska [20] has proved that CNTs functionalization can increase the adsorption of metal ions, this surface modification can introduce some structural defects resulting in inferior properties of the tubes. On the other hand, comparing this process with a single noncovalent functionalization, the first one comes out as more expensive due to high temperature and pressure conditions.

Noncovalent functionalization promotes the dispersion of CNTs in aqueous solutions leaving the electronic structures and CNTs properties unchanged. The use of surfactants is included in this category. However, the use of surfactants alone is not enough to reach a perfect dispersion. It is necessary to apply some mechanical methods simultaneously, such as sonication [21].

Surfactants are compounds that have the function of decreasing the surface tension on surfaces. Once they are amphiphilic, which means that they are composed of a hydrophilic head and a hydrophobic tail, they adsorb on the hydrophobic particle surface and promote their dispersion in aqueous solution. This type of compounds is classified according to the charge of their hydrophilic region as cationic, anionic or non-ionic. In this way, if we are studying an adsorption of a surfactant with an opposite charge from the solid surface, we have the Coulomb attraction as driving force between the hydrophilic area and solid surface. However, there is also another possibility, when a non-ionic surfactant adsorbs on a solid surface, the driving force responsible for that phenomenon are Van der Walls forces.

This adsorption will spontaneously stop when a Critical Micelle Concentration (CMC) is reached. CMC is defined as the concentration of surfactants above which micelles form. In studies where the adsorption of a second type of particles, such as metal ions, is priority, it is essential not to reach CMC, or the metal ions will not be allowed to reach CNTs adsorption sites and the efficiency of the process will be reduced.

Kun et al. [22] studied the influence of surfactant (SDBS) concentration on the dispersion of purified SWCNTs (P-SWCNTs). Two suspensions with the same P-SWCNTs concentration were prepared, one with 5000mg/L of SDBS and another one with 1000mg/L of SDBS. These suspensions were dispersed in the same sonication conditions. It is possible to conclude that stably dispersed concentration (C_e, mg/L) grows with the surfactant concentration and with the sonication energy, E (J/mL). That concentration represents the quantity of P-SWCNTs dispersed in 1000 mg/L of SDBS solution. In terms of average hydrodynamic diameter, A_{HD} (nm), it is possible to get a decrease of the diameter of the CNTs particles in suspension due to the good dispersion reached - **Figure 4 (a).**

Kun et al. [22] compared also a P-SWCNTs dispersion with functionalized CNTs dispersions: hydroxylated CNTs (H-SWCNTs) and carboxylated CNTs (C-SWCNTs). A better dispersion of those suspensions (maintaining the SDBS concentration) was reached - **Figure 4 (b).** However, when the supplied sonication was higher, the added value of this functionalization became insignificant compared to P-SWCNTs dispersions, which means that the functionalization is more efficient only with low sonication energy - **Figure 4 (b).**

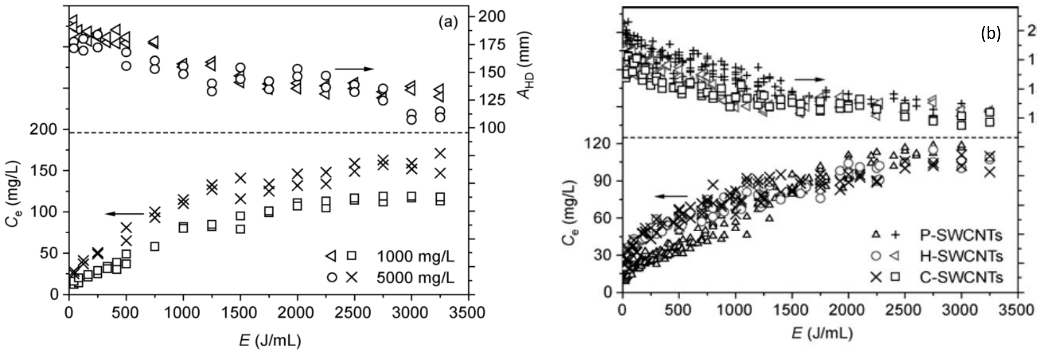

Figure 4 *(a) Stably dispersed concentration (Ce,mg/L) and average hydrodynamic diameter (A_{HD}, nm) for a suspension of 400mg/L of P-SWCNTs added to a SDBS solution (1000mg/L and 5000mg/L) in function of sonication energy (E,J/mL). Suspensions dispersed with an output sonication power of 600W. (b)Same conditions to H-SWCNTs and C-SWCNTs dispersions with same conditions as P-SWCNTs (adapted from Kun et al.* [22]*)*

Mechanical Methods

As mentioned previously, the use of a surfactant to disperse MWCNTs is not always fully effective, and it is therefore necessary to add to the process the use of mechanical energy, such as sonication or heating.

Under certain conditions, sonication can damage CNTs electronic structure. The dispersion of SWCNTs can be done also by heating. Therefore, Yamamoto et al. [19] tried to disperse a suspension of 0.5 mg of SWCNTs with 6 mg of dispersant at 170ºC. This method revealed more efficient in terms of reaching a good dispersion without disrupting the CNTs structure. However, depending on the situation, this method can be more expensive than sonication, which means that in certain cases sonication can be applied.

In sonication, the ultrasound equipment converts the voltage into mechanical vibration of the particles. When ultrasound propagates via a series of compression, attenuated waves are induced in the molecules of the medium through which it passes. Although the energy created is small, the cumulative effect causes the dispersion of particles into the medium. The shock waves promote the “peeling off” of individual nanoparticles located on the outer part of nanoparticles bundles and thus results in the separation of individualized nanoparticles. One disadvantage in this process is the increase of temperature, since the MWCNTs aggregation will be promoted, which means that it is necessary to remove the heat from the dispersion [17].

Sonication time is one parameter with an important influence in dispersion efficiency. It is expected that the longer sonication time, within limits, the better CNTs dispersion and smaller the suspended CNTs particle size. To assure a good dispersion and by applying an economical process, it is possible to predict the energy necessary to reach the goal. The Equation (1) shows the relation between the power of sonicator, the volume of the suspension to disperse and the sonication time [22].

$$E = P\frac{t}{V} \tag{1}$$

Where E is the sonication energy (J/mL);

P is the output power of the sonicator (W);

t is the sonication time (s);

V is the volume of the suspension (mL).

In the same study developed by Kun et al. [22], mentioned previously, the influence of sonication time in P-SWCNTs dispersion was obvious. The longer sonication time, the more P-SWCNTs were dispersed and the smaller the size of the dispersed CNTs particles. In the same way, a better dispersion and smaller particle size can be reached with the increase of sonication energy - **Figure 5.**

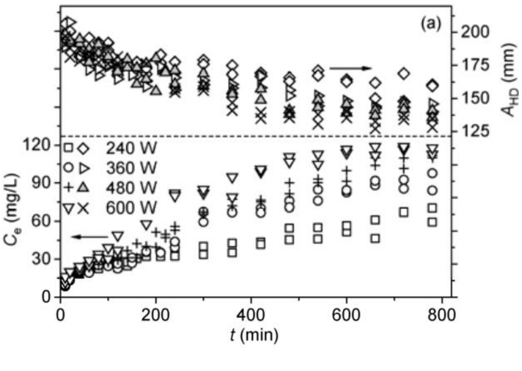

Figure 5 *Stably dispersed concentration (Ce,mg/L) and average hydrodynamic diameter (A_{HD}, nm) of P-SWCNTs in SDBS solution, at sonicator output powers of 240, 360, 480 and 600W in function of sonication time (t, min). (adapted from Kun et al. [22])*

2.2 Heavy Metals

2.2.1 Background

The first contact between mankind and metals dates to the end of Neolithic, when the Man discovered gold and copper (6000 BC and 4200 BC) [23]. With this discovery, civilizations could create simple tools, coins, jewelry and other useful materials for their everyday life. In this way, civilizations had a notable development due to the extraction of metals and the expansion of metallurgic activities, leading to industrial, technologic, and economic growth.

The continuous search for better conditions of life led societies to an unsustainable exploration of natural resources, such as mineral extraction activities. Regarding the mining activities, even though minerals are a commonly found resource in Nature, the situation got to an even more alarming point due to the continuous inadequate treatment of these metals, which consequently raised the concentration levels of such metals to a point that the ecosystems can no longer support. We can conclude that anthropogenic activities like mining, industrial exploration, and agriculture have an important role in environment contamination [24].

Metals are compounds characterized by their shine, hardness, and good electrical and thermal conductivity. We talk about heavy metals when materials have density around 5 times greater than water [25]. These compounds are seen as too dangerous for the environment and human health due to their toxicity. Toxicity depends on the route of exposure (inhalation, ingestion of food and drinks or absorption by contact) and the solubility of the metal in question. Some heavy metals such as zinc are present in some organic reactions, however there are others such as arsenic, lead, and mercury that are slowly metabolized and excreted from living bodies [24], which also implies *bioaccumulation* of heavy metals. They have the ability of denaturing proteins, blocking functional groups, combining and replacing compounds, modifying the normal performance of physiological functions, hindering transport properties by biding cell membranes or even forming complexes with polysaccharides [7]. Prolonged use of these compounds can cause cell intoxication, several types of cancer and mutagenic problems.

Once these heavy metals reach the groundwater, they can easily affect human health due to their bioaccumulation in ecosystems. Residues of these kinds of materials will start a contamination cycle – metals in the soil will be dragged by rainwater to groundwater, thus reaching water resources that are consumed by aqueous streams. Thus, contaminated fish and plants, once they become included in human food chain, will unavoidably bring to heavy metal ingestion by humans. Since these compounds cannot be metabolized, they will be accumulated in our bodies causing many diseases.

2.2.2 Heavy Metals in Portugal

In Portugal, heavy metal pollution is directly related not only to bad sanitation or mining activity but also to industrial development. It is essential to ensure that all places where the mining activity is not active is recovered, avoiding environment contamination by metals [26]. On the other hand, in the case of industrial complexes, it is necessary to pay a special attention to wastewaters, their treatment, and their final destination.

According to Inácio et al. [27] and Barbosa et al. [28] in Continental Portugal, the concentrations registered in the previous years refer to zinc, copper, lead, nickel, cadmium, mercury and in some places arsenic. If we take a closer look at industrial activity distribution throughout the country, we can conclude that the biggest industrial complexes are located in the urban areas of *Porto, Aveiro* (*Estarreja*), *Lisbon*/*Setúbal*, *Leiria* and *Santarém*. On the other hand, according to *Caxaria* [29] mining exploitation is still active in the region of *Alentejo*, specifically in *Neves-Castro*, *Aljustrel*, and *Panasqueira*. There are also some exploitations conducted in the North of Portugal – *Aveiro* and *Bragança*.

After a previous research about water contaminations in Portugal, we could conclude that we can still see problems associated to *copper, nickel, lead* and *zinc*.

Copper

The chemical symbol of this metal is Cu, atomic number equal to 29 and density of 8.9 g/cm^3 [30]. This metal is one of the most exploited on our territory due to its durability, corrosion resistance, malleability and easy handling. As zinc or nickel, copper can be found in human organisms as an enzyme co-factor [31] [32], but this compound in high concentrations can become toxic, causing gastrointestinal distress, red cells destruction leading to anemia, liver and kidneys problems, and in extreme cases high levels of copper can cause Wilson's disease[1] [33].

According to the Annual Report on Water and Wastewater Services in Portugal from 2015 [34], 4 samples from a total of 3 935 were registered as exceeding the permissible limit values as established by the Portuguese legislation. The maximum value collected was 2.40 mg/L of Cu^{2+}, while the established limit is 2 mg/L [35].

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[1] Wilson's disease is a genetic problem that does not manifest itself until adolescent age and it is characterized by the inability of eliminating copper from human body. The patient liver is incapable of producing enough bile, responsible for the excretion of excess copper. Then, it is accumulated in other tissues, for example in brain tissues, which causes neurological problems or vision problems (Kayser-Fleischer eye ring). [63]

Nickel

As copper, nickel is another metal extracted from national territory, especially in *Neves-Corvo* mines. This compound is represented by Ni, it precedes copper in periodic table with the atomic number of 28 and it has a density approximately equal to copper (8.9 mg/cm^3) [36].

One of the first effects of human exposure to nickel are allergic reactions, such as hypersensitivity. Since nickel is commonly used in jewelry and coins, its contact with skin can cause redness and eczemas. When inhaled, this metal can cause respiratory inflammations. In more extreme cases, high concentrations of nickel will promote free radicals formation and Ni^{2+} will function as a tumor precursor inhibiting regular activity of some cells [37]. According to International Agency for Research on Cancer (IARC), nickel is inserted in Group 1 of carcinogenic compounds [38].

In 2014, the maximum concentration of nickel found in Portugal was 0.26 mg/L, when the exposure limit established according to *Decreto-Lei nº306/2007* is 0.02 mg/L [35].

Lead

Lead's chemical symbol is Pb, it has 82 as atomic number and its density is around 11.34 g/cm^3 [39].

In the last years, lead was one of the metals found in drinking water, which can be attributed to the old plumbing system due to the fact that the first plumbing constructed in the country contained a considerable percentage of lead. With the passing of time, those water systems experienced oxidation, which liberated lead ions into the water reaching Portuguese water taps [40].

On other hand, mining exploitation of lead is situated in *Aveiro* (*Braçal* and *Malhada* mines) [41], which explains the high values of this compound registered in Annual Report on Waters [34], as already mentioned. According to the Report, the maximum values found were equal to 0.28 mg/L, when the national permissible exposure limit is 0.01mg/L.

Health dangers associated with this metal are the inhibition of some essential elements in our organism, for example, proteins (hemoglobin) and calcium (causing calcium homeostasis[2] and possibly osteoporosis). As is the case with other heavy metals, lead can cause neurological problems [42].

Zinc

In Continental Portugal, zinc is at the same extraction level as copper or nickel. The biggest source for its extraction is in *Neves-Corvo* and *Aljustrel* mines, although we can find some deposits in the central zone (*Lousal*, for example) [43].

This metal is next to copper in the periodic table with atomic number 30 and it is expressed by Zn. Compared with other metals already mentioned, zinc has lower density equal do 7.11 g/cm^3 [44].

Unlike other metals, there are no records of specific values for zinc contamination by ERSAR[3]. However, according to a report elaborated by *Estradas de Portugal*, the maximum level of zinc found in waters near A6 (*Nó de Borba*) was 0.5 mg/L and 0.68mg/L near EN10 (*Reta do Cabo*). However, in all study cases presented in this document, the author speaks about zinc traces [28].

As it was already mentioned, zinc in small quantities is essential to normal activity of human body. However, a long exposure to this metal can cause digestive problems at stomach level or pancreas, it can disturb protein metabolism and cause arteriosclerosis [44].

2.2.3 Water treatment

Last years, the issues associated with toxic metal contaminated water have been receiving a special attention. The legislation is more and more inflexible and straight and new processes of water decontamination are in continuous development such as chemical precipitation, ion exchange, adsorption, biosorption, membrane filtration and others. Science of polymers and surfactants are one of the most studied areas to apply in water treatment [45].

Chemical precipitation is one of the basic techniques chosen due to its relative simplicity and low cost of precipitant [46]. The present technique is based on transforming a soluble compound into an insoluble form (precipitate). Besides hydroxide precipitation, there are other precipitation types also applied, as carbonate or

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[2] "Calcium homeostasis refers to the regulation of the concentration of calcium ions in the extracellular fluid" [64]

[3] Portuguese authority responsible for wastewater control

sulfite treatments. Usually, this process is accompanied by flocculation or coagulation techniques.

Dean et al [47] could reach an almost complete removal (~90%) of heavy metals as iron manganese, zinc, copper, nickel and cobalt with hydroxide precipitation. However, metals as mercury, cadmium and lead were not completely successful, which required adding limewater, for example, in order to precipitate these heavy metals.

On the other hand, considerable disadvantages are associated with this technique. Firstly, the fact that in some cases the addition of chemicals, as lime, may increase the production of sludge. Secondly, some metal hydroxides are amphoteric and when we have a mixture of metals, there is no optimal pH to work with and the efficiency of the process may be in doubt. Besides, this method is sensible to other complexing agents, inhibiting the process [48].

Ion exchange is based on exchanging of ions between two electrolytes or between an electrolyte solution and a complex. This technique is known by its high removal capacity and fast kinetics. Resins, as strong ($-SO_3H$) or weak (-COOH) acidic resins, are commonly used due to their specific ability to exchange its cations with the cations in the wastewaters [48]. Besides synthetic resins, natural zeolites are also applied since they are in abundance in nature and cheap in terms of costs, although they are usually applied in laboratory studies. It is necessary more research work in this area to apply in large scale.

In present, adsorption is recognized as an effective and economic method, even in terms of industrial scale. Moreover, in most cases it is a reversible process and it is possible to regenerate adsorbents. Including in this technique, it is activated carbon adsorbents and carbon nanotubes.

Activated carbon is characterized by its high surface area resulting from the large micropore and mesopore volume. However, it is quite expensive their commercialization, especially if we are talking about industrial wastewater treatment. In this way, developing composites with activated carbon, as adding alginates, tannic acids or surfactants can be turn the process more effective. On the hand, it is important to search for alternative sources, converting carbonaceous materials, as eucalyptus bark, for example, into activated carbon.

Nowadays, carbon nanotubes have been studying in several scientific areas due to their properties. Adsorption of particles is one of the studies developed especially due to the high surface area of these nanoparticles.

2.2.4 Metal ion adsorption by MWCNTs

Stabilization of MWCNTs suspension assuring that a good dispersion is reached has a direct influence on MWCNTs performance. Xiaoli Tan et al. [49] studied the effect of anionic surfactant, SDBS, in nickel adsorption. A suspension of 0.8% (w/w) of MWCNTs were dispersed in a SDBS solution (0.98 mmol/L) by a sonicator during 1h at 128W. After the dispersion process, the MWCNTs+SDBS suspension were added to a solution of 0.15 mmol/L of nickel. **Figure 6** shows the influence of surfactant concentration on nickel adsorption.

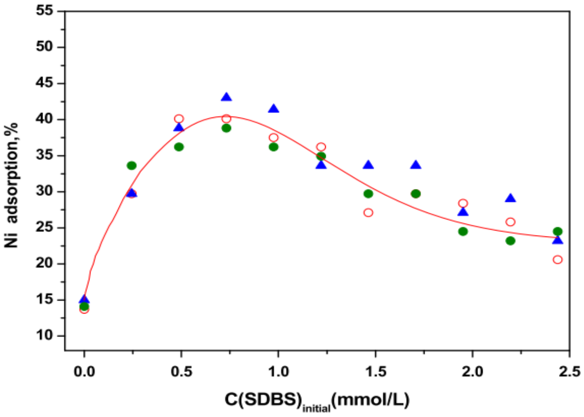

Figure 6 *Effect of SDBS concentration on the adsorption of nickel on MWCNTs. (adapted from Xiaoli Tan et al.* [49]*)*

Xiaoli Tan et al. concluded that the adsorption of nickel increases with the increasing SDBS concentration (at C_{SDBS}<0.73 mmol/L) and then decreases with the increase of SDBS concentration. The effect of SDBS on nickel adsorption may be attributed to the formation of cation-SDBS complex on the accessible adsorption sites on MWCNTs surfaces. On the other hand, the decrease observed may be explained by the possible tendency of SDBS to form micelles at MWCNTs surfaces. For this reason, it is important to know the surfactants CMC in order to maximize the metal ion adsorption.

Functionalization of CNTs, as already mentioned in sub section 2.1.4, is an efficient technique of CNTs stabilization. In this way, removal of particles by functionalized CNTs has been studied. Lu and Liu [51, 52] developed a few tests of heavy metal ions removal, as Ni (II) and Zn (II), applying oxidized SWCNTs and oxidized MWCNTs. For example, relatively to Ni (II), **Figure 7A** and **Figure 7B** shows the sorption isotherms of Ni (II) by raw and oxidized SWCNTs and raw and oxidized

MWCNTs, respectively. C_e represents the equilibrium Ni (II) concentration (mg dm^{-3}) and q_e are correlated with the isotherm of Langmuir and Freundlich (mg g^{-1}), representing the capacity of Ni (II) sorption by CNTs.

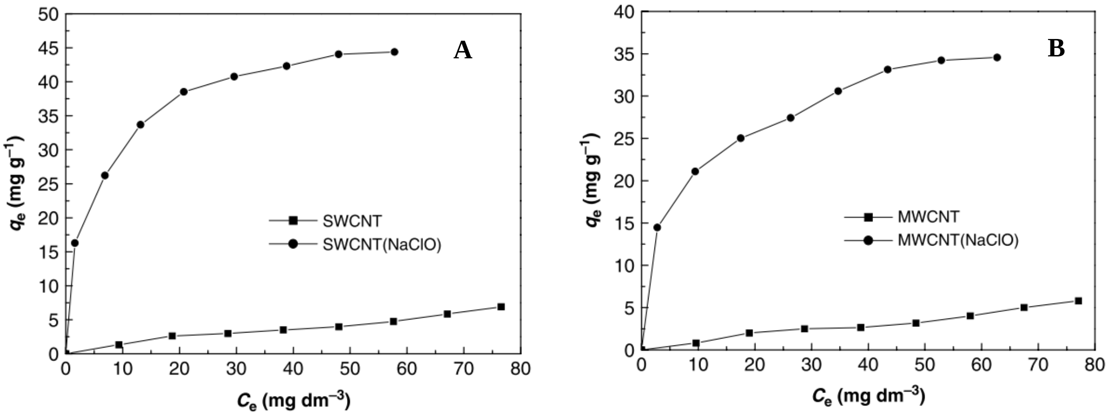

Figure 7 *Sorption isotherms of Ni (II) by raw and oxidized SWCNTs (A) and raw and oxidized MWCNTs (B).* [50]

It is quite clear the difference between raw and oxidized CNTs in Ni (II) removal. The fact that functional groups and acidic sites changes the CNTS surface properties, increasing the hydrophilicity, improved a better Ni (II) sorption onto oxidized CNTs. On its time, the cation removal was higher when oxidized SWCNTs were applied, comparing to oxidized MWCNTs. Lu and Liu [50] explained that this result might be attributed to the fact that SWCNTs contain more surface total acidic sites than oxidized MWCNTs, and also because the zeta potential of oxidized SWCNTs is more negative than that of oxidized MWCNTs. These two points will increase the electrostatic attraction for the SWCNTs than for the MWCNTs.

This study showed possible to reach good results in terms of particles removal. However, the functionalization step of CNTs involves high temperatures, what makes this process expensive. Thus, raw MWCNTs will be applied in present study.

2.3 National Legislation

Although Portugal does not have a specific law covering water preservation, pollution and recovery, there is a law referring to the use of water for human consumption. The first registered legislation in the Official Journal dates from 1990, when for the first time, in accordance with European Legislation, government defined reference values of toxic compounds that waters could contain, treatments to apply according to their class and other points (*Decreto-Lei* DL n^{o} 74/1990).

After eight years, it was time to review this legislative document and elaborate a new one – DL nº 236/1998 [53]. This document approaches all essential topics that national entities should evaluate, clarifies the competences of each entity and redefines parameters values of toxic compounds in water intended for human consumption.

On the other hand, in 2001 the old intervention program called PRESGRI 99 (strategic plan for industrial waste management) was reviewed according to *Decreto-Lei* DL nº 89/2002. PRESGRI 2001 arose with the objective of analyzing all industrial pollution sources on the national territory, identified all residues produced by industries, prepared intervention plans coordinated by local authorities and assured that values of pollution legislated by government are respected. PRESGRI was a route to assure 3R's policy: Reduce, Reutilize, and Recycle [54].

Even with the best results reached along the years [34], it was necessary to pay more attention to the issues of microbiological parameters, revision of the control program, definition of new control parameters according to different national areas, e.g. water hardness or tendency of forming cyanobacteria colonies, or even the application of a more rational sampling in some specific locations. In this way, in 2007, a new legislative document was drawn (DL nº 306/2007), which is still in use and which will be applied in this work for the purpose of target values – **Table 1**.

***Table 1** Maximum concentration for each heavy metal ion in water, according to national legislation (DL nº306/2007 and DL nº 236/98)*

Metal Ion	C_{max} **(mg/L)**[35,53]
Pb^{2+}	0.01
Cu^{2+}	2.00
Ni^{2+}	0.02
Zn^{2+}	3.00

3 Characterization of Materials and Experimental Procedure

3.1 Overview

This chapter presents in detail all the materials used and which techniques were chosen in this work in order to reach the main objective: removal of metal ions from aqueous solutions by multiwalled carbon nanotubes.

All tests performed were developed in laboratory, respecting as much as possible certain operatory conditions in order to ensure the homogeneity and reproducibility of the samples.

Firstly, it was necessary to characterize the materials applied, starting with the surfactants characterization. This characterization was focused on determination of hydrodynamic diameter, molecular weight and zeta potential of three different types of surfactants.

Then, once the dispersion of CNTs in aqueous solutions is quite difficult to reach, it is necessary to optimize the operatory conditions of these tests. Ultrasound energy and addition of surfactants were the techniques chosen to disperse these suspensions. Those dispersions were characterized measuring the diameter of suspended particles by Dynamic Light Scattering (DLS), to make sure that there is no MWCNTs aggregates.

After characterization steps, optimal dispersions were added to metal ions solutions, starting the adsorption tests. The results of those adsorptions were analyzed with atomic absorption spectrometry, making possible to conclude about the efficiency of MWCNTs dispersions in metal ions removal.

3.2 Materials

3.2.1 Multiwalled Carbon Nanotubes

To proceed with this study, multiwalled carbon nanotubes (MWCNTs) CN7000, produced by Nanocyl were used. The choice of MWCNTs has to do with economic factors, since MWCNTs are much less expensive than SWCNTs. So, considering the interest on innumerous applications, this was a determinant factor. Also, so far only MWCNTs are able to proceed at an industrial level.

According to data provided by the supplier, these MWCNTs have a mean dimeter around 9.5nm, a mean length around 1500nm and specific surface between 250 000 and 300 000 m^2/kg. They have 90% of pure carbon and 10% of metallic oxides. Casaleiro, in 2014 [55] completed MWCNTs characterization regarding density and zeta potential, reaching the results of 1.7g/cm^3 and -25.2mV, respectively.

3.2.2 Surfactants

It was seen in section 2.1.2 that CNTs are extremely hydrophobic what requires the use of surfactants to promote their dispersion in aqueous solutions. In this way, three types of surfactants were chosen, so it was possible to study not only their influence in CNTs dispersion but also their influence in metal ions removal. **Table 2** lists the surfactants applied during the tests, SDBS (anionic), Pluronic F-127 and Glycerox (non-ionic) and polyDADMAC MMW (cationic) and the data provided by the supplier – Sigma-Aldrich for all of them, except for Glycerox that was provided by aquaTECH ©.

Table 2 *Surfactants applied during the tests and data provided by the supplier.*

Surfactant (-)	Concentration (wt%)	Charge (-)	Chain Type (-)
SDBS	-	Anionic	Linear
Pluronic F-127	-	Nonionic	Linear
PolyDADMAC MMW	20	Cationic	Linear
Glycerox	31	Nonionic	Linear

These surfactants were characterized for hydrodynamic diameter (size), molecular weight and zeta potential. This characterization has an important role in this study once we can do a better interpretation of surfactants performance not only in terms of MWCNTs dispersion but also in terms of influence in adsorption mechanisms.

Usually, size information is seen as one of the most important characteristics of molecules, especially in cases like adsorption on other particles once they will influence adsorption sites in MWCNTs structure. However, it is important to pay attention when a measurement is developed. It is normal to get different results since materials are composed by irregular particles with different dimensions. In this way, it is necessary to define an equivalent dimension of the particle which is directly related to its size.

Zeta potential plays an important role in terms of electric potential between the surfactant and the particles surface.

This study was performed with ZetaSizer Nano equipment by Malvern, UK, available on *Laboratório de Tecnologia de Sólidos* of Chemical Engineering Department of *Faculdade de Ciências e Tecnologias da Universidade de Coimbra.* The results reached are presented below in section 3.3.1.

3.2.3 Metal Ion Solutions

In section 2.2.2 it was possible to know what metals exist in higher concentrations in Portugal, their chemical information and their negative effects in human health. They are Cu, Ni, Pb and Zn.

To prepare the metal ion solutions, it is necessary to dissolve the respective salts with deionized water as solvent. In this way, solutions of Copper (II) chloride dehydrate $CuCl_2 \cdot 2\ H_2O$, nickel sulfate (II) $Ni(SO_4) \cdot 6\ H_2O$, lead nitrate (II) $Pb(NO_3)_2$ and zinc sulfate $Zn\ SO_4 \cdot 7\ H_2O$ were prepared. **Table 3** lists these salts and their respective molecular weight.

Table 3 *Salts and respective molecular weight.*

Salt	**Molecular Weight (g/mol)**
$CuCl_2 \cdot 2\ H_2O$	170,48
$Ni(SO_4) \cdot 6\ H_2O$	262,86
$Pb(NO_3)_2$	331,21
$Zn\ SO_4 \cdot 7\ H_2O$	287,50

3.3 Experimental Procedures

3.3.1 Characterization Techniques

Zetasizer Nano

Zetasizer Nano, or ZSN, is an equipment that allows characterizing particles in a liquid medium, measuring three fundamental morphological parameters: Particle size, Zeta potential and Molecular weight in the case of polymers [56].

Size measurement

Brownian motion is defined as the random movement of particles suspended in a fluid resulting from their collision with the molecules in the liquid (or gas). Knowing that smaller particles moves slowly than bigger ones, ZSN can study that movement on time by taking “pictures” of the sample in different moments, using the Dynamic Light Scattering (DLS) technique.

DLS consists in illuminate the particles with a laser and analyze the intensity of fluctuations in the scattered light. It is necessary to have enough particles that can scatter the light but on other hand avoid the formation of aggregates and consequently the multiple scattering. This information can be controlled once ZSN software provides that information on *Quality Report* by the *Count Rate* value.

After the analysis, ZSN gives the value of D_z (Z-average) which is the intensity weighted harmonic mean size of the hydrodynamic diameter distribution. To measure this intensity, ZSN software obeys to Rayleigh’s approximation that relates the size of particles with the intensity of scattering, assuring no multiple scattering occurs.

This measurement was applied in this study in order to know the size of the molecules of surfactant and the quality of MWCNTs dispersions to compare the efficiency of surfactants in these dispersions.

Molecular weight measurement

Opposing to Size Measurement, Molecular weight measurement applies a process called Static Light Scattering (SLS). In the same way that DLS, particles in the sample are illuminated by the laser and consequently the light will be scattered in all directions. But instead of measuring the time dependent fluctuations in the scattering intensity, SLS will measure the time-averaged intensity of scattered light.

This measurement is based on Rayleigh equation (Equation (2)) that describes the intensity of light scattered from particle on solution.

$$\frac{KC}{R_\theta} = \left(\frac{1}{M} + 2A_2C\right)P(\theta) \qquad (2)$$

Where $\boldsymbol{R_\theta}$ is the Rayleigh ratio (the ratio of scattered light to incident light determined using a standard component, toluene in this case);

$\boldsymbol{M}$ is the sample molecular weight;

A_2 is the second virial coefficient and describes the interaction strength between the particles and the solvent;

C is the concentration;

$P(\theta)$ is the angular dependence of the sample scattering intensity;

K is the optical constant defined by the Equation (3):

$$K = \frac{2\pi^2}{\lambda_o^4 N_A}\left(n_o \frac{dn}{dc}\right)^2 \tag{3}$$

Where N_A is Avogadro's Number;

λ_o is the laser wavelength;

n_o is the solvent refractive índex;

$\frac{dn}{dc}$ is the differential refractive index increment and represents the change in refractive index as a function of the change in the polymer concentration.

This measurement requires preparation of different sample concentrations, once they will be compare with toluene first measurement. The equipment software supplies the so called *Debye Plot*, with the relation between the intensity of scattered light $\left({}^{K}/_{CR_\theta}\right)$ and those concentrations (*C*) at one angle. From this graphical representation, it is possible not only to determine the Absolut Molecular Weight,$\left({}^{1}/_{M}\right)$, but also the virial coefficient, *A*$_2$. The first parameter is calculated based on the intersection of the Debye line with axis null concentration and the second one corresponds to the gradient of the same line (**Figure 8**). On the other hand, it is possible to analyze if there is multiple scattering effect, which occur if the intensity of the scattered light decreases between two consecutive points when concentration increases. A solution to this problem is diluting the sample.

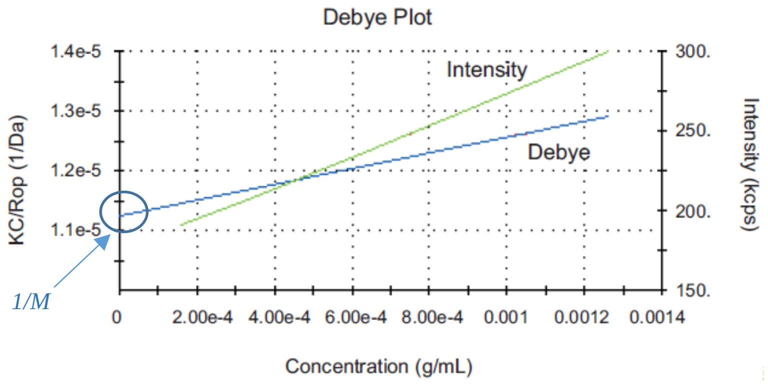

Figure 8 *Representation of Absolute Molecular Weight (1/M) on Debye plot (adapted from Malvern ZSN user manual).*

Zeta Potential measurement

The interaction between the particle and the molecules that surround it will create a variation of counter ions concentration around the particle surface and consequently create an electrical double layer. Paying attention to **Figure 9,** it is possible to understand that liquid layer surrounding the suspended particle distribute its ions in two parts: an inner region called *Stern layer* and an outer region called *Diffuse layer*. Once in *Stern layer* ions are strongly attached to the particle and when the particle moves, these ions will be drag with it. The same does not happen with the ions beyond the equilibrium boundary or *Slipping plane*. Therefore, zeta potential is defined as the potential created by this boundary and explains the stability of certain solution.

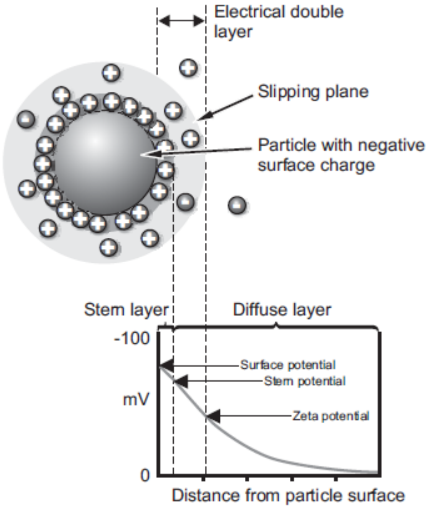

Figure 9 *Representation of ion layers distribution around the suspended particle and their respective potential according to distance from particle surface (adapted from Malvern ZSN user manual).*

If we think about a certain suspension where all the particles have the same large zeta potential, they will tend to repel each other and there is no tendency to flocculate.

The main factor that have direct influence in zeta potential measurements is pH. When zeta potential is equal to zero this means that the suspension is unstable and it is called the *Isoelectric Point*.

The zeta potential of a particle in suspension is measured based first on *Electrophoresis* phenomena described by Henry equation - Equation (4). When an electric field is applied across a suspension, charged particles will be attracted towards the electrode with opposite charge. On other hand, the viscous forces of the medium will contradict this movement and consequently slow them down. When an equilibrium is reached the velocity or Electrophoretic Mobility of particles will be constant and it is time to apply Henry's equation:

$$U_E = \frac{2\varepsilon\, z\, f(ka)}{3\eta} \tag{4}$$

Where $\boldsymbol{U_E}$ is the Electrophoretic Mobility;

$\boldsymbol{\varepsilon}$ is the dielectric constant;

$\boldsymbol{z}$ is zeta potential;

η is the viscosity;

f(ka) is the Henry's function which normally takes two possible approximations, 1.5 or 1.0.

Those two approximations are chosen depending on samples type. In the case of aqueous samples, f(ka) will be equal to 1.5 and it refers to *Smoluchowski* approximation. On other hand, when samples are non-aqueous, Henry's function will be equal to 1.0 and it refers to *Huckel* approximation.

Malvern's Zetasizer Nano based on Laser Doppler Velocimetry (LDV) measures the electrophoretic mobility, U_E, by the ELS (Electrophoretic Light Scattering). A light beam passes throw the sample and the light scattered, by the particles, will be combined with a reference beam at an angle of 17º. This behavior will produce a fluctuating intensity signal proportional to the speed of the particles. A digital signal processor is used to convert the characteristic frequencies in the scattered light. From the particle velocity, proportional to electrophoretic mobility, the particle zeta potential can be calculated using Henry Equation.

Refractive index measurement

As it was mentioned before, to apply the Molecular Weight equation used in the measurements it is necessary to know the refractive index of the sample. This measurement was done with a Refractometer (Atago RX-5000 CX) available in *Laboratório de Tecnologia de Sólidos* of Chemical Engineering Department of *Faculdade de Ciências e Tecnologias da Universidade de Coimbra*.

The speed of light when it moves through a medium slows down its velocity once it is constantly absorbed and reemitted by the atoms of the material. The ratio between the speed of light in targeted medium and in vacuum, which remains constant, is defined as the *Index of Refraction* or *Refractive Index* (RI) [57].

This measurement requires a first step of calibration with the solvent used (deionized water) at 25ºC. After this calibration, the different concentrations prepared are measured and with RI values obtained it is elaborated a regression curve (refractive index as function of surfactant concentration). The slope of this curve will correspond to the value of $^{dn}/_{dC}$.

Atomic Absorption Spectrometry

A final stage of this study is measuring metal ion concentrations in order to conclude about efficiency of MWCNTs in their removal from aqueous solutions.

Absorption Atomic Spectrometry (AAS) is an analytical technique that make use of the wavelengths of light specifically absorbed by an element. This absorption correspond to the energy needed by that element to move from one energy level to another one more energetic [58].

AAS is based on atomization of the sample, which means that the sample is converted into ground state free atoms in the vapor state. When a source of light (a specific lamp according to the metal) passes through this vaporized sample, the atoms will absorb the respective frequency of light and a different beam of electromagnetic radiation emitted from excited atoms is passed through the vaporized sample. The concentration of the sample will be measure based on radiation flux between the white (without sample) and the sample.

The equipment applied during all study was Atomic Absorption Spectrometer Perkin Elmer 3300, which detection limit in terms of concentration for each metal ion is presented in **Table 4.**

Table 4 *Detection Limit in terms of concentration (ppm) for each heavy metal ion.*

Metal Ion	Detection Limit (ppm)
Pb (II)	0.0670
Cu (II)	0.0750
Ni (II)	0.0670
Zn (II)	0.0057

3.3.2 Characterization of Surfactants

The study started with the size measurement of the surfactants, where different concentrations of surfactant were tested and according to quality report provided by ZSN it was possible to move forward with zeta potential and molecular weight measurements.

Hydrodynamic diameter of molecules, Dz

In general, the procedure developed was quite simple and applied to all characterizations. First, surfactants were dissolved in 100mL of deionized water to get a solution concentration of 0.5% (w/w), 0.5g/100mL, during 3hours in stirring plates (600rpm) in order to get a good dissolution.

Then, samples of these initial solutions were collected by a syringe and filtered (porosity of 0.45μm) into a square glass cell, appropriate for ZSN equipment. The measurement was carried out according to some previously defined parameters such as chamber temperature equal to 25ºC, 120s of stabilization and five measurements in minimum to ensure the reproducibility. It is extremely important to pay attention to possible presence of bubbles inside the cell, due to sensibility of the equipment.

In the end, according to count rate provided by ZSN quality report, it is necessary to decrease or increase the initial concentration. These new solutions were mixed during approximately 30 minutes and analyzed in the same conditions.

When ZSN software provides a “Good Quality Report”, it means that we have found viable conditions to describe molecules size. The concentration that matched with ZSN Quality Criteria were 0.03% (w/w) for SDBS, 0.5% (w/w) for Pluronic and 0.1% (w/w) for PolyDADMAC MMW– Appendix A.1. The next measurements of zeta potential and molecular weight will have these concentrations as reference.

Zeta Potential, z

The procedure followed was the one already described above, with exception of the measuring cell where the sample was collected. In this case, instead of using a square glass cell, the cell chosen was DTS1070 containing two electrodes. Again, the sample was collected with a syringe and a filter of 0.45μm.

In case of SDBS, it was necessary to increase the initial concentration of 0.03% (w/w) to 0.05% (w/w). All zeta potential distribution graphics can be found in Appendix A.2.

Molecular Weight, M

As explained in subsection 3.3.1, it is necessary to prepare solutions with different concentrations, besides toluene as white sample. It is usual to prepare two samples with higher concentrations than the solution used for size measurement and two samples below.

To proceed with this measurement it is necessary to know additional information as RI for each surfactant concentration. Then, it was possible to build a plot of RI values as function of concentration, in order to determine the value of dn/dc through a regression line – Appendix A.3.

Besides this additional step, it is necessary to insert all concentration values measured into the ZSN software in order to generate the Debye plot for each molecular weight calculus. Cell preparation follows the same procedure than size measurement. The Debye plots generated in this study can also be seen at Appendix A.3.

Table 5 shows the results obtained in this first set of tests. It is important to say that polyDADMAC MMW characterization was performed by Patrícia Costa, 2016 [59].

Table 5 *Summary of surfactant characterization.*

Surfactant	**Dz (nm)**	**Dz^{av} (nm)**	**z (mV)**	**z^{av} (mV)**	**M (kDa)**	**M^{av} (kDa)**
SDBS	80.96	81.02	-66.80	-66.97	370	363
	80.61		-66.70		358	
	81.49		-67.40		361	
Pluronic F-127	6.910	6.920	-0.460	-0.430	8.18	9.49
	6.950		-0.350		10.0	
	6.910		-0.470		10.3	
PolyDADMAC MMW	48.87	48.58	70.10	69.47	201	240
	48.13		69.00		250	
	48.74		69.30		269	

3.3.3 Characterization of MWCNTs dispersions

Once the three types of surfactants are characterized, it is time to proceed to the characterization of MWCNTs dispersions.

It was explained in section 2.1.4 (Stabilization of Carbon Nanotubes) the important role that a good CNTs dispersion plays in order to optimize their properties. In this way, three parameters were changed in order to study their influence on CNTs dispersions. Those parameters were sonication time, sonication intensity and surfactant concentration. This last parameter was based on comparative study between surfactants.

Once a good result was reached for Glycerox (as reference), the same ultrasound conditions were applied and the dispersions characterized in the ZSN equipment for each surfactant.

In this section, it was studied also the performance of SDBS, Pluronic F-127 and polyDADMAC MMW at same concentration (0.03% (w/w)) in MWCNTs dispersions (0.01% (w/w) and 0.05% (w/w)). After this first approach, the concentration of surfactant applied in the dispersions might be optimized to proceed with the adsorption step.

Characterization of ideal dispersions

To reach a MWCNTs suspension well dispersed three parameters were studied: sonication time, sonication intensity and surfactant concentration. This study was based on two MWCNTs concentrations: 0.01% (w/w) and 0.05% (w/w), corresponding to 0.015g and 0.075g for a volume of surfactant solution equal to 150mL. These MWCNTs concentrations were chosen based on Figueiredo [60] study, where he could reach a good quality dispersion of 0.01% (w/w) of MWCNTs with 2% of Glycerox as surfactant, with 5 minutes of ultrasonic energy, thus an adsorption test could be made under these conditions. In this way, this test was the reference to start the optimization. On the other hand, Lu and Liu [51,52] studied the efficiency of Ni (II) and Zn (II) removal applying 0.01% (w/w) and 0.05% (w/w) of oxidized CNTs. The maximum sorption reached in these two studies were with 0.05% (w/w) of MWCNTs.

Glycerox is a nonionic surfactant already studied in MWCNTs dispersions [60]. However, due to logistic issues it was not possible to obtain reproducible batches of this surfactant, so this surfactant was used only to optimize sonication conditions in the beginning of laboratory tests. After this optimization, it was possible to fix sonication parameters and adjust surfactant concentration for this situation.

Glycerox was provided as an aqueous solution with concentration equal to 31% (w/w), so a weight of 9.7g were added to a beaker which was filled with deionized water until 150mL. This solution was stirred during 3h at 500rpm promoting a good dissolution.

Dispersion of MWCNTs in this surfactant were prepared for ultrasound tests for both MWCNTs concentrations (0.01% (w/w) and 0.05% (w/w)) with the same surfactant concentration (2% (w/w)):

Test 1- Ultrasonic energy during 5 minutes at 90% intensity;

Test 2- Ultrasonic energy during 5 minutes at 75% intensity;

Test 3- Ultrasonic energy during 10 minutes at 75% intensity;

Test 4- Ultrasonic energy during 15 minutes at 75% intensity.

These tests were performed using a probe-sonicator (Sonics Vibracell VC505). It works with a frequency of 20kHz and a maximum power of 500W.

Temperature is another important parameter that should be maintained around 20ºC. Casaleiro [55] verified that when applying ultrasounds to disperse a suspension, the temperature could increase until 47ºC, promoting undesirable effects in MWCNTs dispersions. **Figure 10** shows the ice bath with a water flux prepared for each test during all dispersions.

Figure 10 *Ice bath with water flux prepared during MWCNTs dispersions, using an ultrasound equipment.*

The efficiency of each test was analyzed in terms of particle size distribution, with the ZSN equipment. A sample was collected into a squared glass cell with a Pasteur pipette and the hydrodynamic diameter was measured, as described in 3.3.1. Glycerox reached an optimal performance for both MWCNTs concentrations in the conditions of test 4 (ultrasonic energy during 15 minutes at 75% intensity). This result can be analyzed in Chapter 4. For the other tests, the results are presented in Appendix B.

After sonication tests with Glycerox, concentration of SDBS, Pluronic F-127 and polyDADMAC MMW were optimized in terms of MWCNTs dispersion. The surfactant concentration for each type started with 0.03% (w/w), as explained below, and then adjusted according to ZSN quality reports (Size measurement).

All surfactants solutions were prepared in deionized water and mixed at 600rpm at least 3 hours for full dissolution. All results about MWCNTs dispersions for each surfactant will be discuss in the next chapter.

Comparative study between surfactants

According to Jiaxing Li et al [61] it was possible to reach not only a good result of metal ion adsorption but also a good MWCNTs dispersion, applying SDBS as surfactant in an amount of 0.03% (w/w). SDBS was thus chosen as the reference for this comparative study between surfactants. Therefore, for each surfactant a concentration equal to 0.03% (w/w), was always considered and their performance in dispersion of 0.01% (w/w) and 0.05% (w/w) of MWCNTs was studied.

In the case of SDBS and Pluronic F-127, they were weight 0.045g and added to 150mL of deionized water, to obtain a solution of 0.03% (w/w). The polyDADMAC MMW was provided as an aqueous solution with a concentration of 20% (w/w). To prepare a solution of 0.03% (w/w) it is necessary to weight 0.225g of polyDADMAC MMW and add 150mL of deionized water. The solutions prepared were mixed for at least 3hours at 600rpm.

When the surfactant solutions were totally dissolved, they were added to MWCNTs. Then, these suspensions were dispersed applying ultrasonic energy (Test 4), as explained previously. The size of the MWCNTs in these dispersions were measured using Zetasizer Nano equipment. The data corresponding to each surfactant can be seen in Chapter 4.

For the surfactants other than SDBS, the optimal surfactant concentration for the dispersion was determined as 0.03% (w/w) in the case of polyDADMAC MMW for both concentrations of MWCNTs, and for Pluronic F-127, 0.03% (w/w) in the case of 0.01% (w/w) of MWCNTs and 1% (w/w) in the case of 0.05% (w/w) MWCNTs. Those values are indicated in **Table 8** of sub-section 3.4.

3.3.4 Adsorption of Metal Ions

To prepare metal ions solutions, four different salts were dissolved. They were copper (II) chloride dihydrate, nickel sulfate (II), lead nitrate (II) and zinc sulfate.

One of the objectives described previously was to remove a specific concentration of each salt. **Table 6** shows the metallic compound, its respective maximum concentration found in Portugal and the target required by National Legislation.

Table 6 *Metal ions maximum concentration registered in 2014 in Portugal and respective maximum concentration allowed by national legislation (DL nº306/2007)*

Metal Ion	$C_{\mathbf{max,observed}}$ **(mg/L)**	$C_{\mathbf{max,\ allowed}}$ **(mg/L)**[35]
$\mathbf{Pb^{2+}}$	0.28	0.01
$\mathbf{Cu^{2+}}$	2.40	0.05
$\mathbf{Ni^{2+}}$	0.26	0.02
$\mathbf{Zn^{2+}}$	-	3.00

Once heavy metals have a high density, it is extremely difficult to prepare directly such low concentration solutions. In this way, a larger amount of each metal was weighted and then several dilutions were done until reaching the target concentration. Metal salts are extremely easy to dissolve in water, thus the solutions were mixed during approximately 30minutes.

In the end, a sample of 50mL was taken from each of the solutions prepared and added to a beaker of 250 mL. MWCNTs suspensions previously dispersed by each surfactant tested were added to the same beaker, already containing metal ion solutions, and carried on under agitation of 100 rpm. During the tests, samples of 10 mL were taken and filtered, first with a membrane filter of 1.0 μm and filtered again by a membrane filter of 0.45 μm. The adsorption of cations by MWCNTs was quantified by AAS.

3.4 Test Plan

Although a few extra studies were developed, such as the effect of the type of surfactant in MWCNTs adsorption, for example, a test plan based on adsorption tests was developed in order to reach the main objective of this work: heavy metal removal from aqueous solutions by MWCNTs.

Firstly, the MWCNTs dispersion tests were optimized. It was possible to disperse 0.01% (w/w) and 0.05% (w/w) of MWCNTs (0.015g/150mL and 0.075g/150mL, respectively), applying ultrasonic energy during 15 minutes and an intensity of 75%, with a concentration of Glycerox equal to 2% (w/w).

Then and before proceeding with adsorption tests, the concentration of surfactants were optimized, starting with a concentration of 0.03% (w/w) of SDBS as reference. A comparative study between surfactants performance were developed. All three surfactants, with a concentration of 0.03% (w/w), were applied to disperse 0.01% (w/w) and 0.05% (w/w) of MWCNTs, at same sonication conditions. **Table 7** shows the test plan developed to study the influence of the surfactant type in MWCNTs dispersions.

Table 7 *Test plan for comparative study between SDBS, Pluronic F-127 and PolyDADMAC MMW performance in MWCNTs dispersions.*

Surfactant (-)	Surfactant Concentration (% w/w)	MWCNTs Concentration (% w/w)
SDBS	0.03	0.01
		0.05
Pluronic F-127	0.03	0.01
		0.05
	1	
PolyDADMAC MMW	0.03	0.01
		0.05

According to Quality Report provided by ZSN software, in the case of adsorptions with 0.01% (w/w) of MWCNTs, this surfactant concentration was the optimum one. However, in case of polyDADMAC MMW, it was visible the existence of some aggregates. In this way, the concentration of this surfactant was increased to 0.1% (w/w).

When MWCNTs concentration was equal to 0.05% (w/w), the concentration of SDBS stayed unchanged as well as for Pluronic F-127. However, this last surfactant showed again some aggregates, what lead to the need to increase its concentration to 1% (w/w). In terms of polyDADMAC MMW, the concentration was increased to 0.5% (w/w), 1% (w/w) and 2% (w/w), but without better results, what means that adsorptions were carried on with a dispersion of not so good quality.

Once optimal concentrations of surfactants were defined, it was possible to start adsorption tests. The adsorption of Pb (II) by 0.01% (w/w) and 0.05% (w/w) of MWCNTs were taken as reference. The other metal ion solutions were treated with the MWCNTs suspension that provided better results on Pb(II) adsorption. Every ion metal solution were treated by optimal dispersions during 7days and samples of 10mL were taken at 4h, 18h, 24h and 7 days after the start.

Table 8 presents the test plan of adsorption tests.

Table 8 *Test plan for metal ion adsorption tests.*

Surfactant (-)	**Surfactant Concentration (% w/w)**	**MWCNTs Concentration (% w/w)**	**Metal ion (-)**	**Metal ion concentration (mg/L)**
SDBS	0.03	0.01	Pb^{2+}	2.98
		0.05		2.98
		0.01	Cu^{2+}	2.38
		0.01	Ni^{2+}	2.64
		0.01	Zn^{2+}	3.43
Pluronic F-127	0.03	0.01	Pb^{2+}	3.33
	1	0.05		3.33
	0.03	0.01	Cu^{2+}	5.41
	0.03	0.01	Ni^{2+}	2.64
	0.03	0.01	Zn^{2+}	3.43
PolyDADMAC MMW	0.03	0.01	Pb^{2+}	3.33
		0.05		3.33
	0.03	0.01	Cu^{2+}	5.41
	0.03	0.01	Ni^{2+}	3.74
	0.03	0.01	Zn^{2+}	3.80
SDBS + Pluronic F-127	0.03 + 0.03	0.01	Pb^{2+}	2.98
		0.05		
SDBS **Pluronic F-127**	0.03	0.01	Pb^{2+} Cu^{2+} Ni^{2+} Zn^{2+}	3.69 6.58 2.64 3.30

4 Results and Discussion

4.1 Overview

Chapter 4 presents and discusses the results obtained during the laboratory tests described in Chapter 3.

In first place, the optimization results of sonication conditions applied to MWCNTs dispersions and the optimal concentration for each surfactant in order to reach a good MWCNTs dispersion will be presented. It will be presented also a comparative study in terms of surfactants performance in the dispersion of MWCNTs.

Afterwards, the results of adsorption tests will be presented. These results include the effect of MWCNTs concentration on heavy metal ions adsorptions, the study of the competitive adsorption between heavy metal ions and also the effect of using a mixture of surfactants, SDBS (anionic) and Pluronic F-127 (non-ionic) in MWCNTs dispersions and in adsorption of Pb (II).

In the end, it will be presented an elaborated discussion of the results.

4.2 MWCNTs dispersions

4.2.1 Characterization of ideal dispersions

In the first sonication tests, the temperature of the dispersions could reach 45ºC, what required the use of a controlled ice bath with a flux of water. When this parameter was controlled, the temperature of the tests remained in a range between 18ºC and 25ºC.

The size distribution of the MWCNTs dispersions for the tests 1, 2 and 3 corresponding to different tests of sonication conditions and using Glycerox as surfactant (see subsection 3.3.3) can be seen in Appendix B.1. In case of test 4, it was not possible to measure the hydrodynamic diameter of particles, once the ZSN equipment was not available. This means that the quality of the dispersion was analyzed at “naked eye” and confirmed with an optical microscope, model OLYMPUS BHS.

The optimal conditions reached with the sonication treatment for 2% (w/w) of Glycerox corresponded to an ultrasonic energy of 75% of intensity during 15 minutes, corresponding to test 4. All the other tests showed not only a disagreement with the quality criteria of the software but also MWCNTs aggregates were visible in dispersions, especially for the higher concentration of MWCNTs.

These conditions were then applied to disperse 0.01% (w/w) and 0.05% (w/w) of MWCNTs with SDBS, Pluronic F-127 and polyDADMAC MMW. All tests started with a concentration of 0.03% (w/w) of surfactant, which, according to Jiaxing Li et al [61], was the optimal concentration for SDBS as explained before, and based on Quality Report provided by the ZSN software, concentrations was increased starting from that base value until a good dispersion was reached.

For a concentration of 0.01% (w/w) of MWCNTs, SDBS and Pluronic F-127 were efficient with a concentration of 0.03% (w/w). In the case of polyDADMAC MMW, the ZSN software provided also a Good Quality Report for a concentration of 0.03% (w/w), although aggregates were visible at “naked eye”. In this way, the concentration of this surfactant was increased to 0.1% (w/w), but it was still visible some aggregates in the top of the dispersion and the Quality Report was worst, so we kept the same concentration of 0.03% (w/w).

When the concentration of MWCNTs was increase to 0.05% (w/w), the concentration was increase to 1% (w/w) for Pluronic F-127 and to 0.5% (w/w), 1% (w/w) and 2% (w/w) for polyDADMAC MMW. In the first case, when the concentration of Pluronic F-127 was increase, it was possible to reach a better MWCNTs dispersion. On the other hand, the dispersion of MWCNTs applying higher concentrations of polyDADMAC did not show to be better than for the tests with lower concentrations, what means that a concentration of 0.03% (w/w) was applied in all adsorption tests.

The results of size distribution for each MWCNTs concentration, for the optimal conditions, can be seen in Appendix B.2.

Table 9 shows the optimal concentrations to apply in adsorption tests for SDBS, Pluronic F-127 and polyDADMAC MMW.

Table 9 *Optimal concentration for SDBS, Pluronic F-127 and polyDADMAC MMW to apply in the adsorption tests for each MWCNTs concentration.*

Surfactant (-)	Surfactant Concentration (% w/w)	MWCNTs Concentration (% w/w)
SDBS	0.03	0.01
	0.03	0.05
Pluronic F-127	0.03	0.01
	1	0.05
PolyDADMAC MMW	0.03	0.01
	0.03	0.05

After 7 days of adsorptions tests under slowly agitation of 100rpm, samples were taken from adsorption tests applying SDBS and Pluronic F-127, in order to analyse possible modifications in the MWCNTs dispersions. According to Quality Report the hydrodynamic diameter agreed with quality criteria. However, in both cases there were visible some aggregates in the top of the suspension: the value provided by ZSN software were 165.0 nm in the case of SDBS and 156.8 nm for Pluronic F-127. These Quality Reports and the summary values can be seen at Appendix B.2 as well.

4.2.2 Comparative study between surfactants

As explained in subsection 3.3.3, the performance of three surfactants in MWCNTs dispersion was studied, applying the same concentration (0.03% w/w) and the same sonication conditions (75% of intensity during 15minutes – Test 4).

A similar size distribution was reached in the three tests, although in the case of polyDADMAC MMW, the curve is slightly positioned to the right of the scale (see Appendix C). This means that higher values of hydrodynamic diameter were detected, what was proved with the visible aggregates - **Figure 11**. Appendix C shows the size distribution of particles provided by the ZSN software, when the concentration of MWCNTs was equal to 0.01% (w/w) and 0.05% (w/w).

Figure 11 *Aggregates of MWCNTs after dispersion of 0.01% (w/w) of MWCNTs with polyDADMAC MMW at a concentration of 0.03% (w/w).*

Pluronic F-127 had a similar behavior as SDBS, what means that an increase of MWCNTs concentration might be studied starting with the 0.03% (w/w) of surfactant, in order to conclude which surfactant shows a better performance on MWCNTs dispersion.

Even if the Quality Report provided by the ZSN software showed a positive result for both nonionic and cationic surfactants, Pluronic F-127 and polyDADMAC MMW (see Figure C2), **Figure 12** raised some doubts since a few aggregates could be seen at "naked eye".

The results of size distribution for dispersions with 0.05% (w/w) of MWCNTs can be seen in Appendix C as well.

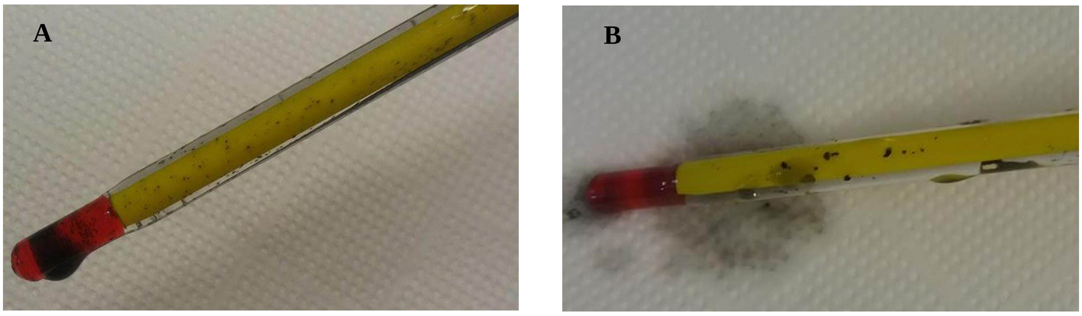

Figure 12 *Aggregates of MWCNTs in suspensions with a concentration of 0.05% (w/w) of MWCNTs and 0.03% (w/w) of Pluronic F-127 (A) and polyDADMAC MMW (B).*

Table 10 presents the summary of the hydrodynamic diameters measured for 0.01% (w/w) and 0.05% (w/w) of MWCNTs dispersions for each surfactant at 0.03% (w/w): SDBS, Pluronic F-127 and polyDADMAC MMW.

***Table 10** Summary of the results of hydrodynamic diameter for each surfactant with a concentration of 0.03% (w/w) and concentrations of MWCNTs equal to 0.01% (w(w) and 0.05% (w/w).*

Surfactant (-)	**MWCNTs Concentration (%)**	**Dz (nm)**	**Dz^{av} (nm)**
SDBS	0.01	178.5	180.5
		183.0	
		179.9	
	0.05	187.3	187.6
		187.8	
		187.6	
Pluronic F-127	0.01	184.9	187.3
		185.3	
		191.7	
	0.05	220.6	219.9
		216.1	
		222.9	
PolyDADMAC MMW	0.01	314.8	307.7
		305.8	
		302.6	
	0.05	280.8	277.6
		274.9	
		277.0	

Paying attention to **Table 10** it is possible to conclude that Pluronic F-127 had a similar performance as SBDS when dispersing 0.01% (w/w) of MWCNTs. However, when the concentration of MWCNTs increase to 0.05% (w/w), the hydrodynamic diameter tends to increase slightly which is a possible explanation for the existence of some MWCNTs aggregates, as observed.

In the case of polyDADMAC MMW, both dispersions registered higher values of hydrodynamic diameter, around 300 nm, 1.7 times higher than SDBS.

4.3 Adsorption of metal ions by MWCNTs

4.3.1 Influence of MWCNTs concentration in adsorption tests

For each optimal concentration of surfactant presented in **Table 9** in subsection 4.2.1, concentrations of 0.01% (w/w) and 0.05% (w/w) of MWCNTs were studied in the adsorption tests in order to conclude about the influence of MWCNTs concentration in the adsorption of metal ions. These set of tests was based on Pb (II) adsorption.

Figure 13 shows the comparative study between two MWCNTs concentrations, for each surfactant.

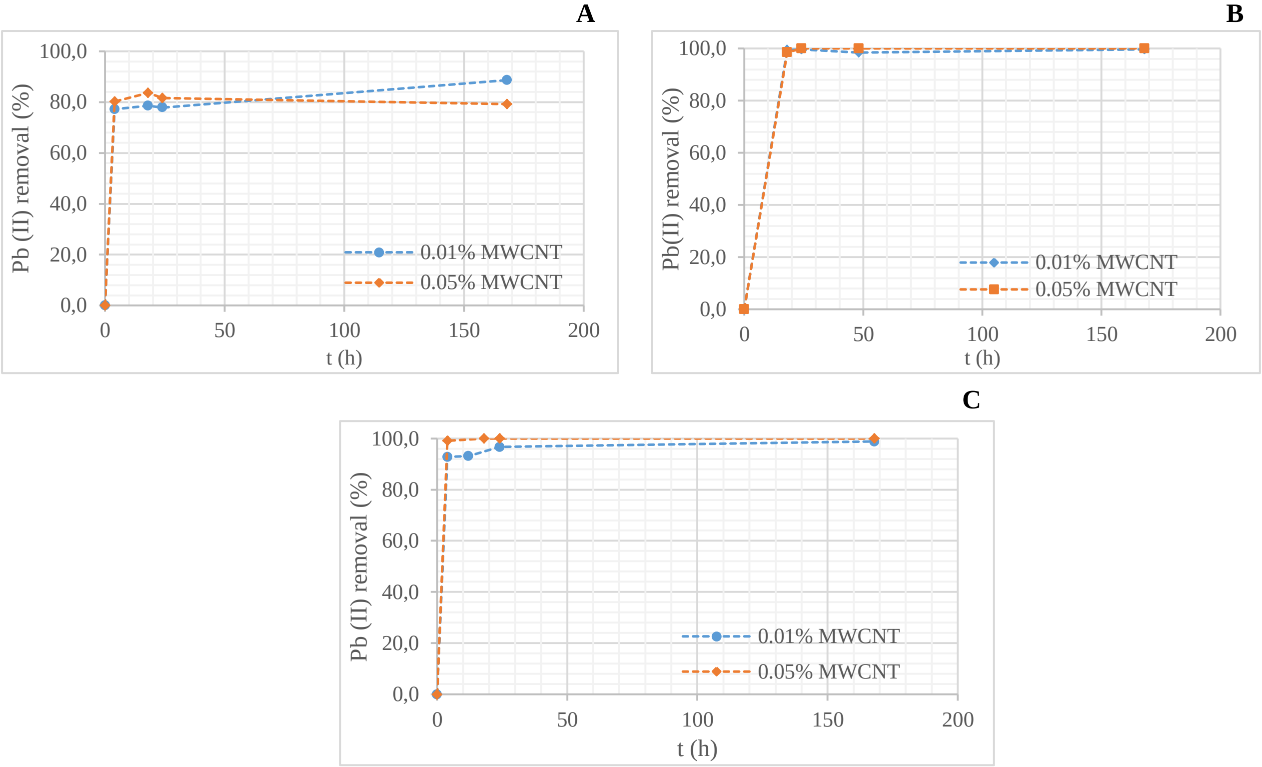

Figure 13 *Pb (II) removal by MWCNTs from an aqueous solution. MWCNTs suspensions dispersed by SDBS (A), Pluronic F-127 (B) and polyDADMAC MMW (C). The initial concentration of Pb (II) was 2.98mg/L in SDBS test and 3.33mg/L in Pluronic F-127 and polyDADMAC MMW tests. Surfactant concentrations described in Table 9.*

Figure 13 shows that the behavior of the Pb (II) removal applying 0.01% (w/w) or 0.05% (w/w) of MWCNTs is quite similar. Only in the case of SDBS, 0.01% (w/w) of MWCNTs showed to reach a higher removal of this metal ion.

This means that it is not necessary to apply 0.05% (w/w) of MWCNTs in metal ions removal, when it is possible to reach around 99% of removal with a concentration of MWCNTs of 0.01% (w/w). The minimum concentration of Pb (II) reached was 0.01 mg/L for the dispersion with 0.01% (w/w) of MWCNTs stabilized with Pluronic F-127.

For a MWCNTs concentration of 0.05% (w/w) the final concentration was even lower, both with Pluronic F-127 and polyDADMAC MMW but below the detection limit of the atomic absorption equipment (see **Table 4** in subsection 3.3.1).

The summary of these graphics can be seen at Appendix D.

4.3.2 Metal ion removal

As showed in subsection 4.3.1, the difference between the efficiency of applying a higher or a lower concentration of MWCNTs in adsorption tests is not significant. In this way, all adsorption tests were developed with a concentration of 0.01% (w/w) of MWCNTs. **Figure 14** shows the metal ions removal curves for each surfactant. In Appendix E it is possible to see the table summarizing this study.

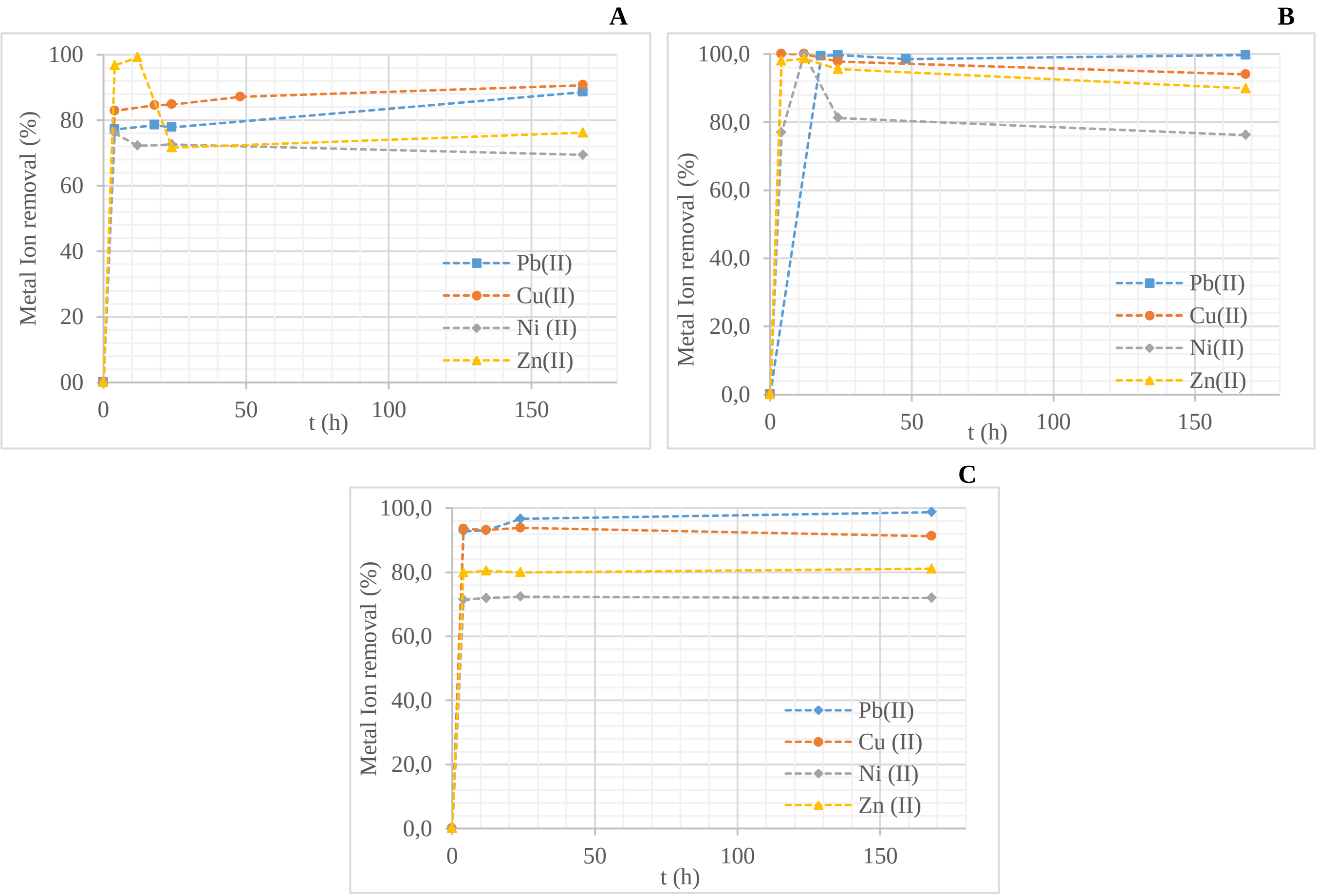

Figure 14 *Metal Ion removal by suspensions of 0.01% (w/w) of MWCNTs dispersed by SDBS (A), Pluronic F-127 (B) and PolyDADMAC MMW (C). All surfactants concentration were equal to 0.03% (w/w).*

It is quite easy to see that all adsorptions could reach high values of removal, superior to 80%, especially Pb (II) and Cu (II), when applying any surfactant. However, in the case of Ni (II) and Zn (II), after 18h of tests it was registered a release of these metals from MWCNTs adsorption sites.

In general, for Pb (II) it was possible to decrease an initial concentration of 2.98 mg/L to 0.34mg/L in case of SDBS tests, from 3.33 mg/L to 0.01 mg/L when dispersing MWCNTs with Pluronic F-127 and in case of polyDADMAC MMW tests it decreased also from 3.33mg/L to 0.04 mg/L. It is important to notice that the target required by National Legislation for this heavy metal is equal to 0.01 mg/L, what means that when applying Pluronic F-127 this goal was reached and with polyDADMAC MMW the result was quite close to that value. For the test with SDBS the final concentration was still on order of magnitude above the target. With this anionic surfactant, it was also performed a test with a higher concentration of Pb (II), equal to 11.26mg/L, and it was possible to reach the final concentration of 0.36mg/L of Pb (II), which corresponds to 97% of metal ion removal. So, even if SDBS does not allow reaching the target concentration, it can contribute to a higher removal of Pb (II).

In the case of Cu (II), in tests performed with Pluronic F-127 and polyDADMAC MMW its removal showed to be lower than for Pb (II). It was possible to decrease from a concentration of 2.38 mg/L to 0.22 mg/L for SDBS tests and 0.47mg/L in the case of polyDADMAC MMW. When applying Pluronic F-127 as surfactant, at 18h of adsorption the removal reached 100%, however since this moment it was registered a desorption of this metal, reaching 0.32mg/L in the end, what is possible related with hydrodynamic forces induced by stirring conditions.

About the adsorption of Zn (II), Pluronic F-127 showed to be more efficient than SDBS, reducing an initial concentration of this metal from 3.43mg/L to 0.35mg/L, when the anionic one only could reduce to 0.63mg/L. At 18h of Zn (II) adsorption, it was possible to reach a removal of 99% and 98% for tests performed by SDBS and Pluronic F-127, respectively. In the end, these removal goals decrease to 76% for the first surfactant mentioned and 89% for the second. A possible reason for this desorption phenomenon is the hydrodynamic effects resulted from stirring movements. In the case of polyDADMAC MMW it was possible to reduce the amount of Zn (II) to a final concentration of 0.718 mg/L (81%).

Finally, for Ni (II) adsorption tests, Pluronic F-127 was capable of reducing the initial concentration of Ni (II) of 3.74 mg/L until 0.63 mg/L (76%). PolyDADMAC MMW and SDBS had a similar performance, since it was possible to reduce around 72% and 69% of Ni (II), respectively. In the same way as Zn (II) adsorption tests, this metal showed to reach 100% of removal with Pluronic F-127 as surfactant but after 18h it suffered a significant desorption until 76%, once again, probably due to hydrodynamic forces resulted from stirring conditions.

To conclude the influence of hydrodynamics, another adsorption test were performed with Pluronic F-127 with 0.03% (w/w) of concentration and 0.01% (w/w) of MWCNTs but with no continuous stirring. Samples were taken after stirring the suspension for 3 minutes at 100rpm and going on, afterwards, without further stirring. **Figure 15** compares the result of Ni (II) adsorption in these conditions with a test that applies agitation at 100rpm during the whole time. In Appendix E.2, it is possible to see a summary of both results.

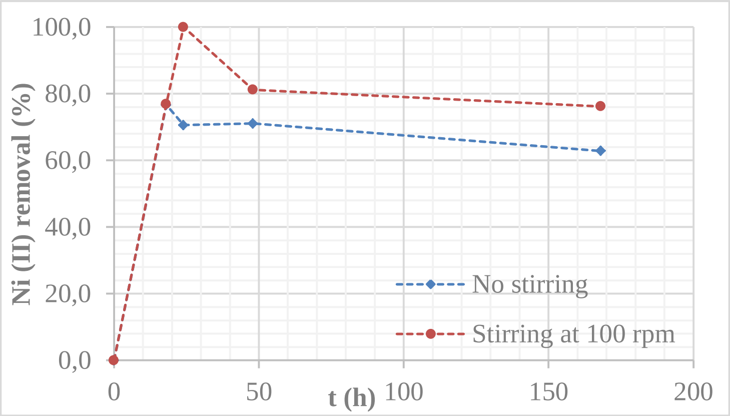

Figure 15 *Ni (II) removal applying a suspension of 0.03% (w/w) of Pluronic F-127 and 0.01% (w/w) of MWCNTs, with stirring at 100rpm and no stirring. Initial concentration of metal ion equal to 2.64mg/L.*

The test where no stirring was applied did not show to be more efficient in terms of metal ion removal. For the same initial concentration of Ni (II) (2.64mg/L), when applying a stirring of 100 rpm it was possible to reach a final concentration of 0.63mg/L, contrary to “No Stirring” test that only decreased Ni (II) concentration to 0.98mg/L.

However, when “No Stirring” conditions are applied, Ni (II) ions remained stuck in MWCNTs and almost any fluctuations of its concentration in the medium were registered, confirming that the hydrodynamics can have an effect in the adsorption of cations, both positive or negative. It means that perhaps it will be possible to reach a high removal of heavy metal ions until 18 hours and then stop the stirring in order to avoid its release from MWCNTs adsorption sites. Additionally, the stirring velocity is an important parameter to analyze in the future.

4.3.3 Mixture of SDBS and Pluronic F-127

A mixture of 0.03% (w/w) of SDBS and 0.03% (w/w) of Pluronic F-127 was prepared in order to study their combined influence in MWCNTs dispersions and their influence in Pb (II) removal, since they both presented good results in the adsorption tests and, additionally, one has a negative charge and the other is nonionic (Pluronic F-127)

With the same sonication conditions studied in subsection 4.2.2 (Test 4), this solution was used to disperse 0.01% (w/w) and 0.05% (w/w) of MWCNTs. Once these suspensions were prepared, they were added to a 50mL of Pb (II) solution of 50mL and mixed during 7days, like in the other adsorption tests already described.

Table 11 shows the hydrodynamic diameter measured by the ZSN equipment for the two suspensions. In Appendix F.1 it is possible to see the respective size distribution provided by ZSN software.

Table 11 *Hydrodynamic diameter of particles in suspensions of 0.01% (w/w) and 0.05% (w/w) of MWCNTs dispersed by a solution of 0.03% (w/w) of SDBS and 0.03% (w/w) of Pluronic F-127.*

MWCNTs Concentration (%)	Dz (nm)	Dz^{av} (nm)
0.01	177.5	179.1
	178.1	
	181.8	
0.05	191.2	189.8
	191.2	
	186.9	

It was possible to reach a low value for the hydrodynamic diameter in both dispersions. It means that a good dispersion was obtained as proved by the quality report presented in Appendix F. The result for a concentration of MWCNTs of 0.05% (w/w) is better that the one obtained previously with Pluronic F-127 alone (**Table 10**).

The results corresponding to single solutions of SDBS and Pluronic F-127 were 180.5 nm and 187.3 nm, respectively, for a dispersion of 0.01% (w/w) of MWCNTs and 187.6 nm and 219.9 nm, respectively, for a dispersion of 0.05% (w/w) of MWCNTs. These results correspond to 0.03% (w/w) of surfactant. If we compare these tests with the mixture of surfactants, it is possible to see that the main difference is for the test applying 0.05% (w/w) of MWCNTs. When applying Pluronic F-127 alone with a concentration of 0.03% (w/w), it was not possible to reach a good quality dispersion of 0.05% (w/w) of MWCNTs suspension, while with the mixture of surfactants the hydrodynamic diameter decrease from 219.9 nm to 189.8 nm, reaching a good dispersion with no visible aggregates.

These suspensions with a good dispersion level were applied to remove Pb (II) from an aqueous solution. The respective adsorption test is represented in **Figure 16**. Its summary is presented in Appendix F.2.

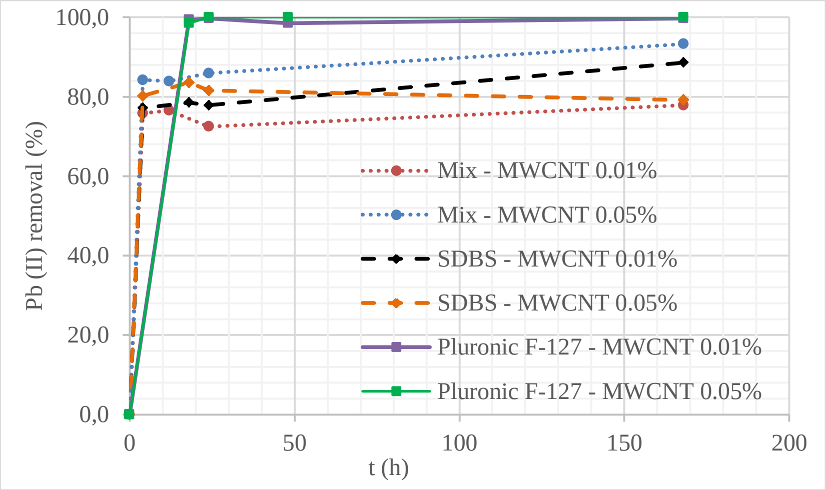

Figure 16 *Pb(II) removal applying a suspension of 0.01% and 0.05% of MWCNTs dispersed by a solution of 0.03% SDBS and 0.03% of Pluronic F-127. Pb(II) initial concentration was 2.98mg/L.*

In subsection 4.3.1 about the influence of MWCNTs concentration in metal ion removal, it was possible to see that there is no significant effect of increasing its concentration. However, when the suspensions of MWCNTs were dispersed by a mixture of the two surfactants, it was possible to reach a higher removal in tests with 0.05% (w/w) of MWCNTs, around 93%. It was possible to decrease from an initial concentration of Pb(II) of 2.98mg/L to 0.66 mg/L with a suspension of 0.01% (w/w) of MWCNTs and to 0.20 mg/L in case of applying a suspension of 0.05% (w/w) of MWCNTs.

This must be related to the better dispersion of MWCNTs when the two surfactants are used in combination. If in one way the anionic surfactant, SDBS, showed to have a good influence in metal ion attraction, the small dimensions of Pluronic F-127 helped reaching a good dispersion of MWCNTs and consequently a high Pb (II) removal.

However, if we compare these results with single surfactants solutions, it is possible to see that in the suspension with Pluronic F-127 the efficiency of metal ion removal was higher than with this mixture of SDBS and Pluronic F-127. Even if in that case the concentration of surfactant had to be higher for 0.05% (w/w) of MWCNTs suspensions, as it can be seen in subsection 4.2.1. When only 0.01% (w/w) were used in the removal, the single surfactants performed always better than the combination of the two surfactants for the same concentration of MWCNTs. A possible explanation for these results can be attributed to the surface area of MWCNTs that is available to receive metal ions, since, in fact, the concentration of the surfactants was doubled, thus covering a larger area of the MWCNTs surface.

4.3.4 Competitive adsorption between metal ions

Since SDBS and Pluronic F-127 showed to reach a high heavy metal removal, these two surfactants were used to disperse 0.01% of MWCNTs, in order to treat an aqueous solution with Pb (II), Ni (II), Cu (II) and Zn (II). Both solutions with a concentration of surfactant equal to 0.03% (w/w). The results of these tests can be seen in and a summary table is presented in Appendix G.

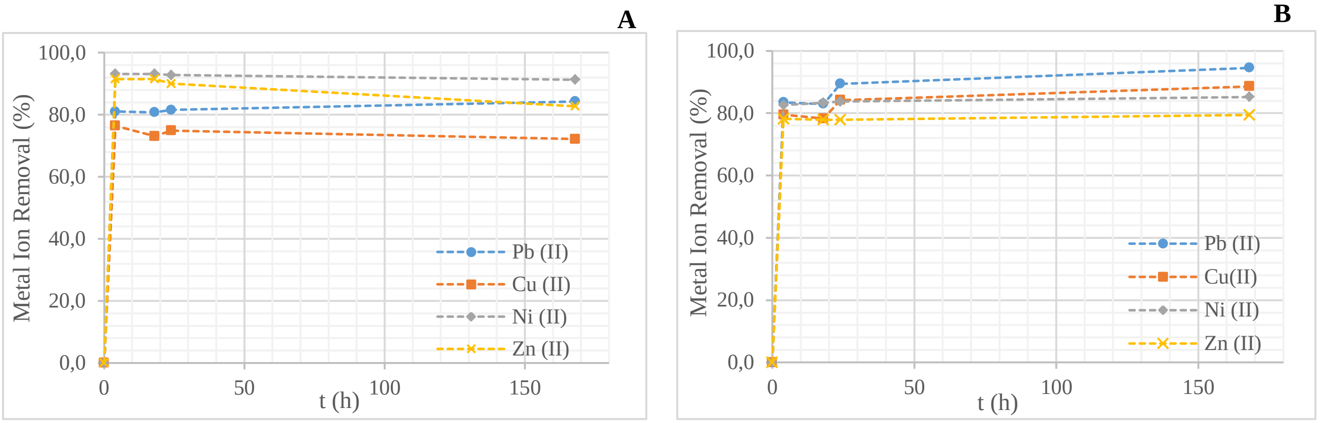

Figure 17 *Metal ion removal by adsorption in suspensions with 0.01% (w/w) of MWCNTs and 0.03% (w/w) of SDBS (A) and 0.03% (w/w) of Pluronic F-127 (B). Pb(II) initial concentration equal to 3.69 mg/L, Cu (II) equal to 6.58 mg/L, Ni (II) 2.64mg/L and Zn (II) equal to 3.30 mg/L.*

According to **Figure 17**, it was possible to remove high percentages of all heavy metals even if they are combined in a single water. It is not visible a significant difference between the surfactants, although when applying Pluronic F-127, it was possible to reach more than 80% of removal for all metal ions. This suspension could decrease Pb (II) concentration from 3.69 mg/L until 0.2 mg/L, followed by Cu (II) which initial concentration was 6.58 mg/L and final was 0.75 mg/L, Ni (II) concentration could decrease from 2.64 mg/L to 0.39 mg/L and finally Zn (II) that decreased from 3.30 mg/L to 0.68 mg/L.

In the case of SDBS, Cu (II) removal showed to be less efficient than for the other heavy metal ions removal. In this test, it was only possible to decrease Cu (II) concentration from 6.58 mg/L to 1.83 mg/L. The higher removal in this test was Ni (II) with a decrease in its concentration from 2.64 mg/L to 0.23 mg/L. Ni (II) was followed by Pb (II) that started with a concentration equal to 3.69 mg/L and ending equal to 0.58 mg/L. Lastly, Zn (II) concentration decreased from 3.30 mg/L until 0.57 mg/L.

In general, in Pluronic F-127 tests, the efficiency of heavy metal adsorptions followed the same trend as in the adsorption tests of the individual metals, each at a time, described previously in subsection 4.3.2. It means that it was reached a higher removal for Pb (II), followed by Cu (II), Ni (II) and Zn (II), even if Ni (II) showed a higher adsorption here than previously. On the other hand, in the SDBS test, Ni (II) and Zn (II) showed to reach here (in the mixture) a higher percentage of removal comparing to Pb (II) and Cu (II), contrary to what happened in the one at a time tests (subsection 4.3.2).

4.4 Discussion of Results

As predicted, MWCNTs showed to have a strong tendency to form aggregates in order to decrease their surface energy. In this way, sonication energy was applied to promote a good MWCNTs dispersion. Once Glycerox showed to have a good performance in MWCNTs dispersions, as showed by Figueiredo [60], sonication conditions were studied applying this non-ionic surfactant. It is important to notice that it could be an interesting study to perform adsorption tests with this surfactant, although, due to logistic issues, this surfactant was only applied in sonication conditions studies.

Therefore, the optimal conditions of sonication applied were 15 minutes with an intensity of energy of 75%. In this step, it was essential to apply an ice bath, since the increase of temperature was significant, reaching in some cases 45ºC. This heating showed to have an important role in MWCNTs aggregation.

Dispersion of MWCNTs was performed applying different surfactants: anionic (SDBS), non-ionic (Pluronic F-127) and cationic (polyDADMAC MMW), and their performance was compared not only in terms of MWCNTs dispersion but also in terms of heavy metal ions removal.

Although SDBS had a negative zeta potential, it was the surfactant with the best performance in MWCNTs dispersions. It means that with a lower concentration (0.03% (w/w)) it was possible to disperse both concentrations of MWCNTs (0.01% (w/w) and 0.05% (w/w)). In this case, the good quality of dispersion was reached due to hydrophobic forces between the surfactant tail and the nanotubes. On the other hand, with Pluronic F-127 and polyDADMAC MMW, probably the binding between MWCNTs surface and their structure was based on Van der Waals and Coulomb Law by electrostatic forces where the surfactant head remained in contact with the nanotube walls.

In terms of adsorption of heavy metal ions, SDBS has the higher hydrodynamic diameter, fact that influences the availability of adsorption sites on the MWCNTs surface. This surfactant has the advantage of reaching a kind of trap for these cations, once the head of the surfactant structure (with negative charge) will attract the positive charge of Pb (II), Cu (II), Ni (II) and Zn (II).

Because Pluronic F-127 is an extremely small surfactant comparing with other two surfactants, when the concentration of MWCNTs was increased to 0.05% (w/w), 0.03% (w/w) of Pluronic F-127 could not avoid the formation of MWCNTs aggregates. Contrary to SDBS, Pluronic F-127 has a zeta potential close to zero due its non-ionic nature. In this way, the complex Pluronic F-127/MWCNTs will not repel other complexes and, if the hydrodynamic effect is not sufficient, Van der Waals forces from MWCNTs will attract other MWCNTs and consequently form aggregates. This did not happen with SDBS, once its negative zeta potential will be strong enough to repel other SDBS/MWCNTs complexes and remain dispersed for a long time (7 days after adsorption tests, for example).

Still in terms of Pluronic F-127 performance, this surfactant showed to have a great potential in heavy metal ion removal reaching in some cases 100% of removal, even if in the case of Ni (II) a desorption was noticed after 18h of adsorption test. Since Pluronic F-127 is a much smaller molecule, it leaves a lot of free sites on the MWCNTs surface for adsorption of the metal cations. Thus, as long as dispersion is good enough, metal removal is high. Regarding the desorption of Ni (II) after 18h, it can be related with the lower molecule size and electronegativity of this metal, which promotes the desorption induced by the hydrodynamic forces related with stirring conditions.

The cationic surfactant, polyDADMAC MMW, was the surfactant where total disaggregation of MWCNTs was not possible, even when an increase of surfactant concentration was introduced. Aggregates were always visible at “naked eye” and an increase of hydrodynamic diameter of particles (polyDADMAC MMW/MWCNTs) was registered. For this reason, this surfactant showed to be the surfactant with worst performance in heavy metal ions adsorption tests, although, it was still possible to reach 98% of Pb (II) removal and 91% of Cu (II) removal.

MWCNTs concentration was also studied in terms of adsorption efficiency. It was expected that adsorption capacity increase when MWCNTs concentration increases as well. In the first tests of single surfactants solutions, this point was not proved, once the adsorption of Pb (II) was similar with both concentrations of MWCNTs. However, when the dispersion of 0.01% (w/w) and 0.05% (w/w) of MWCNTs was performed by a solution of SDBS mixed with Pluronic F-127 (0.03% (w/w) for each surfactant), it was possible to reach 90% of Pb (II) removal with the higher MWCNTs concentration and only 78% with the lowest MWCNTs concentration. This result might be attributed to the fact that with a mixture of surfactants, a better MWCNTs dispersion is performed for the higher concentration of nanotubes, and consequently, a higher metal ion removal can be reached. The presence of Pluronic F-127 will improve the MWCNTs dispersion and SDBS will attract the cations to the complex Pluronic F-127/SDBS/MWCNTs. However, metal ions removal showed to be more efficient in single tests, possibly due to the fact that the surface area of MWCNTs available to receive cations is higher with only one single surfactant than when applied a solution of two surfactants. Thus, since in this case the concentration of surfactant was doubled, in dispersions with one single of surfactant it can become easier for cations to reach the MWCNTs adsorption sites. Apparently, the trapping effect of SDBS was not dominant. It is important to study lower concentrations for the mixtures of surfactants.

In all adsorption tests performed, especially in the test with competition between heavy metal ions, Pb (II) was the metal with higher removal registered, with the exception when SDBS was applied as surfactant, even if the difference, in this case, is not very significant. It was possible to reach 99% in single tests performed by both Pluronic F-127 and polyDADMAC MMW and 90% when all metal ions are in competition. This might be explained not only by the high electronegativity that characterized Pb (II), 2.33 of Pauling scale, but also by its higher atomic radius (175 pm), which hinders desorption [62].

In general, the capacity of being removed from the aqueous solutions by MWCNTs followed the sequence: Pb (II), Cu (II), Zn (II) and Ni (II). However, in conditions of heavy metal ions competition, Ni (II) reached a higher removal than Zn (II) for both surfactants. Zn (II) is the metal with the lowest electronegativity. Still, in terms of competition between metals, MWCNTs become less capable of retaining heavy metal ions, as expected, once MWCNTs surface is occupied by competing metal ions. The decrease of Ni (II) and Zn (II) adsorption capacity might be attributed to the fact that Pb (II) and Cu (II) have more affinity with active adsorption sites on MWCNTs than Ni (II) and Zn (II), due to higher electronegativity of Pb (II) and Cu (II). On the other hand, Ni (II) and Zn (II) are ions with smaller atomic radius, 124 pm and 134 pm respectively [62], compared with Pb (II) and in the same way that this smaller ions are attracted by the complex surfactant/MWCNTs, they are also easily released by Brownian movements. Nevertheless, it is important to notice that even with competing ions in the solution, the overall removal is quite higher.

It is also important to mention that the difference showed by SDBS, that did not follow the adsorption sequence Pb (II) > Cu (II) > Zn (II) > Ni(II), could be explained by the atomic radius of metal ions. It means that, as already mentioned, SDBS, as an anionic surfactant, can work as a trap for cations. This may conduct to a strong binding between surfactant and the smaller metal ions, instead of binding of this ions with MWCNTs adsorption sites.

Another point to mention is the fact that Cu (II) and Ni (II) share similar properties of electronegativity and atomic radius. The first one has an electronegativity equal to 1.90 in Pauling scale and an atomic radius of 128pm, while the second one has an electronegativity of 1.91 and an atomic radius of 124pm. For these reason, their removal by MWCNTs suspensions are quite similar in most cases [62].

Finally, comparing the results obtained during this study with National Legislation, it is possible to highlight the behaviour of Zn. Although, its removal percentage did not exceed 90% with Pluronic F-127, its final concentration respected the target established (3 mg/L) when applying all surfactants. Pb (II) was the metal with higher removal registered. It was possible to respect the National Legislation (0.01 mg/L) when 0.01% (w/w) of MWCNTs were applied with Pluronic F-127. However, in tests where polyDADMAC MMW was applied, Pb (II) removal was 0.04 mg/L. For Cu (II) and Ni (II) the targets were not reached.

An important fact to refer is the detection limits of AAS equipment that as it can be seen in subsection 3.3.1, are higher than concentrations stablished in the beginning. For this reason, it was not always possible to detect low concentrations of heavy metal ions and thus it is difficult to know if the targets were reached or not.

5 Conclusions and future research

5.1 Conclusions

In this work, aqueous solutions containing heavy metal ions were treated by MWCNTs suspensions, dispersed by three different types of surfactants: SDBS as an anionic surfactant, Pluronic F-127 as non-ionic surfactant and a cationic one, polyDADMAC MMW.

In terms of MWCNTs dispersion, SDBS showed to be the surfactant with the best performance. Not only for the lowest concentration of MWCNTs of 0.01% (w/w) but also for suspensions with 0.05% (w/w) of MWCNTs, it was possible, with the same surfactant concentration of 0.03% (w/w), to separate MWCNTs aggregates.

The same concentration of 0.03% (w/w) of Pluronic F-127 and polyDADMAC MMW were used to disperse MWCNTs suspensions. The first surfactant was effective when applied in suspensions with 0.01% (w/w) of MWCNTs, but when MWCNTs concentration increase to 0.05% (w/w), it was necessary increase its concentrations to 1% (w/w). On the other hand, polyDADMAC MMW did not show to be able to disperse completely none of both MWCNTs concentrations, where few aggregates were visible even if the hydrodynamic radius were reasonable. Higher concentrations were tested in this case, although there were always visible MWCNTs aggregates. Therefore, it is possible to state that the efficiency of surfactants in MWCNTs dispersions followed the sequence SDBS > Pluronic F-127 > polyDADMAC MMW.

Optimal concentration for each surfactant were applied to perform heavy metal ion adsorption tests. The influence of MWCNTs concentration in adsorption tests was studied. It was possible to conclude that when a MWCNTs dispersion was performed by single surfactants, the difference between 0.01% (w/w) and 0.05% (w/w) of MWCNTs was not significant. However, when a solution of surfactants (SDBS + Pluronic F-127) was prepared, a good quality dispersion for both MWCNTs concentrations could be reached and a higher metal ion removal was obtained with 0.05% (w/w) of MWCNTs.

All surfactants showed to be efficient in heavy metal ions dispersion. MWCNTs suspensions dispersed by Pluronic F-127 revealed to be the best ones in heavy metal ions removal. It could remove from aqueous solutions 99% of Pb (II), 100 % of Cu (II), 90% of Zn (II) and 76% of Ni (II), although, after 18 hours, a significant desorption was registered for Ni (II), the smallest molecule, possibly due to hydrodynamic forces produced by stirring conditions. The influence of hydrodynamic forces in desorption phenomena was proved, by conducting studies with and without stirring. The desorption of Ni (II) registered during the study might be a problem when applied to real water treatment. It is important to study the optimal adsorption time in order to avoid the later release of heavy metal ions to the medium, once they have been trapped by the nanotubes.

On the other hand, SDBS worked as a “trap” to the cations due to its anionic nature. However, it did not follow the general adsorption sequence Pb (II) > Cu (II) > Zn (II) > Ni (II). This surfactant could remove 90% of Cu (II), 88% of Pb (II), 76% of Zn and 69 % of Ni (II). Therefore, SDBS has a great power to disperse MWCNTs but in terms of adsorption tests it was worst than by Pluronic F-127 and in some cases by polyDADMAC MMW. Therefore, the trapping effect of SDBS was not predominant in the cations removal. It seems that metal ions were preferably captured by the MWCNTs surface. The third surfactant, polyDADMAC MMW, could not total disaggregate MWCNTs but it was possible to reach a removal of 99% of Pb (II), 90% for Cu (II), 80% for Zn (II) and 71% for Ni (II). Thus, polyDADMAC MMW showed to have a positive influence in terms of metal ions adsorption. Perhaps the lower number of molecules adsorbed on the MWCNTs surface ends up leaving more active adsorption sites on the nanotubes surface for the metal ions capture.

For all adsorption tests, Pb (II) was the heavy metal ion with more affinity with complexes surfactant/MWCNTs. In this way, a competitive test between all heavy metal ions was performed for SDBS and Pluronic F-127. Once again, 84% and 94% of Pb (II) was removed by SDBS/MWCNTs and Pluronic F-127/MWCNTs, respectively. Its high electronegativity might be in the origin of this affinity. Ni (II) and Zn (II) were the metals with a minor removal registered by Pluronic F-127 and polyDADMAC MMW. These results might be explained by the fact that these two metals have a lower electronegativity and also a smaller atomic radius, comparing with Pb (II), and thus desorption competes more easily with adsorption. On the other hand, with SDBS as surfactant in the competitive test, Ni (II) showed the highest adsorption (93%), possibly due to its smaller atomic radius, which makes electrostatic attraction to this anionic surfactant easier.

5.2 Future Research

All work developed match with the objectives stablished. However, other studies can be performed in order to understand other points of this vast subject. Some suggestions are presented below:

- Surfactants have shown an important role in adsorption tests, not only because they influence MWCNTs dispersion but also because they reduce the available active adsorption sites on MWCNTs surface. Thus, studying the influence of surfactant concentration in heavy metal ions adsorption can be important;

- Especially with Pluronic F-127, stirring conditions showed to have a significant influence in desorption of cations. The removal of heavy metal ions were higher in these conditions. Therefore, it is suggested to study the optimal stirring conditions (time and speed of stirring);

- PolyDADMAC MMW showed to be less efficient in MWCNTs dispersion, although, the results of adsorption tests related to this surfactant were higher than 70%. It will be interesting to study lower concentrations of MWCNTs in order to find out the concentration for which this cationic surfactant can be efficient;

- Once MWCNTs are so efficient in heavy metal ion removal, the same study conditions could be applied to remove other pollutants as bacteria and virus;

- In certain point of adsorption tests, it is expected the saturation of MWCNTs. In this way, it will be interesting to perform desorption tests in order to become the reutilization of MWCNTs possible;

- It is also important to evaluate the possibility of developing a matrix to contain the MWCNTs during the removal tests which will allow, afterwards, their easy removal from the contaminated water.

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Appendix

Appendix A

Surfactants characterization

Characterization of surfactants (SDBS, Pluronic F-127 and polyDADMAC MMW) based on hydrodynamic diameter, molecular weight and zeta potential.

A.1 – Size measurements

SDBS

Since the quality report was not accepted for the initial solution of 0.5% (w/w), it was necessary to dilute this solution in three new solutions 0.25% (w/w), 0.05% (w/w) and 0.03% (w/w).

From these three tests performed, positive results were reached with concentrations of 0.05% (w/w) and 0.03% (w/w), although the best was with the lowest concentration (0,03% (w/w)) – **Figure A1**.

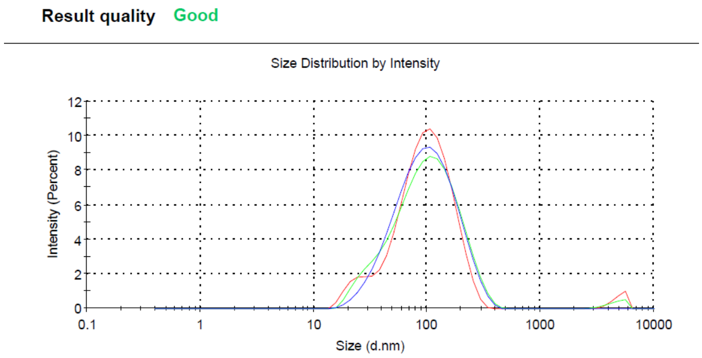


Figure A1 *Intensity of scattered light as a function of the size of molecules of SDBS for a concentration equal to 0.03% (w/w).*

Pluronic F-127

A good quality report was immediately reached with a concentration of Pluronic F-127 equal to 0.5% (w/w) - **Figure A2.**

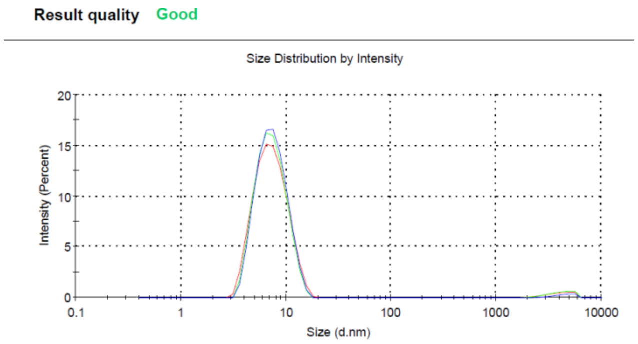
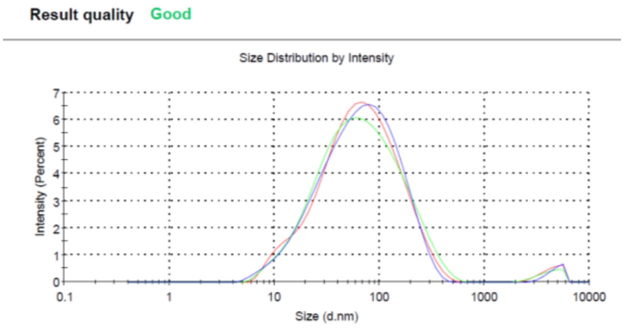


Figure A2 *Intensity of scattered light as function of the size of molecules of Pluronic F-127 for a concentration equal to 0.5% (w/w).*

PolyDADMAC MMW

In case of polyDADMAC MMW, Patrícia Costa [59] could reach a good quality report with a surfactant concentration equal to 0.1% (w/w). **Figure A3** shows the size distribution of this polymer.



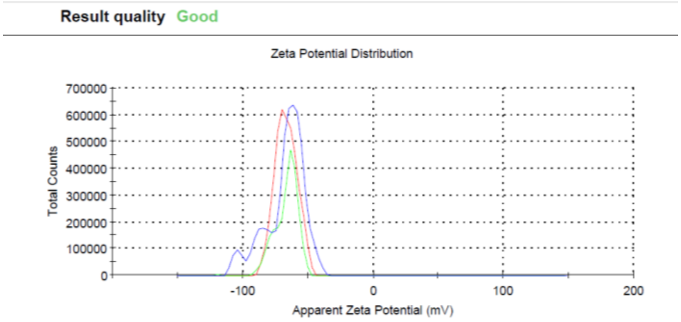
Result quality Good

Figure A3 *Intensity of scattered light as function of the size of molecules of PolyDADMAC MMW for a concentration equal to 0.1% (w/w).*

A.2 – Zeta Potential measurements

SDBS

In terms of zeta potential measurement, the optimal concentration reached in order to obtain a Good Quality report was 0.05% (w/w). **Figure A4** shows the result provided by ZSN software.



Result quality Good

Figure A4 *Zeta potential distribution of SDBS at a concentration equal to 0.05% (w/w).*

Pluronic F-127

Zeta potential measurement of Pluronic F-127 was performed with the same concentration than size measurement (0.5% (w/w)). Although the quality report have failed, Pluronic F-127 is a nonionic surfactant, thus difficult to measure, and by analyzing the **Figure A5**, the result agrees with this information.

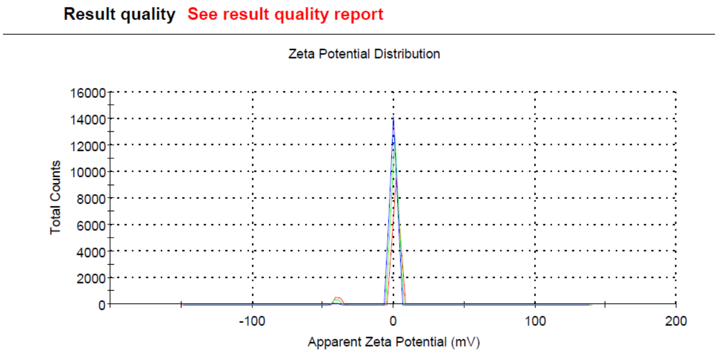


Figure A5 *Zeta potential distribution of Pluronic F-127 at a concentration equal to 0.5% (w/w).*

PolyDADMAC MMW

In case of zeta potential of polyDADMAC MMW, Patricia Costa could reach a good quality report with a concentration of 1% (w/w). **Figure A6** shows the Zeta potential distribution provided by ZSN software.

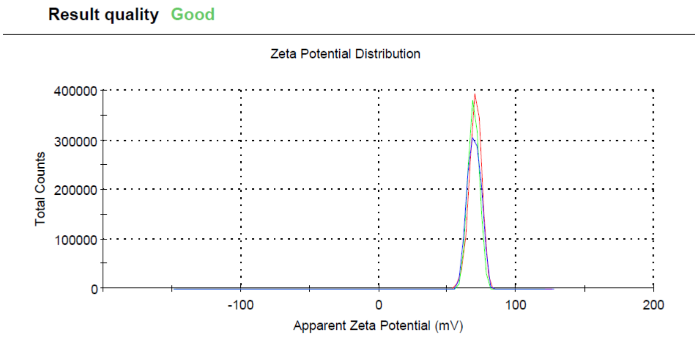


Figure A6 *Zeta potential distribution of polyDADMAC MMW at a concentration equal to 1% (w/w).*

A.3 – Molecular Weight measurements

SDBS

Molecular weight measurement was developed according to Refractive Index as function of SDBS concentration as presented in **Table A1** and Linear Regression Curve described in **Figure A7**.

Table A1 *Refractive Index for each concentration. of SDBS*

SDBS Concentration (g/mL)	Refractive Index
0	1.33251
0.0001	1.33253
0.0002	1.33254
0.0003	1.33257
0.0004	133257
0.0005	1.33261
0.0006	1.33261

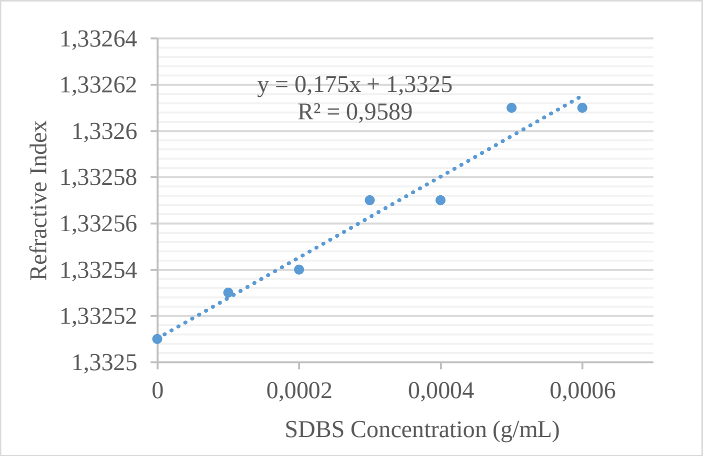
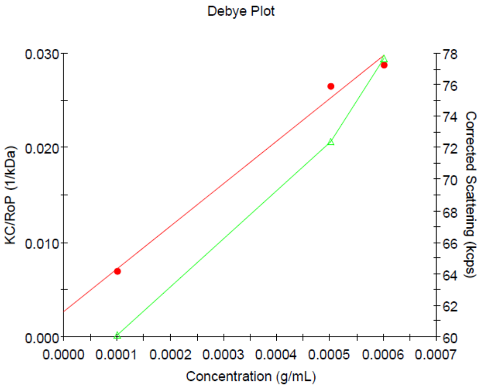
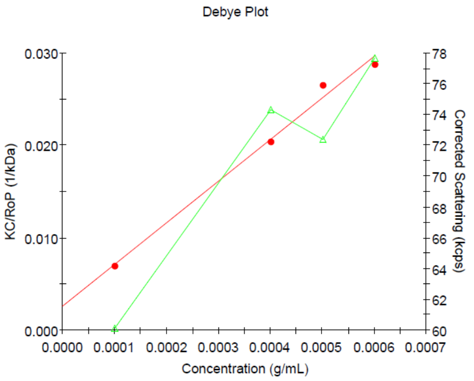


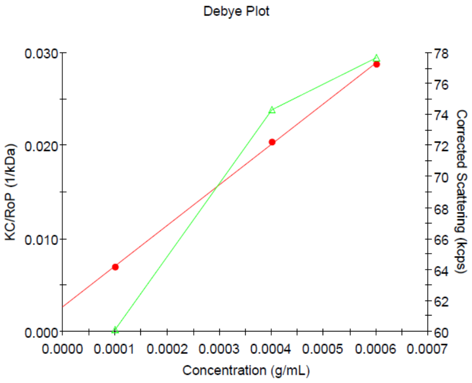
Figure A7 *Determination of the dn/dC parameter to the surfactant SDBS*



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0001	60.2	0.00704	358±148	0.0991
0.0005	72.4	0.0265		
0.0006	77.7	0.0288		



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0001	60.2	0.00704	370±125	0.991
0.0004	74.3	0.0204		
0.0005	72.4	0.0265		
0.0006	77.7	0.0288		



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0001	60.2	0.00704	361±38.7	1.000
0.0004	74.3	0.0204		
0.0006	77.7	0.0288		

Pluronic F-127

In case of Pluronic F-127, Molecular Weight measurements were developed according to Refractive Index as function of Pluronic F-127 concentration as presented in **Table A2** and Linear Regression Curve described in **Figure A8**.

Table A2 *Refractive Index for each concentration of Pluronic F-127.*

Pluronic F-127 Concentration (g/mL)	Refractive Index
0	1.33251
0.0005	1.33255
0.0010	1.33262
0.0025	1.33282
0.0050	1.33317
0.0100	1.33386
0.0150	1.33458

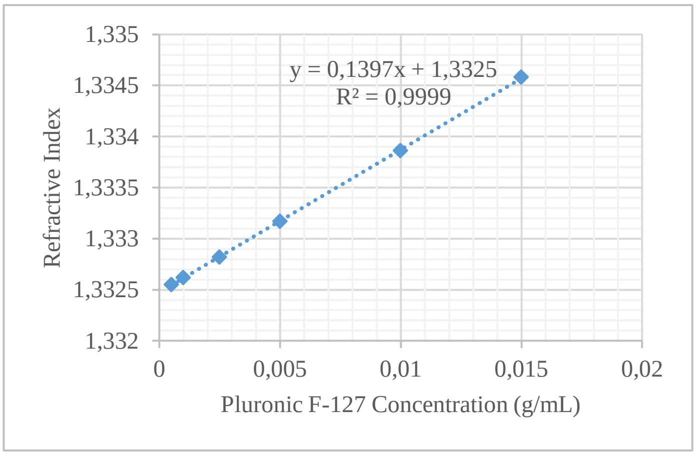
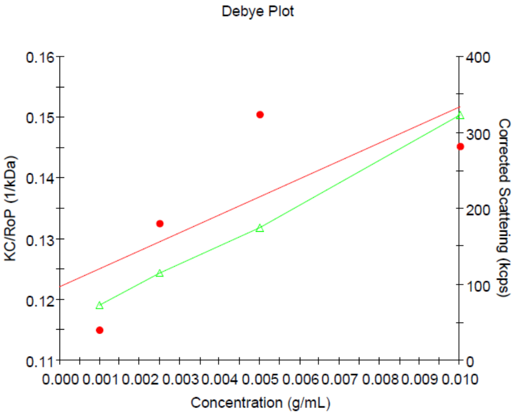
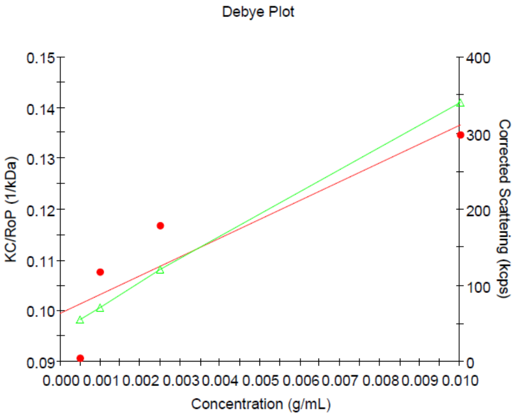


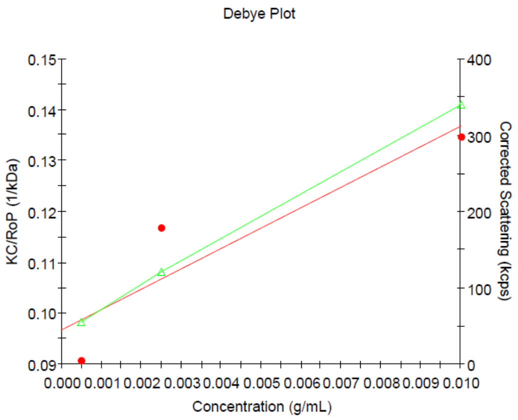
Figure A8 *Determination of the dn/dC parameter to the surfactant Pluronic F-127*



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0005	56.3	0.0909	10.0±0.639	0.800
0.0010	71.9	0.108		
0.0025	121.9	0.117		
0.0100	340.1	0.135		



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0010	73.7	0.115	8.18±0.668	0.549
0.0025	115.8	0.133		
0.0050	175.4	0.150		
0.0100	323.2	0.145		



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0010	56.3	0.0909	10.3±1.05	0.826
0.0025	121.9	0.117		
0.0100	340.1	0.135		

PolyDADMAC MMW

For last, molecular weight measurements for polyDADMAC MMW were developed according to Refractive Index as function of polyDADMAC MMW concentration as presented in **Table A3** and Linear Regression Curve described in **Figure A9** [59].

Table A3 *Refractive Index for each concentration of polyDADMAC MMW..*

PolyDADMAC MMW Concentration (g/mL)	Refractive Index
0	1.33251
0.0001	1.33353
0.00025	1.33356
0.0005	1.33359
0.0010	1.33369
0.0015	1.33380
0.0020	1.33389

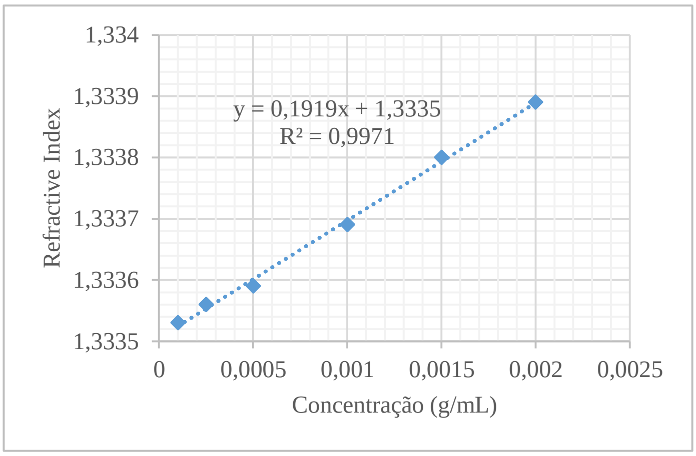
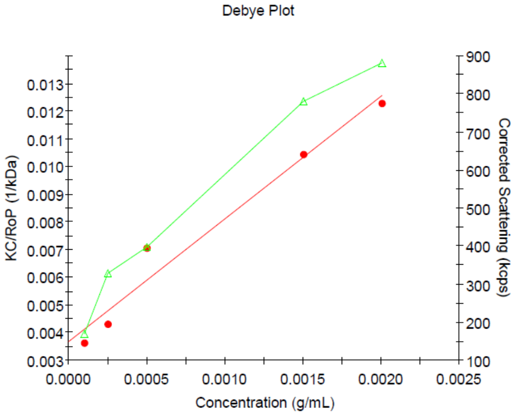
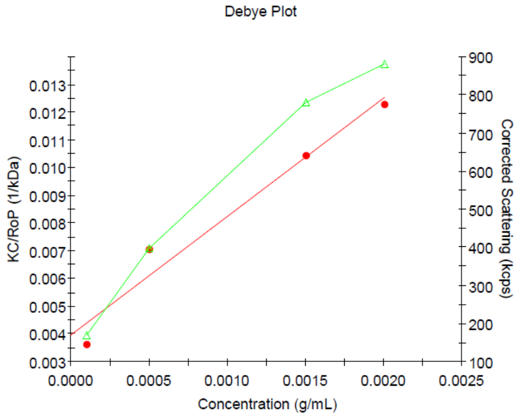


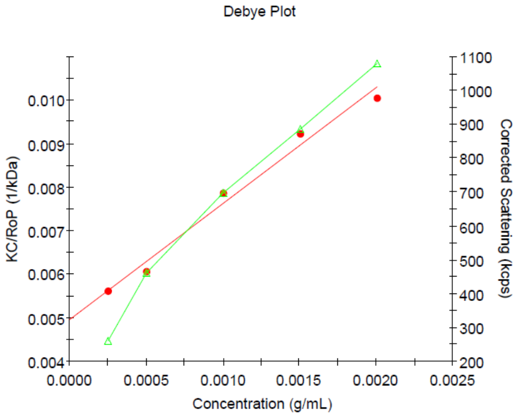
Figure A9 *Determination of the dn/dC parameter to the surfactant polyDADMAC MMW*



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0001	172.0	0.0909	269±34.4	0.967
0.00025	330.4	0.00434		
0.0005	398.8	0.00708		
0.0015	780.2	0.0105		
0.0020	880.8	0.0123		



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.0001	56.3	0.0909	250±39.0	0.965
0.0005	398.8	0.00708		
0.0015	780.2	0.0105		
0.0020	880.8	0.0123		



Concentration (g/mL)	Corrected Scaterring (kcps)	KC/RoP (1/kDa)	M (kDa)	R^2
0.00025	263.3	0.00564	201±9.35	0.984
0.0005	463.1	0.00608		
0.0010	699.3	0.00787		
0.0015	886.3	0.00923		
0.0020	1079.4	0.0100		

Appendix B

MWCNTs dispersions

Conditions of MWCNTs dispersions as sonication conditions and concentration of surfactants were studied.

Appendix B.1 – Optimization of conditions of sonication

Four different tests of MWCNTs dispersion applying ultrasonic energy were conducted. For each test, two MWCNTs concentrations 0.01% (w/w) and 0.05% (w/w) were studied. The concentration of Glycerox was fixed at 2% (w/w). The results are presented below.

- Test 1: Ultrasounds applied during 5 minutes at 90% of intensity

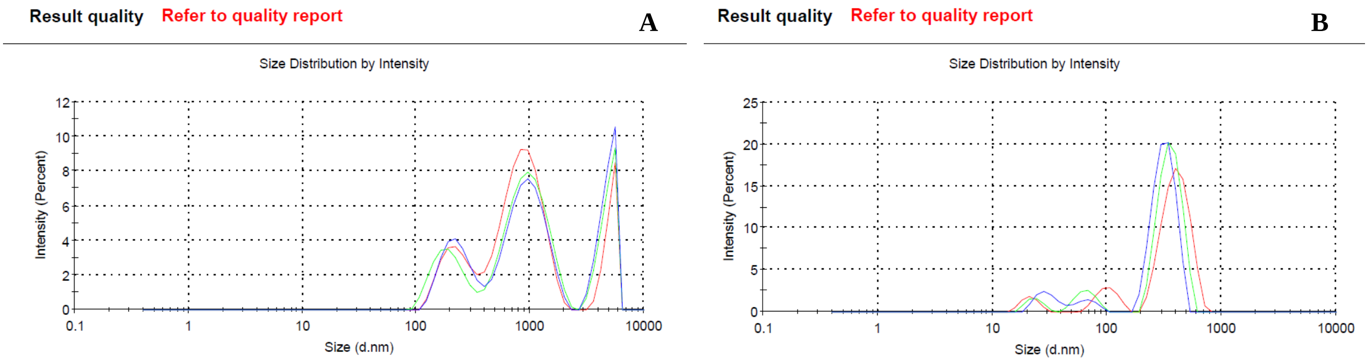


Figure B1 *Intensity of scattered light as function of the size of the particles in MWCNTs suspensions. Glycerox concentration of 2% (w/w) and MWCNTs concentration equal to 0.01% (w/w) (A) and 0.05% (w/w) (B).*

- Test 2: Ultrasounds applied during 5 minutes at 75% of intensity

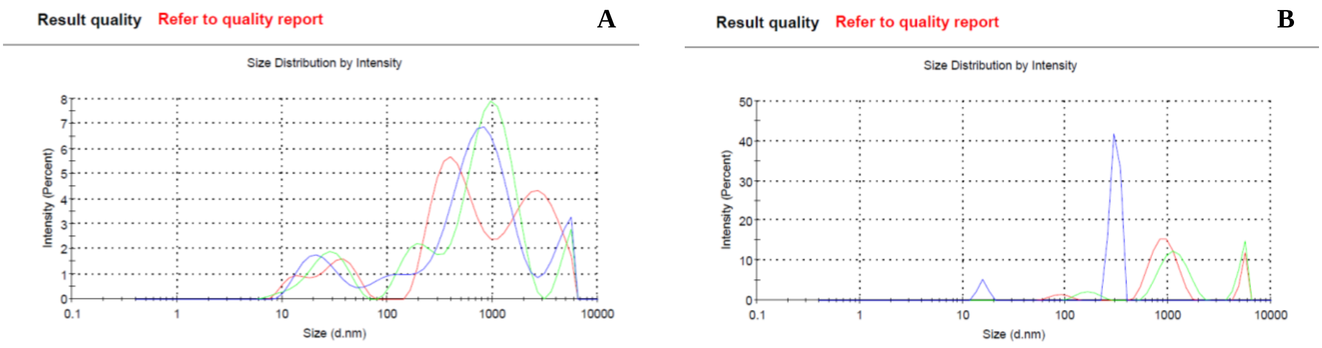


Figure B2 *Intensity of scattered light as function of the size of the particles on MWCNTs suspensions. Glycerox concentration of 2% (w/w) and MWCNTs concentration equal to 0.01% (w/w) (A) and 0.05% (w/w) (B).*

- Test 3: Ultrasounds applied during 10 minutes at 75% of intensity

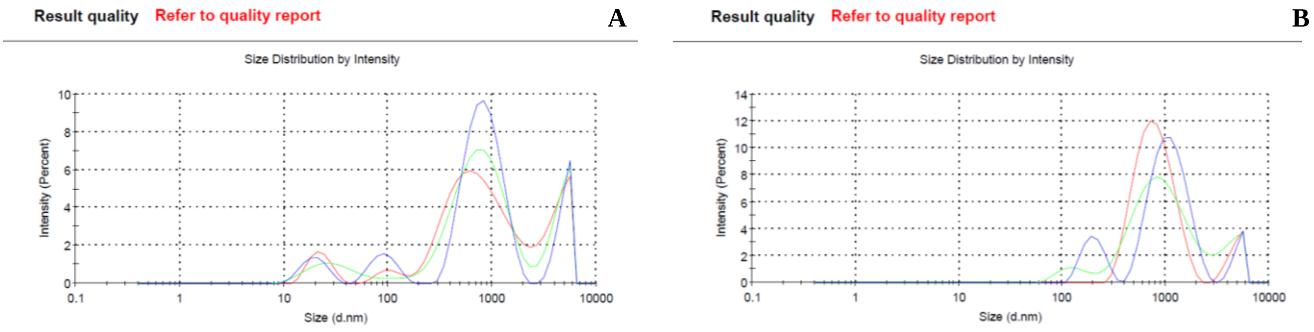


Figure B3 *Intensity of scatered light as function of the size of the particles on MWCNTs suspensions. Glycerox concentration of 2% (w/w)and MWCNTs concentration equal to 0.01% (w/w) (A) and 0.05% (w/w) (B).*

Table B1 summarizes all the hydrodynamic diameters of the suspensions provided by the ZSN software for each sonication test and for each surfactant applied.

Table B1 *Summary of Hydrodynamic Diameter of the particles in MWCNTs suspensions for each dispersion test.*

Test	**MWCNTs Concentration (%)**	**Dz (nm)**	**Dz^{av} (nm)**
1	0.01	706.3	718.2
		732.8	
		715.5	
	0.05	1007	1033
		1081	
		1011	
2	0.01	257.2	265.7
		283.4	
		256.4	
	0.05	1441	1821
		1480	
		2542	
3	0.01	528.3	536.4
		539.1	
		541.8	
	0.05	584.9	631.1
		643.0	
		665.5	

Appendix B.2 – Optimization of surfactant concentration in MWCNTs dispersions

In case of 0.01% (w/w) of MWCNTs dispersions, the study started with a concentration of 0.03% (w/w) for all surfactants, being the size distributions presented in **Figure B4**. Then the concentration of polyDADMAC MMW was increase to 0.1% (w/w) –**Figure B5**.

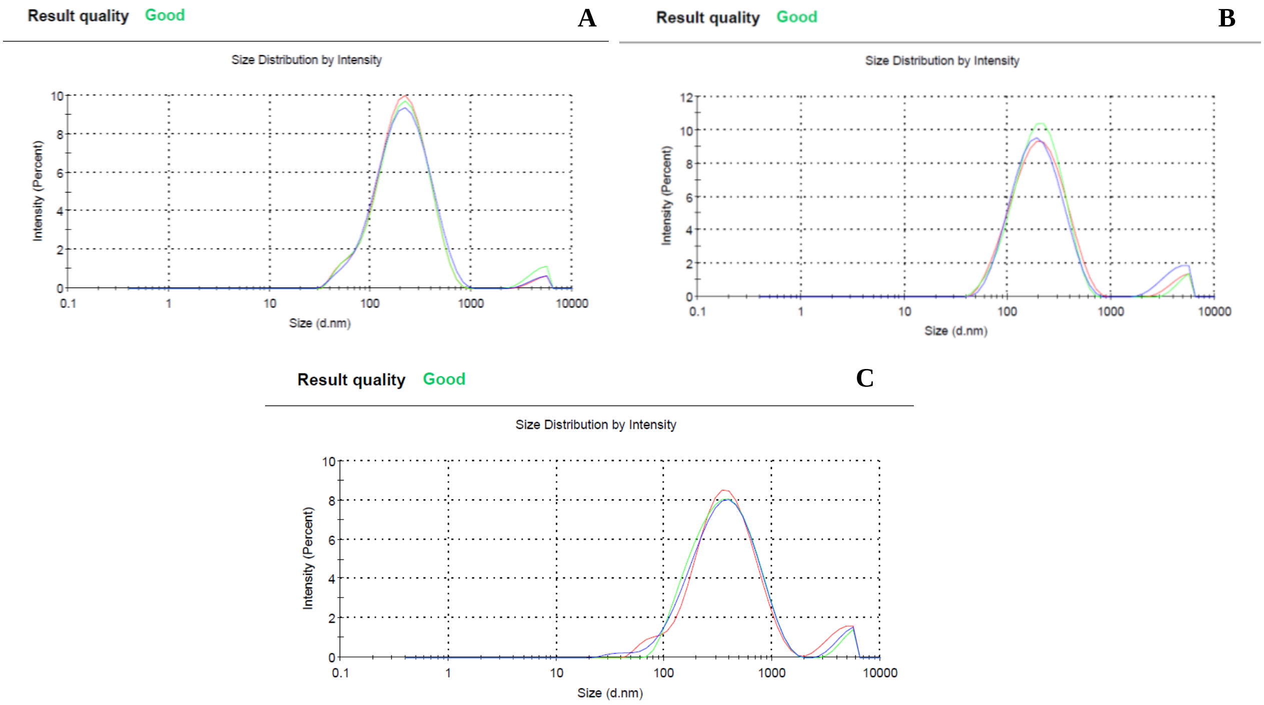


Figure B4 *Intensity of scattered light as a function of the size of the particles in 0.01% (w/w) of MWCNTs dispersions, applying SDBS (A), Pluronic F-127 (B) and polyDADMAC MMW (C) with a concentration equal to 0.03% (w/w).*

Figure B5 *Intensity of scattered light as a function of the size of the particles in 0.01% (w/w) MWCNTs dispersions applying 0.1% (w/w) of polyDADMAC MMW.*

In the case of 0.05% (w/w) of MWCNTs, SDBS reached a good dispersion also when applied 0.03% (w/w), however, the concentration of Pluronic F-127 and polyDADMAC MMW were increased. For Pluronic F-127 the concentration applied was 1% (w/w) and 0.5% (w/w), 1% (w/w) and 2% (w/w) for polyDADMAC MMW- **Figure B6** and **Figure B7**.

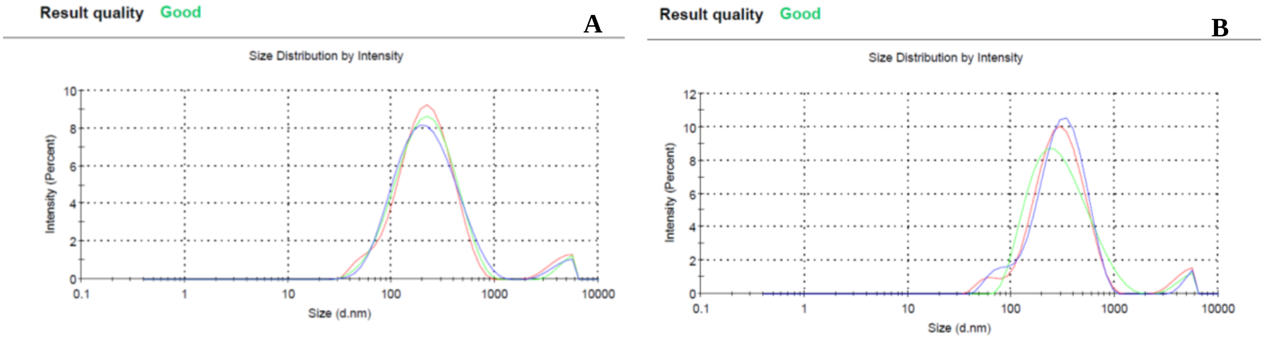


Figure B6 *Intensity of scattered light as function of the size of the particles in a dispersion of 0.05% (w/w) of MWCNTs, applying 0.03% (w/w) of SDBS and 1% (w/w) of Pluronic F-127 as surfactants.*

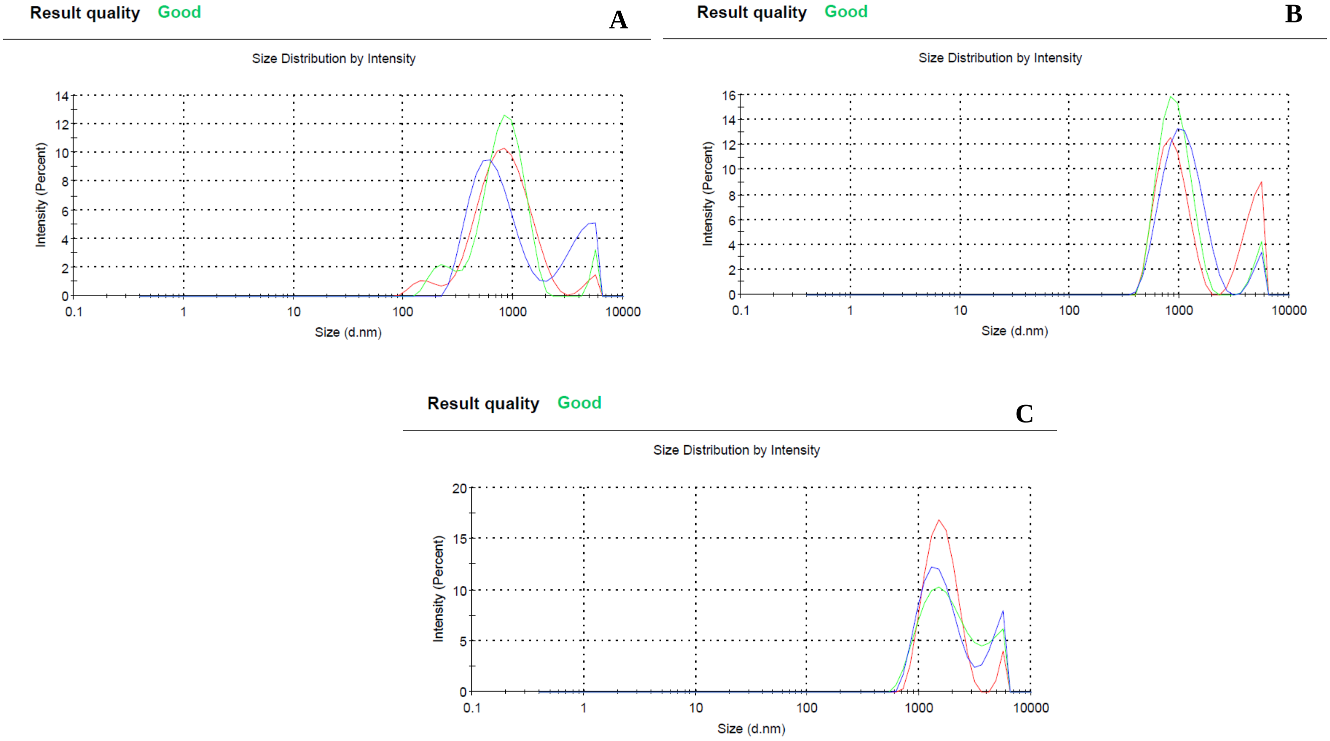


Figure B7 *Intensity of scattered light as function of the size of molecules in a dispersion of 0.05% (w/w) of MWCNTs applying 0.5% (w/w) (A), 1% (w/w) (B) and 2% (w/w) (C) of polyDADMAC MMW as surfactant.*

Table B2 summarizes all hydrodynamic diameters provided by the ZSN software for each dispersion test and for each surfactant studied.

Table B2 *Summary of hydrodynamic diameter for MWCNTs dispersions with concentrations of 0.01% (w/w) and 0.05% (w/w), applying different surfactants (SDBS, Pluronic F-127 and polyDADMAC MMW).*

Surfactant	Surfactant concentration (w/w %)	MWCNTs concentration (w/w %)	Dz (nm)	Dz^{av} (nm)
SDBS	0.03	0.01	178.5	180.5
			183.0	
			179.9	
		0.05	187.3	187.6
			187.8	
			187.6	
Pluronic F-127	0.03	0.01	184.9	187.3
			185.3	
			191.7	
	1	0.05	278.2	288.5
			295.8	
			291.5	
PolyDADMAC MMW	0.03	0.01	314.8	307.7
			305.8	
			302.6	
	0.1		336.6	363.0
			372.7	
			379.6	
	0.5	0.05	675.5	771.0
			847.5	
			790.0	
	1		1263	1123
			1027	
			1080	
	2		1874	1868
			1833	
			1898	

After 7days of adsorption tests under slowly agitation (100rpm), samples with 0.01% (w/w) of MWCNTs and 0.03% (w/w) of surfactant were taken and analyzed in the ZSN equipment – **Table B3**. The dispersions with polyDADMAC MMW were not analyzed, at this time, once the quality of the dispersions were not acceptable in terms of visible MWCNTs aggregates.

Table B3 *Hydrodynamic diameter for dispersions of 0.01% (w/w) of MWCNTs and 0.03% (w/w) of surfactant, after 7 days of adsorption test.*

Surfactant	Dz (nm)	Dz^{av} (nm)
SDBS	161.5	165.0
	164.1	
	169.5	
Pluronic F-127	156.5	156.8
	158.6	
	155.2	

Appendix C

Comparative study of dispersion performance between SDBS, Pluronic F-127 and polyDADMAC MMW

Figure C1 shows the quality report provided by the ZSN software for dispersions of MWCNTs with a concentration of 0.01% (w/w) applying surfactants with a concentration of 0.03% (w/w).

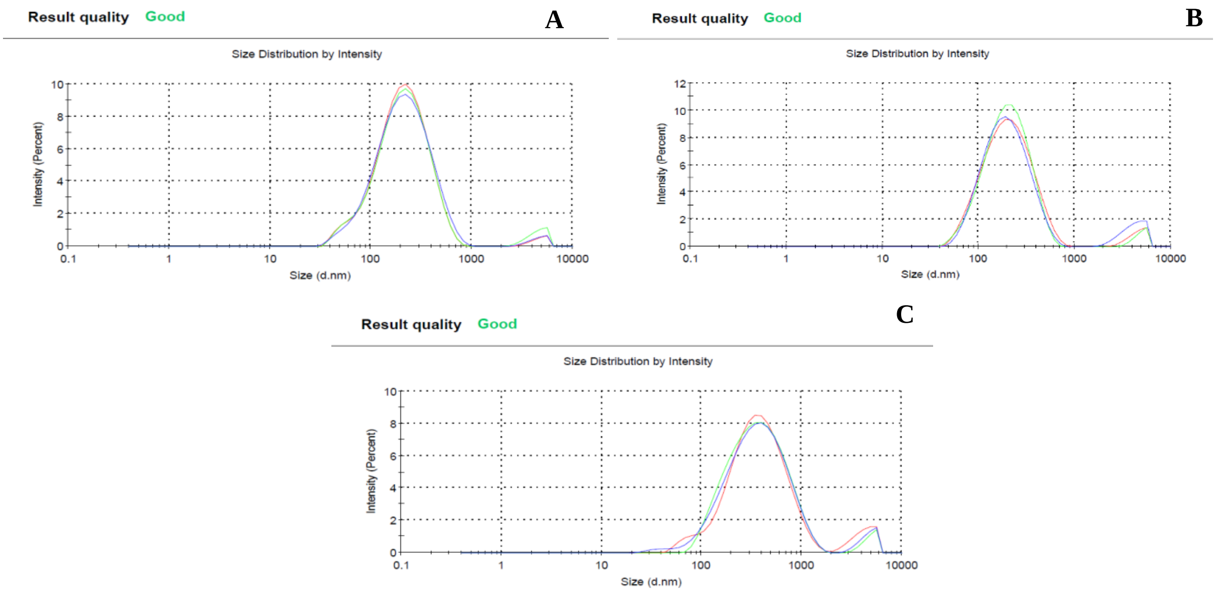


Figure C1 *Intensity of scattered light as a function of the size of the particles in a dispersion of 0.01% (w/w) of MWCNTs applying SDBS (A), Pluronic F-127 (B) and polyDADMAC MMW (C) as surfactant. Concentration of surfactants equal to 0.03% (w/w).*

The surfactant concentration was maintained equal to 0.03% (w/w) and a higher concentration of MWCNTs was studied (0.05% (w/w)). **Figure C2** shows the quality report provided by ZSN software for these dispersions of MWCNTs.

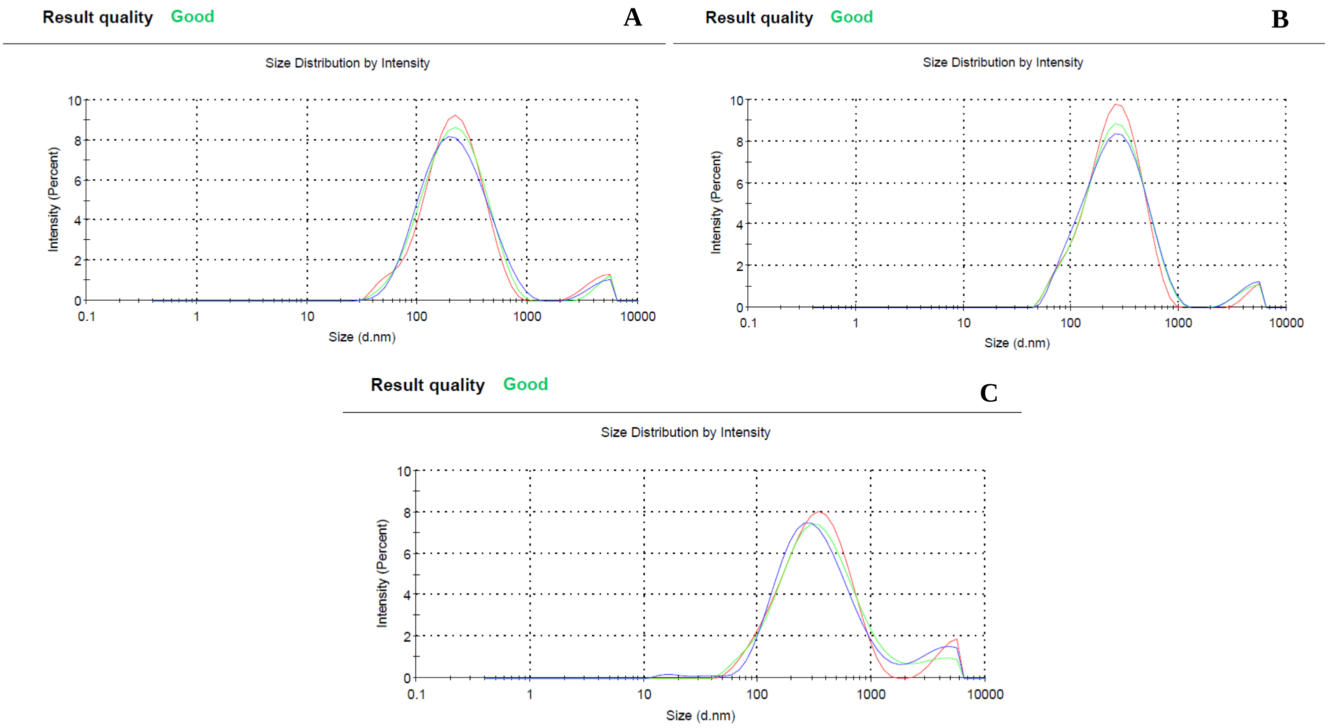


***Figure C2** Intensity of scattered light as a function of the size of the particles of SDBS (A), Pluronic F-127 (B) and polyDADMAC MMW (C) for a concentration of surfactant equal to 0.03% (w/w) and 0.05% (w/w) of MWCNTs.*

Appendix D

Influence of MWCNTs concentration in adsorption tests

Two concentrations (0.01% (w/w) and 0.05% (w/w)) of MWCNTs were studied in order to conclude about their influence in heavy metal ions removal.

Table D1 *Summary of Pb (II) removal applying MWCNTs suspensions with concentrations of 0.01% (w/w) and 0.05% (w/w), for each surfactant. SDBS and polyDADMAC MMW were applied with a concentration of 0.03% (w/w) for both MWCNTs concentrations, Pluronic F-127 with a concentration of 0.03% (w/w) for 0.01% (w/w) of MWCNTs and 1% (w/w) for 0.05% (w/w) of MWCNTs.*

		Pb (II) Concentration (mg/L)		**Pb (II) Concentration (% removal)**	
Surfactant	**Time (h)**	**0.01% (w/w) MWCNTs**	**0.05% (w/w) MWCNTs**	**0.01% (w/w) MWCNTs**	**0.05% (w/w) MWCNTs**
SDBS	0	2.98	2.98	0.00	0.00
	4	0.68	0.59	77.2	80.2
	18	0.64	0.49	78.5	83.6
	24	0.66	0.55	77.9	81.5
	168	0.34	0.62	88.6	79.2
Pluronic F-127	0	3.33	3.33	0.00	0.00
	4	0.02	0.05	99.4	98.5
	18	0.01	0.00	99.7	100
	24	0.05	0.00	98.5	100
	168	0.01	0.00	99.7	100
PolyDADMAC MMW	0	3.33	3.33	0.00	0.00
	4	0.24	0.03	92.8	99.1
	18	0.23	0.00	93.1	100
	24	0.11	0.00	96.7	100
	168	0.04	0.00	98.8	100

Appendix E

Metal ions removal from aqueous solutions

Solutions of Pb (II), Cu (II), Ni (II) and Zn (II) were treated with MWCNTs suspensions in order to decrease the concentration below an established target.

Appendix E.1- Influence of different surfactants in heavy metal ion removal

All tests below were performed with a surfactant concentration of 0.03% (w/w) and 0.01% (w/w) of MWCNTs.

Table E1 *Removal of Pb(II), Cu (II), Ni (II) and Zn (II) by a suspension of 0.03% (w/w) of SDBS and 0.01% (w/w) of MWCNTs.*

	SDBS								
	Pb(II)			**Cu (II)**		**Ni (II)**		**Zn (II)**	
	h	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**
t0	0	2.98	0.0	2.38	0.0	2.64	0.0	3.43	0.0
t1	4	0.68	77.2	0.409	82.8	0.633	76.0	0.087	96.7
t2	18	0.64	78.5	0.368	84.6	0.733	72.2	0.022	99.2
t3	24	0.66	77.9	0.363	84.8	0.723	72.6	0.749	71.6
t4	168	0.34	88.6	0.222	90.7	0.808	69.4	0.629	76.2
Target (mg/L)		0.01	-	0.05	-	0.02	-	3.00	-

Table E2 *Removal of Pb(II), Cu (II), Ni (II) and Zn (II) by a suspension of 0.03% (w/w) of Pluronic F-127 and 0.01% (w/w) of MWCNTs. Initial concentration of heavy metal ions: 3.33 mg/L, 5.41 mg/L, 2.64mg/L and 3.43mg/L, respectively.*

	Pluronic F-127								
	Pb(II)			**Cu (II)**		**Ni (II)**		**Zn (II)**	
	h	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**
t0	0	3.33	0.00	5.41	0.00	2.64	0.00	3.43	0.00
t1	4	0.02	99.4	0.00	100	0.61	77.0	0.07	98.0
t2	18	0.01	99.7	0.00	100	0.00	100	0.05	98.6
t3	24	0.05	98.5	0.12	97.8	0.50	81.2	0.15	95.5
t4	168	0.01	99.7	0.32	94.0	0.63	76.2	0.35	89.9
Target (mg/L)		0.01	-	0.05	-	0.02	-	3.00	-

Table E3 *Removal of Pb(II), Cu (II), Ni (II) and Zn (II) by a suspension of 0.03% (w/w) of polyDADMAC MMW and 0.01% (w/w) of MWCNTs.*

PolyDADMAC MMW									
		Pb(II)		**Cu (II)**		**Ni (II)**		**Zn (II)**	
	h	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**	**mg/L**	**%**
t0	0	3.33	0.0	5.41	0.0	3.74	0.0	3.8	0.0
t1	4	0.24	92.8	0.347	93.6	1.07	71.4	0.762	79.9
t2	18	0.23	93.1	0.370	93.2	1.05	71.9	0.742	80.5
t3	24	0.11	96.7	0.331	93.9	1.03	72.4	0.761	80.0
t4	168	0.04	98.8	0.473	91.3	1.05	72.0	0.718	81.1
Target (mg/L)		0.01	-	0.05	-	0.02	-	3.00	-

Appendix E.2: Influence of stirring conditions on Ni (II) adsorption

The test were performed applying Pluronic F-127 with a concentration of 0.03% (w/w) as surfactant in a suspension of 0.01% (w/w) of MWCNTs.

Table E4 *Ni (II) removal by a suspension of 0.03% (w/w) of Pluronic F-127 and 0.01% (w/w) of MWCNTs, applying stirring and with no stirring. Initial concentration of heavy metal ion equal to 2.64mg/L.*

		Stirring at 100 rpm		**No Stirring**	
	h	**Ni(II) concentration (mg/L)**	**Ni (II) removal (%)**	**Ni(II) concentration (mg/L)**	**Ni (II) removal (%)**
t0	0	2.64	0.0	2.64	0.0
t1	4	0.608	77.0	0.616	76.7
t2	18	0	100	0.776	70.6
t3	24	0.496	81.2	0.763	71.1
t4	168	0.628	76.2	0.98	62.9
Target (mg/L)		0.02			

Appendix F

Mixture of surfactants

A mixture of 0.03% (w/w) of SDBS and 0.03% (w/w) of Pluronic F-127 was prepared in order to study the performance of this solution in MWCNTs dispersions and metal ions removal.

Appendix F.1 – Dispersion of MWCNTs suspensions

Figure F1 shows the size distribution of particles provided by ZSN software for MWCNTs dispersions applying a mixture of SDBS and Pluronic F-127.

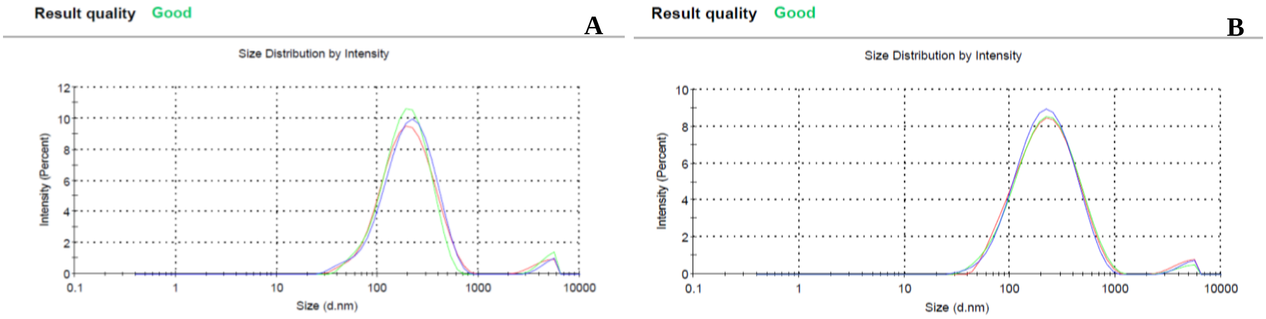


Figure F1 *Intensity of scattered light as a function of the size of the particles in suspensions of 0.01% (w/w) (A) and 0.05% (w/w) (B) of MWCNTs dispersed by a solution of 0.03% (w/w) of SDBS and 0.03% (w/w) of Pluronic F-127.*

Appendix F.2 – Pb (II) removal by MWCNTs suspensions with a mixture of SDBS and Pluronic F-127

Table F1 shows the removal of Pb (II) in tests of 7 days, applying a suspension of 0.01% (w/w) and 0.05% (w/w) of MWCNTs dispersed by a mixture of surfactants. This solution is composed by 0.03% (w/w) of SDBS and 0.03% (w/w) of Pluronic F-127.

Table F1 *Pb (II) removal applying a suspension of 0.01% (w/w) and 0.05% (w/w) of MWCNTs dispersed by a solution of 0.03% (w/w) of SDBS and 0.03% of Pluronic F-127.*

		0.01% of MWCNTs		**0.05% of MWCNTs**	
	h	**Pb (II) concentration (mg/L)**	**Pb (II) removal (%)**	**Pb (II) concentration (mg/L)**	**Pb (II) removal (%)**
t0	0	2.98	0.0	2.98	0.0
t1	4	0.72	75.8	0.47	84.2
t2	18	0.70	76.5	0.48	83.9
t3	24	0.82	72.5	0.42	85.9
t4	168	0.66	77.9	0.20	93.3
Target (mg/L)		0.01			

Appendix G

Competitive adsorption between heavy metal ions

A solution of all metal ions (Pb (II), Cu (II), Ni (II) and Zn (II)) were prepared and treated with two dispersions of 0.01% (w/w) of MWCNTs, one stabilized with 0.03% (w/w) of SDBS and other with 0.03% (w/w) of Pluronic F-127.

Table G1 and **Table G2** show the results of metal ions adsorption tests for each surfactant tested.

Table G1 *Metal ions adsorption by 0.01% (w/w) of MWCNTs applying 0.03% (w/w) of SDBS as surfactant.*

SDBS								
Time (h)	Pb (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)	Pb (%)	Cu (%)	Ni (%)	Zn (%)
0	3.69	6.58	2.64	3.30	0.00	0.00	0.00	0.00
4	0.70	1.55	0.18	0.28	81.0	76.4	93.2	91.5
18	0.71	1.77	0.18	0.28	80.8	73.1	93.2	91.5
24	0.68	1.65	0.19	0.33	81.6	74.9	92.8	90.0
168	0.58	1.83	0.23	0.57	84.3	72.2	91.3	82.7

Table G2 *Metals ions adsorption by 0.01% (w/w) of MWCNTs applying 0.03% (w/w) of Pluronic F-127 as surfactant.*

Pluronic F-127								
Time (h)	Pb (mg/L)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)	Pb (%)	Cu (%)	Ni (%)	Zn (%)
0	3.69	6.58	2.64	3.30	0.00	0.00	0.00	0.00
4	0.61	1.35	0.46	0.72	83.5	79.5	82.6	78.2
18	0.63	1.43	0.44	0.73	82.9	78.3	83.3	77.9
24	0.39	1.04	0.43	0.73	89.4	84.2	83.7	77.9
168	0.20	0.75	0.39	0.68	94.6	88.6	85.2	79.4