AMERICAN UNIVERSITY OF BEIRUT

INTEGRATION OF PHARMACEUTICAL WASTES WITH NORMAL COMPRESSIVE STRENGTH CONCRETE: EXPERIMENTAL APPROACH

by
WAEL WAJIH TERMOS

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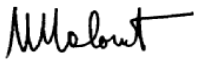

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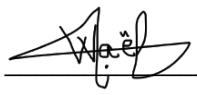

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ABSTRACT
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Title: Integration of pharmaceutical waste with normal compressive strength concrete: Experimental approach

Nowadays, there are growing preoccupations for determining suitable routes for the disposal of pharmaceutical wastes (PW). This study reports the results of an experimental investigation on the influence of Diclofenac (Df) as a partial replacement of Portland cement on the mechanical properties (MP) of the concrete. In addition, the study investigates the potential of hardened concrete at immobilizing the leaching of Df. To that extend leaching in water was assessed at various temperatures; room temperature, 40°C and 60 °C. The analysis of the experimental results showed that it contributes negatively on the compressive strength of the concrete. DF concentrations were determined by high-performance liquid chromatography (HPLC) and revealed that the leached amount of Df produced at early age of 32d, and subsequently decreased sharply to be undetected. On the basis of the experiments performed, it can be concluded that Df decreases the compressive strength of the concrete, and the leached amount of Df increases as the temperature increases.

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INTRODUCTION

1.1. Overview on the pharmaceutical waste management

1.1.1. Disposal of the pharmaceutical wastes

The growing population across the globe is increasing the number of patients, and consequently resulting in the rising volume of pharmaceutical wastes (PW). Thus, with the rising volume of PW, the governments, worldwide, are taking several initiatives for the management of these wastes. Managing pharmaceutical wastes has been of concern to the scientific community and regulatory bodies worldwide [1]. The occurrence of pharmaceuticals in the environment as a result of human use and consumption has now been well established [2].

Over 100,000 tons of pharmaceutical products are consumed globally every year, during their manufacture, use and disposal, Active Pharmaceutical Ingredients (APIs) as well as other chemical ingredients are released into the environment [3]. The effects of active pharmaceutical ingredients (API) on non-target species in the environment are not known. Unwanted pharmaceuticals should be safely disposed at a reduced financial cost to mitigate public and environment health risk [4].

The pharmaceutical compounds may enter the environment by different routes such as discharge of treated wastewater, seepage from landfills sites, sewer lines, runoff from animal wastes etc. Even though the environmental impact of pharmaceuticals in the environment at trace levels has not been clearly determined, the precautionary principle calls for action in the face of uncertainty [5].

The pharmaceutical exposure routes to the environment are manufacturing units, hospital effluents, land applications etc. Moreover, sewage treatment services are not

always successful in removing the active chemicals from waste-water. Consequently, pharmaceuticals find their way into the aquatic environment, where they directly affect aquatic organisms and can be incorporated into food chains [6].

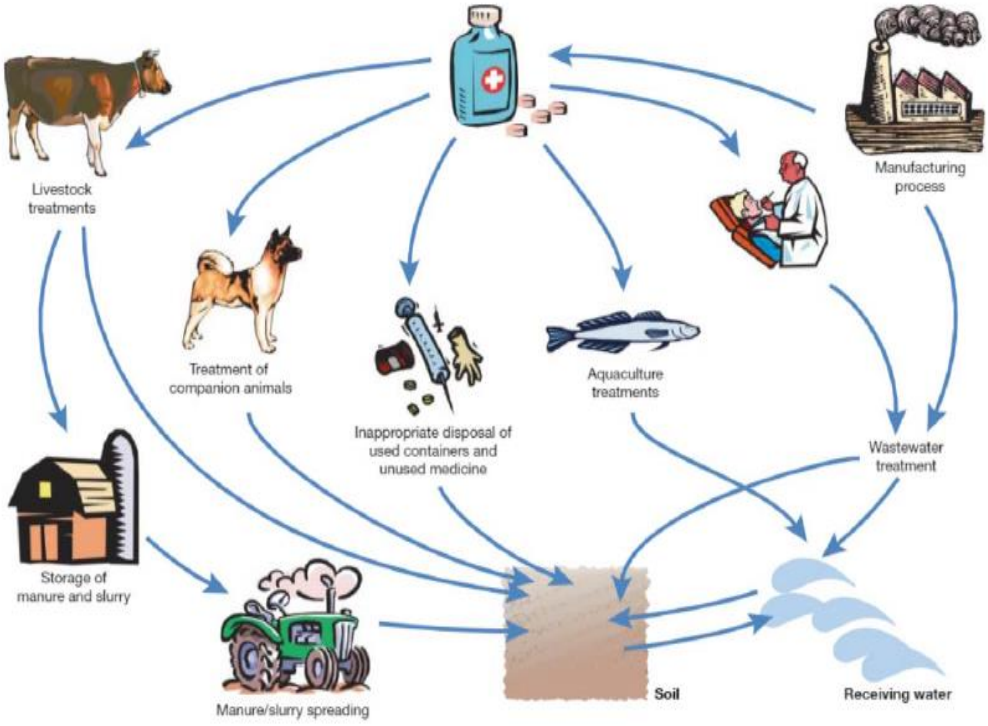

Figure 1. Routes of pharmaceuticals entry into the environment [5]

Over the years, pharmaceuticals such as diclofenac and ibuprofen in trace amounts have been detected in public water systems, ground and surface water. Lack of general knowledge of how to dispose of unused pharmaceuticals leads to improper disposal resulting in accidental toxicity, rising healthcare costs, landfills pilfering/scavenging, water supply pollution, anti-microbial resistance and death [4]. To lessen such effects, regulatory bodies and scientific community worldwide should raise public awareness about safe disposal practices.

1.1.2. Waste management crises in Lebanon

Waste management is still a challenge in Lebanon. The survey states that Lebanon produced 2.04 million tons of MSW in 2013; this means that each person in Lebanon produced 1.05 kilograms of waste per day [7]. Recently, a municipal solid waste (MSW) management crisis and a shortage in landfills and other waste treatment technologies have left municipal waste on the streets and in random sites for months [8]. A vast portion of the estimated 3,000 to 4,500 tons/year of hazardous solid waste produced in Lebanon is mixed with MSW [9].

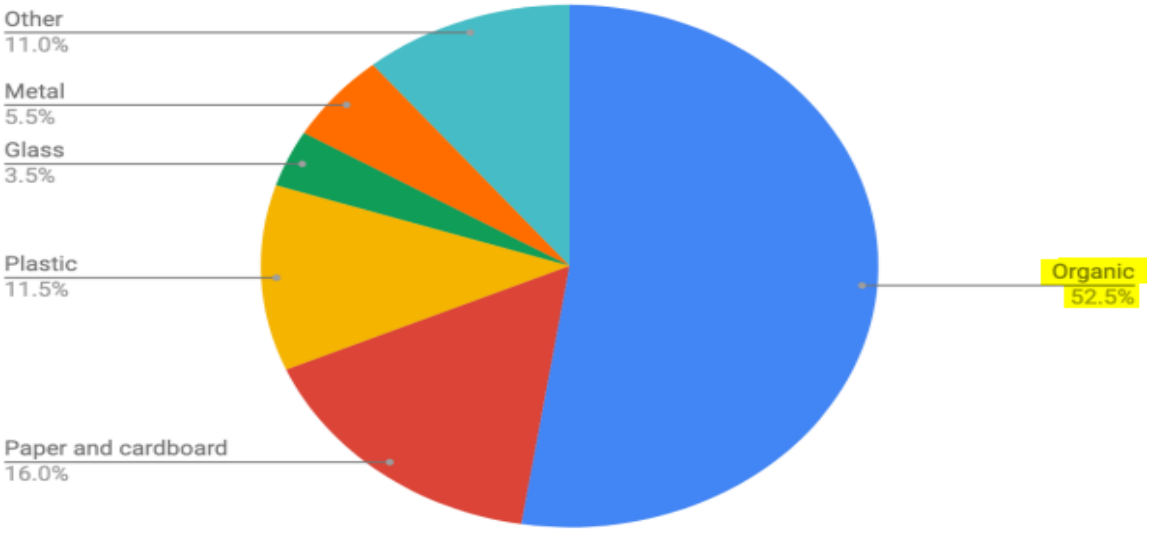

Figure 2. Waste composition in Lebanon [7]

For instance, a recent study reveals that the fate of most waste produced in Lebanese dental clinics is landfilling in MSW landfills [10]. Another study shows that the absence of a well-defined legislation and more stringent controls, most of the industrial and hazardous wastes are being mixed with the municipal wastes and collected in waste collection trucks [11].

The open burning of waste in Lebanon may have serious consequences for the health of people living nearby. A range of scientific studies have documented the dangers that emissions from the open burning of household waste pose to human health. These include exposure to fine particles, dioxins, volatile organic compounds, polycyclic aromatic hydrocarbon, and polychlorinated biphenyls, which have been linked to heart disease, cancer, skin diseases, asthma, and respiratory illnesses. The dangers of open burning of waste are compounded by the fact that Lebanon often does not properly dispose of industrial and healthcare waste, which may be mixed into the municipal solid waste stream [12].

Others show that Tripoli (second city and capital of North Lebanon) is facing an environmental disaster; the actual landfill is over saturated and can collapse in any moment causing dangerous damage in the environment. Landfill must be closed in 2012, but continue to dump waste in reason of lack an alternative new site [13]. Currently, there are no operational built, under construction, or planned hazardous waste landfills [11].

This unprecedented crisis has triggered several local initiatives, from NGOs, private companies and the civil society, to deal with municipal solid waste (MSW) [14], while few establishments export their hazardous waste following the Basel convention [8]. Remaining healthcare waste is disposed with MSW, or through uncontrolled and unauthorized incineration [8]. In particular, pharmaceutical waste, which belongs to the special waste category of healthcare waste [8], is accumulating in pharmaceutical distributors' warehouses with no proper disposal option available.

The lack of wastewater treatment which could remove a portion of pharmaceutical

contaminants and the random hazardous waste disposal practices exacerbate the environmental impact of pharmaceutical waste disposal in Lebanon [15].

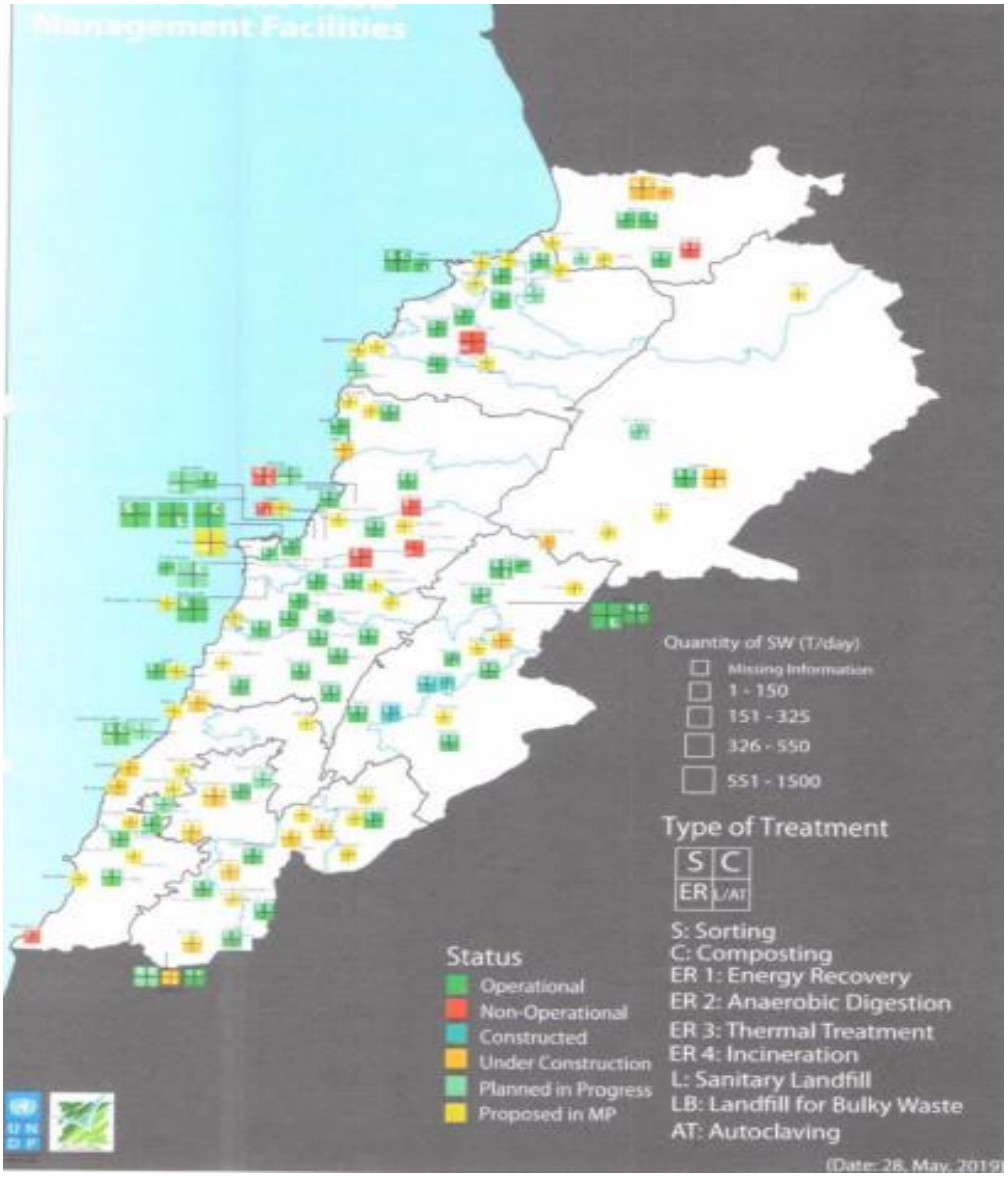

Figure 3. Map showing waste treatment facilities [7].

With the rapid development of global economy, large quantities of solid waste materials have been generated. Owing to economic, technical, and environmental considerations, the use of various solid wastes has become very common in modern concrete construction. Most of these solid wastes contain various hazardous heavy

metals, which can be solidified into the cement concrete [16]. Even though that cement concrete may be successful in immobilizing of these active wastes; some studies in the literature show the risk of heavy metals leaching from the cement products containing solid wastes, especially when exposed to the flowing water or various severe environments [17].

Tackling this issue, this study examines the integration of low compressive strength concrete with active pharmaceutical ingredient (API's) and study the influences on these wastes on the mechanical properties (MP) of the concrete. In addition, it investigates the ability of concrete in immobilizing leaching of Diclofenac. Leaching is quantified by conducting the Tank leaching test (TNT) in water at various temperatures; room, 40 and 60°C.

1.1.3. Advantages of the approach

This approach leads to many vital pros such as:

1.1.3.1. Avoiding Landfills:

Hu li et al said that the biodegradation process is exothermal which resulting in the generation of a considerable amount of heat that is trapped in the landfill. This increases the landfill's temperature, thus creating a vital issue in landfills operation which is the existence of hot spots or enhanced oxidation zones (EOZ), where the temperature can exceed 130°F. The EOZ conditions occur when significant amounts of oxygen infiltrate landfills from the perimeter wells. The development of EOZ in the landfill leads to damage the extraction wells, underground fires, and rapid settlement of the wastes. The landfill gas (LFG) may also create the risk of underground fire, if the

ratio of CH4 and O2 approaches its flammability limit [18]. On the other hand, Karen Slimak showed that many hazardous wastes have high water content which causes a leachate (Leachate is a liquid that forms when landfill waste breaks down and water filters through that waste and picks up toxins [19]). The main problem is in controlling the leachate [20], which comes from rain falling on the top of landfill, groundwater entering the landfill or liquid seeps through the landfill and collects decomposed waste components, chemical reactions take place and produce a toxic leachate "cocktail" [19]. This liquid can contain high level of ammonia, when it finds its way into ecosystems it is nitrified to produce nitrate, this nitrate causes eutrophication, or a lack of oxygen due to increased growth of plant life, in nearby water sources. Eutrophication creates "dead zones" where animals cannot survive due to lack of oxygen [21]. Consequently, the most pressing environmental concern regarding landfills is their release of methane gas. Methane is 84 times more effective at absorbing the sun's heat than carbon dioxide, making it one of the most potent greenhouse gases and a huge contributor to climate change [22].

1.1.3.2. Avoiding Incineration

Gerassimidou et al. studied the leaching of hazardous metals from raw expired drugs and from drug ashes following a simulated incineration test. The leaching tests were performed on solid drugs, packaging, ashed drugs, and ashed packaging. After collecting expired drugs and packaging shells, dating over three years, and including the aforementioned categories of hazardous waste, the samples were dried to ensure a constant weight at 70 °C. After drying and measuring the loss on ignition, the samples were grinded and incinerated at 900 °C. After incineration, the ashes obtained were also

tested. Using the method 4-12B provided by the US department of agriculture, the measurement results for eight metals were obtained: Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. As a conclusion for this experiment, the ashed drugs resulted in the highest number of metals where the concentrations of Cd, Ni, and Pb implied the need for disposing the ashed drugs in a hazardous waste landfill by either building a hazardous waste landfill or upgrading a non-hazardous one. While all other substrates do not require an upgrade to a hazardous waste landfill, the interest lays in the ashed drugs, resulting from the oxidation process in incineration [23]. They showed that even after incineration some metals need to be disposed in hazardous waste landfill, and this process is very expensive if we are going to measure it over the huge amount needed to be disposed every year. In addition, incineration of active wastes leads to the emission of toxic chemicals (acid gasses) in air that creates a health risk from pollutants emitted during combustion especially for those who live near the incinerated area, also it produces hazardous solid waste (toxic substance are more concentrated in the ash produced after incineration) this ash must be landfilled because it contains many hazardous substances [24]. Incineration is a controversial method of waste disposal, due to issues such as emission of gaseous pollutants. It is not suitable for such health care wastes as pressurized gas containers, large amounts of reactive chemical wastes, wastes treated with halogenated chemicals, halogenated plastics such as polyvinyl chloride, wastes with mercury or cadmium or radiographic wastes. Ash produced must be disposed of in a secure landfill. This disposal technique requires investment and operating costs and requires highly skilled operating personnel [25].

1.1.3.3. Wastes immobilization

Saad et al. proved that the eco-board which is composed of polyethylene (PE)/ Polypropylene (PP) reclaimed from Municipal solid waste (MSW) was affective at immobilizing diclofenac DF and reducing its leaching ability. Diclofenac (DF) drug product was embedded in boards of recycled plastic material, and leaching in water was assessed at various temperatures. DF concentrations were determined by high-performance liquid chromatography and revealed a maximum leachable fraction of 4% under accelerated conditions of 70°C, and less than 0.3% following 39 days of exposure at 20°C. The Ensemble Kalman Filter was employed to characterize the leaching behavior of DF. The filter verified the occurrence of leaching through diffusion, and was successful in predicting the leaching behavior of DF at 50°C and 70°C [15].

On the other hand, Yuan, X et al used tank test NEN 7375 to investigate the leaching behavior of heavy metals from the cement pastes containing solid wastes including fly ash (FA) and municipal solid waste incineration fly ash (MSWI) and he Studied the effects of two kinds of curing conditions (standard/Natural) and carbonation on the leaching characteristics of heavy metals [16]. The cement samples were immersed in the acetic acid solution (PH=7 and L/S=3) and the leachates corresponding to each immersion (3,7,14,21,28and 64 days) step were analyzed by inductively coupled plasma (ICP) to quantify the heavy metals. As a conclusion, the leaching of heavy metals becomes undetected after 28d immersion which means most of these metals are produced at early age because metals are solidified within the cement matrix and the cement hydrates dissolve and diffuse into the solution during immersion (good density of cement paste makes the penetration of the solution into the cement paste slow and

difficult with time) [16]. Also, he compared the leached amounts of tank test by parametric values of GB 3838-02 to assess the leaching toxicity and he find that Long-term exposure of cement concrete containing MSWI and FA to water environment may lead to Cr (>0.1) and Cd (>0.01) pollution, where the amount leached of Cr and Cd is 0.19 and 0.019 respectively [16].

1.1.3.4. An integration solution for pharmaceutical waste and concrete

This study reduces the environmental impact of pharmaceutical wastes especially API's which can be solidified into the cement concrete. The solidification process is mainly attributed to the C-S-H phase, which can sorb large amounts of heavy metals, and prevent them from migration due to the low permeability of C-S-H. Owing to the high alkalinity of cement matrix, heavy metals also form the low soluble products to reduce the leaching. In addition to sorption and precipitation, heavy metals may enter the lattice of the hydrates, being firmly bound within the cement matrix [26].

Talah et al. reported in their article "*Effect of Pharmaceutical Wastes Usage as Partial Replacement of Cement on the Durability of High-Performance Concrete (HPC)"* an experimental study of the influence of ash produced from incinerated PW used a partial substitute for Portland cement (10%) on the mechanical properties and durability of HPC. They proved that the sample with higher percentage of PW has higher compressive strength than reference concrete (65MPa instead of 48 after 1 year) according to ASTM C39. Moreover, they noticed that there is reduction of chloride ion penetration, oxygen permeability and increase the durability of concrete, since the test results show that the values of the electric charge for HPC with MP are too small and

the apparent permeability tends to decrease when the compressive strength increases - ASTM C1202. This article deals with HPC which create a gap when it comes to Portland cement since there is a difference in the properties of each type. In addition, they didn't highlight environmental effect of this mixture, for example the long-term leaching of PW from the HPC [27].

The integrated utilization of wastes in cement kiln has multiple advantages. Firstly, the high temperature in cement kiln can completely destroy the hazardous organic substances and benefit the environment. Secondly, the wastes can be alternative fuel and raw materials, which can save energy and resources at the same time. Finally, the co-process of wastes in cement kiln can also receive additional subsidy from the government. However, it should be noted that the application of materials involving wastes might threaten the environment and human health [28].

Pacheco et al. proved that concrete mixture with ceramic aggregates perform better than the control concrete mixture concerning compressive strength, capillary water absorption, oxygen permeability and chloride diffusion thus leading to more durable concrete structures [29]. This helps in solving the ceramic industry waste problem and at the same time leading to a more sustainable concrete industry by reducing the use of nonrenewable resources like cement and aggregates and avoiding environmental problems related to land filled wastes.

1.1.3.5. Leaching ability of these wastes after integration with concrete

Leaching behavior and mechanism are essential to understand, in order to ensure a predictability of the stabilized waste behavior, whether in a landfill or experimentally. Leaching is the process of the release of soluble waste, through the binding membrane,

into the surrounding environment, while dry locations represent the most favorable conditions, groundwater and flow conditions are very prominent in many landfills [30]. Carbonation and low pH conditions are the major inducer of leaching and porosity conditions in cement [31]. To achieve this approach, different experiments were done to investigate the environmental behavior of mine waste rocks by assessing the leaching behavior of two sulfide- mining waste rocks suitable for concrete production. Different tests were carried out: (1) humidity cells test on raw and washed waste rocks, (2) TCLP, SPLP and CTEW-9 on both gold mine waste rocks, and (3) tank leaching test (TNT) on concretes amended with both waste rocks. They tried to decrease the mobility of heavy metals in mine wastes by stabilize/solidify using cement binder. Results showed that the use of these wastes in concrete will lead to reduce the wastes volumes, reduce the energy consumption and the gas emissions and conserve the natural resources since all the contaminants are under the limits fixed by Quebec Environmental Regulation (QER), Environmental Protection Agency (EPA) and Soil Quality Decree (SQD) [32].

To investigated the long-term environmental impact of Eco-Ordinary Portland Cement (EOPC) prepared by municipal solid wastes (MSS) and hazardous wastes (HW), Zhenzhou et al. used leaching test based on modified NEN 7375 lasting 180 days. The cement composites in the compact and ground forms were leached in the deionized water and saline water (leaching solvents) to simulate surface water and marine condition. The cement plant chooses the MSS and HW to substitute part of raw materials to produce cement clinker. The leaching test was conducted in a polyethylene vessel with the liquid–solid ratio of 5:1. During the leaching process, every 10 mL samples was taken after 3, 7, 14, 30, 60, 90, 120, 150 and 180 days. The heavy metals concentrations in the samples were also determined by the ICP-MS (Inductively

coupled plasma mass spectrometry). Results showed that most heavy metals have low leachability and the concentrations of them are much lower than the corresponding regulation except for As which exceeds the limit [28].

In general, leaching is understood and assessed through experimental data since the reactions happening lead to conflicting effects [33]. Leaching tests are classified based on diameter, where powder and granular materials are classified for diameters less than 40 mm, and stabilized waste products for diameters more than 40mm. Such leach tests can form a baseline for predicting long term behavior of leaching [33].

1.1.4. Model organic pharmaceutical compound

The model pharmaceutical used in this study is diclofenac (DF), a widely used nonsteroidal anti-inflammatory drug (NSAID) [34]. Its occurrence in the environment has been well established [35] [36]. The European Commission currently lists DF as a priority hazardous substance [37], and is among the pharmaceuticals placed on a watch list for monitoring and risk assessment purposes [38]. In addition to its relevance as a major environmental contaminant, DF has a relatively high decomposition temperature [38] [39], and a degradation profile following first-order kinetics [40], which makes it a suitable candidate for the leaching studies explored in this work.

1.1.5. Research Objectives

This thesis emphasizes the importance of reducing to reach an end of the disposal of pharmaceutical wastes into the environment. This project tackles the concept of immobilizing solid hazardous waste in concrete after it becomes harden. The model pharmaceutical that will be used in this study is **Diclofenac** (**DF**); nonsteroidal anti-

inflammatory drug. This paper examines the integration of DF with concrete and study the influences of this API on the mechanical properties (MP) of the concrete. In addition, it investigates the ability of concrete in immobilizing the leaching of DF. Leaching is quantified by conducting the Tank leaching test (TNT) in water at various temperatures room, 40 and 60°C to identify the leached amount and compare it with the literature set limits.

The approach suggested by Who for treating expired pharmaceuticals is by exposing them to high temperature by incineration. This mechanism shows no recent cost estimation in which a document published by who in 1999 explains the following:

> "The cost of waste pharmaceutical high temperature incineration: Pharmaceuticals are ideally disposed of by high temperature (i.e. above 1,200ºC) incineration. Such incineration facilities, equipped with adequate emission control, are mainly to be found in the industrialized world. Quotations for disposing of the pharmaceutical waste in Croatia and Bosnia and Herzegovina in this way range from US$2.2/kg to US$4.1/kg. To incinerate the current stockpile of waste pharmaceuticals in Croatia would therefore cost between US$4.4 million and US$8.2 million. Quoted weights of pharmaceutical waste. The gross weights mentioned previously include packaging. Actual pharmaceutical contents may be half, or less than half, of the gross weight." [41] [42]

The previously mentioned costs are exposed to inflation in which oil prices have increased over the years. Due to the absence of proper pharmaceutical waste management process in Lebanon, expired pharmaceuticals are being accumulated in distributers' warehouses and being dumped to landfills and open areas through the municipal waste streams by citizens. Therefore, according to the previous information, the research principles are:

- Experimentally determine the leaching behavior of diclofenac, a model pharmaceutical compound from harden concrete and identify the mechanism of leaching.
- Determine the effect of PW on the mechanical properties of concrete.

CHAPTER 2

EFFECTS OF PHARMACEUTICAL WASTE ON THE MECHANICAL PROPERTIES OF CONCRETE.

2.1. Introduction

This chapter investigates the effects of pharmaceutical waste as a partial replacement of Portland cement on the compressive strength of the concrete specimen. The mix design parameters corresponding to each test are presented in details in table 1 showing the control samples and samples of different percentage replacement of Diclofenac by weight of cement (1%, 2%, 4% & 8%).

2.2. Testing Plan

Figure 4. Concrete Scale Samples

The testing plan for the mechanical properties (MP) of the modified concrete mixes includes only the compressive strength test due to the lack of Diclofenac Sodium as pure material in the country and its high cost. There is a direct relationship between

the amount of diclofenac and that of cement; therefore, the optimal method was using the low compressive strength at 20Mpa in order to decrease the amount of cement which in turn leads to the decrease of the amount of DF used since as previously mentioned DF is pricy. The first step was formulating 5 different mixes with different amounts of Df & cement as shown in table 1. The first one was the control mix containing 0% of Df increasing it gradually to 1,2,4 and 8% of the cement weight in the other mixes. Three replicates were done for each mix in order to attain credibility. Samples were tested after 7 and 28 days to determine the effect of time on the compressive strength of concrete. It is necessary to note that all samples were cured in water before being tested.

Mix Number	% PW	% Cement	Amount of Cement (Kg)	Amount of Diclofenac (Kg)	Amount of Sand (Kg)	Amount of C.A (Kg)
1	0	100	3.19	0	7.44	13.29
2	1	99	3.158	0.0319	7.44	13.29
3	2	98	3.1262	0.0638	7.44	13.29
4	4	96	3.0624	0.1276	7.44	13.29
5	8	92	2.9348	0.2552	7.44	13.29

Table 1.Distribution of the amount of cement & DF over the mixes

To get M20 (f'c=20Mpa) we must use this ratio (1:3:6) where these numbers are related to cement, sand and coarse aggregates respectively. The amount of cement, sand and coarse aggregates (C.A) are calculated in one cubic meter then multiplied by the volume needed in this experiment (0.055 cubic meter of concrete). The amount of cement, sand and C.A needed is 3.19, 7.44 and 13.29 Kg respectively for each mix. For

the first mix zero kg of Df used, while in the second mix 31.9g of cement was replaced by Df, this amount will be 63.8, 127.6 and 255.2g in third, fourth and fifth mix respectively.

Figure 5. Capping of Concrete Cylinders After Demolding

2.3 Concrete Preparation

Formwork preparation plays an important role in the final appearance of the concrete surface. It molds the placed fresh concrete, which in this stage normally is viscous, to the shape specified in the drawing [43].

The specimen's formwork is cylinder of diameter 10cm and height 20cm, according to ASTM C39 "Compressive strength of cylindrical concrete specimens''. Each mix has three replicates at 7 and 28 days. Therefore, the total number of samples is 30 cylinders and 15 cubes of dimensions 6x6x6cm used for leaching test.

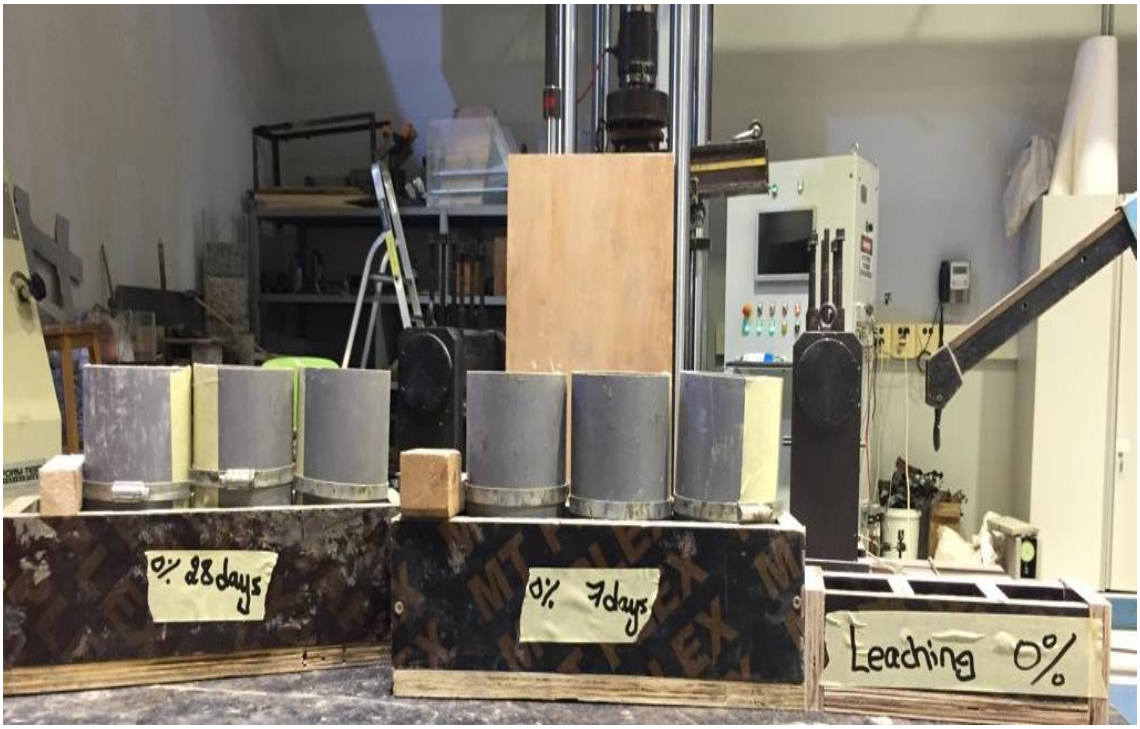

Figure 6. Specimens used for each mix

Before mixing, the materials used in the formation of the concrete mix must be well chosen. A day before mixing, the fine aggregate sieved through #8 to avoid having any large particles inside the mix. In Addition, the C.A washed in order to clean the aggregates from dust particles (Sand) and impurities. These aggregates (Sand & C.A) were placed in an oven for 24 hours to maintain that all particles are dried well. In the or preparing the mixes, the aggregates removed from the oven in the morning to be cooled to the room temperature, since the aggregates used in these mixes were in SSDC (Saturated Surface Dry Condition). The hot aggregates must be avoided in order to prevent the evaporation of the water used in mixing the concrete. The amount of cement and Df were measured precisely for each mix separately the added to the aggregates.

After that, the batching process started following the ASTM C192, the manual mixing took place with a mixing board since the quantity used was small. The C.A mixed with sand and cement until we got a uniform product, then Df distributed uniformly and mixed well with the materials. The mixture was collected at the center of the mixing board and a hollow at the center was made in order to hold the water used, it mixed well using a hand trowel.

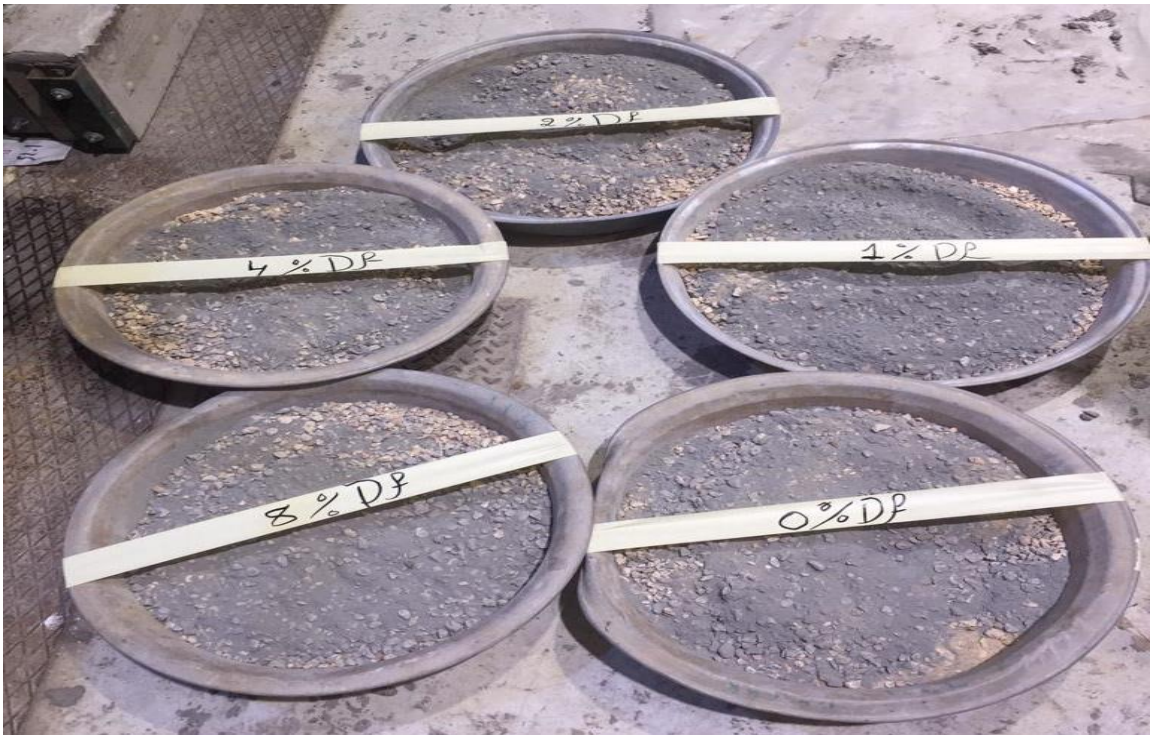

Figure 7. Different percentage of cement and DF for each mix.

Figure 8. Distribution of Df

This concrete mix was filled in the cylinders and cubes (6 cylinders and 3 cubes for each mix). Each mold was filled in three equal layers, rodding each layer 30 times using a 5/8 in tamping rod. The specimens removed from the molds after 24 hours of casting, then these samples were cured continuously using a water tank.

2.4. Concrete Mix Design

Concrete is a composite blend that comprises of cement, sand and aggregate. It is the procedure of finding the exact amount of these materials to reach the target strength and characteristics of concrete. These specifications included the fresh concrete properties, hardened concrete properties (target strength and expected durability) and the maximum size aggregates required. The aim of concrete mix design is to get a durable concrete with acceptable workability and specific compressive strength maintaining the least cost.

The proportions used to create the required strength are mentioned in table 1. The required strength was 10Mpa, so two samples were prepared to identify the appropriate w/c ratio. The first one was with w/c equal to 0.64 while the second one was

0.75 (the w/c was high since we were dealing with low compressive strength). After 2 days, a compressive strength test was done, this test showed that the sample with higher w/c have higher compressive strength which is equal to 11.7 instead of 10.2 for the sample of lower w/c.

Figure 9. compressive strength with different w/c ratio

After all, the amount of sand and C.A was respectively 7.44 and 13.29 for each mix while the amount of cement and diclofenac varies over the mixes. The w/c ratio remains constant but the amount of water added varies between mixes since the amount of cement was not constant (Decreased 1,2,4 and 8 % respectively). This helps in insuring a proper evaluation of the effect of Diclofenac as a partial replacement of cement on the compressive strength of concrete.

2.5 Testing Procedure, Analysis and Results

In this part of the chapter, the compressive strength is the only test done to examine the effect of Diclofenac (Df) on the mechanical properties of the concrete. ACI Committee 207 reapproved on 2002, that concrete's tensile strength usually equal to 6.7 times the square root of the compressive strength [44]. L Zhang et al proved in their study that the cubic curve can explain better the relation between the compressive strength and the tensile strength after they were fitted by SPSS (Statistical Product and Service Solutions), The correlation coefficient is 0.842 [45]. Based on these results and due to the lack of DF in the country, the compressive strength alone can maintain a clear idea about the effect of Df on the strength of the concrete.

To determine the compressive strength of the cylindrical concrete specimens a compressive strength test was done using ASTM C39 [46]. A compressive axial load is applied to molded cylinders until failure occurs. The compressive strength of the specimen is calculated by dividing the maximum load achieved during the test by the cross-sectional area of the specimen [47]. In this test experiment, a compressive axial load is applied to the cylinder at a rate of 1.25mm/min until failure occurs. Capping the cured sample is important to maintain that the test cylinder has smooth, parallel and uniform bearing surface that are perpendicular to the applied axial load during

compressive strength test. In other words, capping avoids irregular surface and stress concentrations which reduces the measured strength of the specimen. Cylinders were capped with Sulphur as mentioned in ASTM C617.

Figure 10. Capping of cylinders before testing

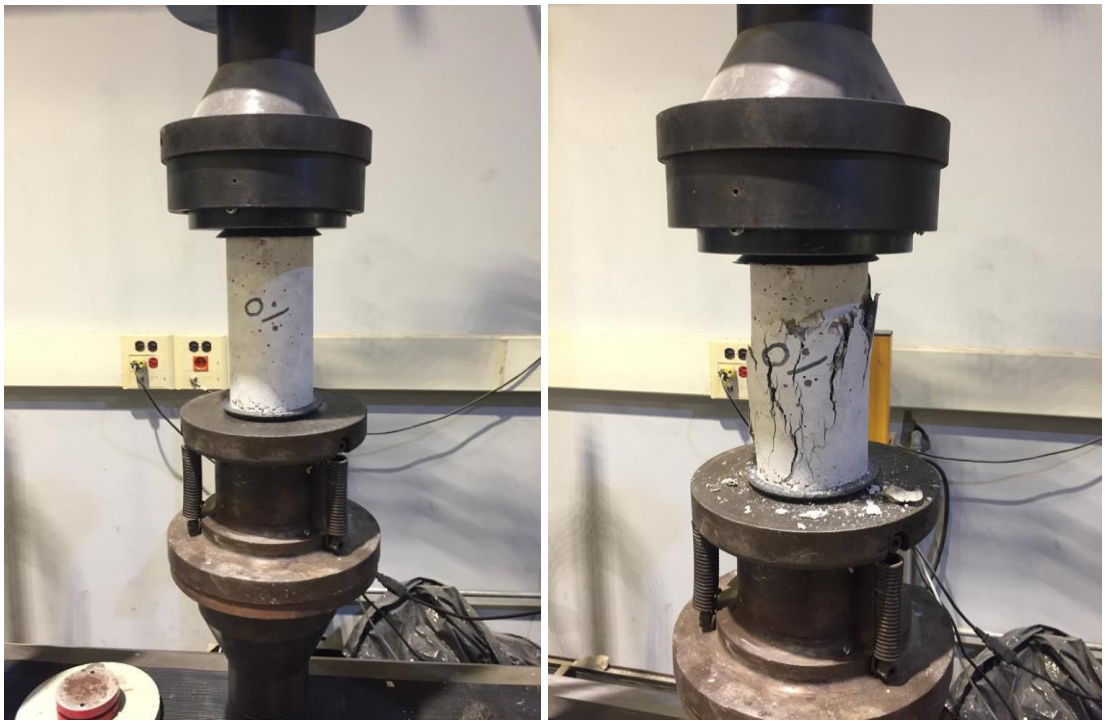

Figure 11. Specimen before and after failure.

Three replicates were tested for each mix after 7 and 28 days as shown in table 2 and 3. The average of these 3 samples was taken as a compressive strength for each mixture. The compressive strength of the control sample (0%) recorded 14.28 Mpa at 7 days and 20.78 after 28days. The addition of the Diclofenac sodium (Df) contributed in lowering the compressive strength of the concrete. The compressive strength of Mix 2 (1%) decreased till 12.549 after 7days and 17.39 after 28days which means it dropped by 12% at day 7 and 16.3% after 28days, while that of mix 3 (2%) registered a slightly increase in compressive strength compared to mix 1 where it reached 12.92 at day 7 and 17.47 at day 28, particularly it decreased by 9.5% and 15.93% After 7 and 28 days respectively. Mix 4 (4%) reported same result as mix 3 after 7 days but the compressive strength decreased slightly till it reached 17.25Mpa after 28days which means it dropped by 16.75% compared to the control concrete. The compressive strength of mix

5 (8%) which contains the highest amount of Df recorded the lowest value which is 8.62 at day 7 and 12.64 after 28 days which means it dropped by 40% after 7 and 28days.

Figure 12. Failure of samples after compressive strength test

After 7 days					
Mix number	Percentage of DF	Samples	Compressive Strength (Mpa)	Strain	Average
Mix 1	0%	1	16.078	0.665	14.28166667
		2	13.821	0.634	
		3	12.946	0.865	
Mix 2	1%	1	12.632	0.7	12.549
		2	12.507	0.657	
		3	12.508	0.493	
Mix 3	2%	1	12.836	0.738	12.92366667
		2	13.852	0.686	
		3	12.083	0.507	
Mix 4	4%	1	12.686	0.691	12.91033333
		2	13.589	0.757	
		3	12.456	0.636	
Mix 5	8%	1	8.311	0.371	8.616666667
		2	8.515	0.447	
		3	9.024	0.652	

Table 2. Results of the compressive strength test after 7 days.

After 28 days					
Mix number	Percentage of DF	Samples	Compressive Strength (Mpa)	Strain	Average
Mix 1	0%	1	18.815	0.561	20.78333333
		2	21.774	0.796	
		3	21.761	0.665	
Mix 2	1%	1	17.161	0.851	17.39333333
		2	17.859	0.773	
		3	17.16	0.829	
Mix 3	2%	1	17.27	0.731	17.47333333
		2	18.024	0.798	
		3	17.126	0.752	
Mix 4	4%	1	16.906	0.752	17.25231
		2	17.173	0.726	
		3	17.669	0.667	
Mix 5	8%	1	13.07	0.744	12.64466667
		2	12.509	0.685	
		3	12.355	0.667	

Table 3. Results of the compressive strength after 28 days.

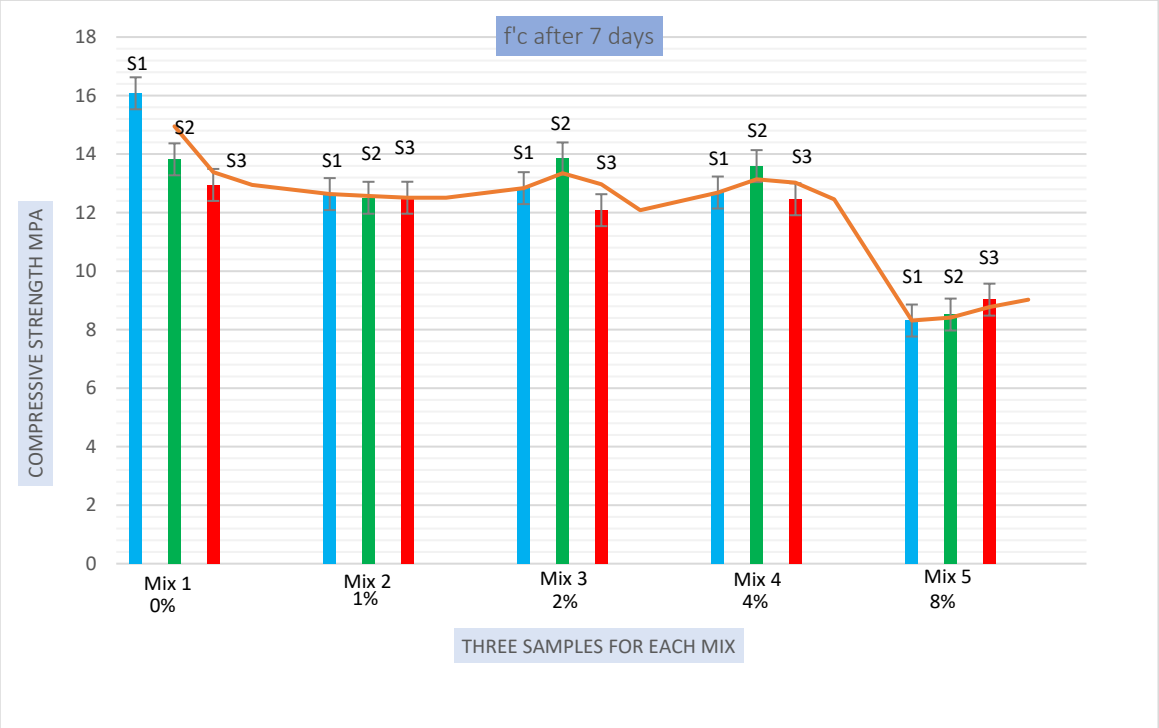

Figure 13. Variation of the compressive strength of every sample in each mix after 7 days

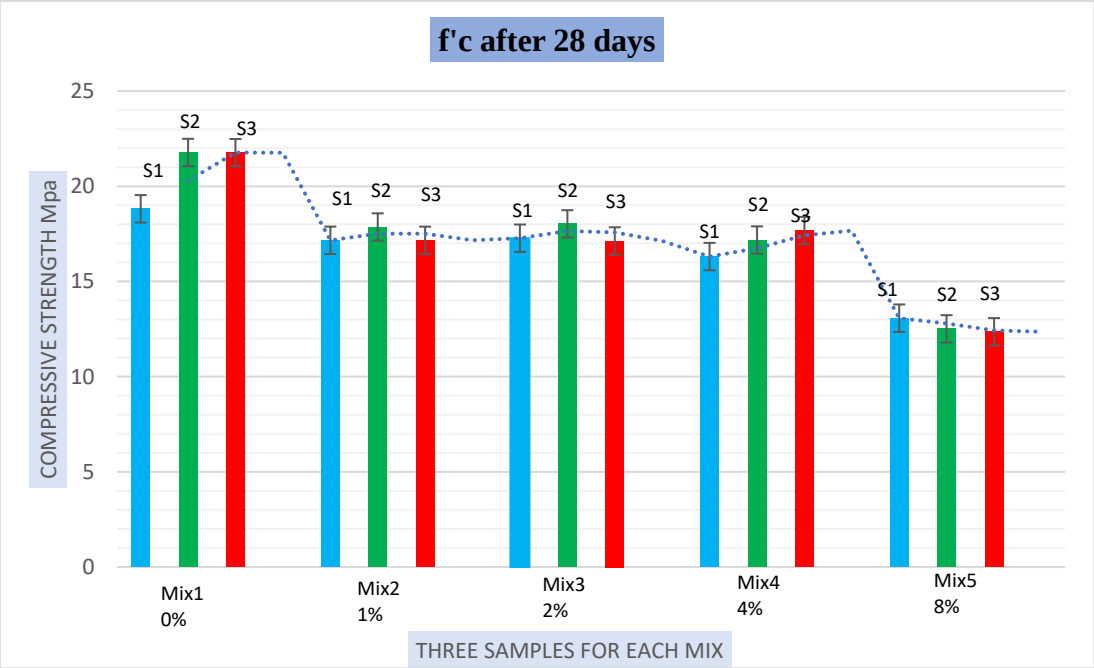

Figure 14.variation of the compressive strength of every sample in each mix after 28 days

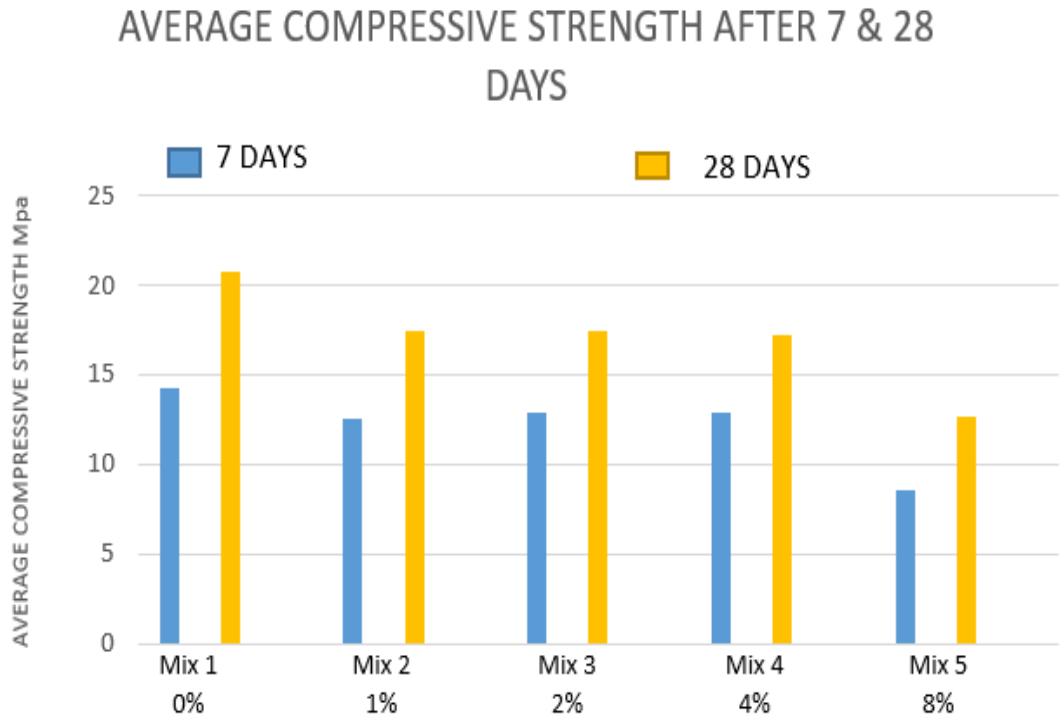

Figure 15. Average compressive strength of each mix after 7 & 28 days.

CHAPTER 3

LEACHING MODEL: STUDYING THE ABILITY OF CONCRETE AT IMMOBILIZING THE DICLOFENAC

In addition to the effect of Diclofenac (Df) as a partial replacement of cement on the mechanical properties of the concrete, an experimental study was done to investigate the leaching behavior of Df from hardened concrete. The leaching test presents the amount of organic pharmaceutical leached from concrete following several experimental conditions.

3.1. Introduction

Recently, there has been a growing interest in identifying suitable routes for the disposal of pharmaceutical waste [1] [2]. This study examines the ability of concrete at immobilizing the pharmaceutical solid waste (Df). Df embedded in the concrete mixture as a partial replacement of cement, the percentages of Df were 0,1,2,4 and 8 distributed over 5 mixes respectively. The leaching test took place in water at various temperatures such as room, 40℃ and 60℃.

3.2. Model organic pharmaceutical compound

The model pharmaceutical used in this study is diclofenac (DF), a widely used anti-inflammatory drug (NSAID) [36]. Its occurrence in the environment has been well established [1] [38]. The European Commission currently lists DF as a priority hazardous substance, [40] and is among the pharmaceuticals placed on a watch list for monitoring and risk assessment purposes [41]. Moreover, Df is a major environmental contaminant since it has a relatively high decomposition temperature [48] [38], and a

degradation profile following first-order kinetics [40], which makes it a suitable candidate for the leaching studies conditions explored in this work.

Furthermore, DF has been identified as a priority contaminant in an environmental risk analysis of pharmaceuticals used in Lebanon [49]. The aim of this study is to quantify the amount of Df leached from the hardened concrete in water at various temperature.

3.3. Materials and Methods

3.3.1. Sample Preparation

For each mix, three cubic samples were prepared 6x6x6cm and tested at different temperatures; one at room, second at 40°C and the third at 60°C. The transversal sides taped using aluminum tape. This ensures leaching occurs only through the top and bottom square faces and allows for the process to be modeled as one-dimensional leaching from a solid. The produced concrete specimens containing DF in the powder form were used for the leaching test.

Figure 16.Transversal tapping of cubic samples using aluminum.

3.3.2. Leaching test

To test the ability of concrete at immobilizing the Df, leaching of Df from concrete was assessed via a static test. Specimens were put in ultra-pure water at a leachant volume to specimen exposed surface area (L/S) of 5cm. A low L/S ratio (5 cm) was selected to increase the DF concentration in solution for enhanced detection with negligible chemical gradient changes between the solid and solution [50]. At the beginning of a testing period, each concrete cubic sample containing Df was introduced into a beaker with water at an L/S of 5 cm. The beaker size was selected to ensure complete water contact of the specimen leaching area and was closed using parafilm and aluminum foil to prevent water evaporation during testing. For accelerated temperature conditions, the water and beaker are preheated to the test condition before introducing the test sample. Temperature was maintained by placing samples in an oven.

Figure 17. Leaching test samples at room temperature.

Figure 18. Leaching test samples at 40°C.

Figure 19. Leaching test samples at 60°C.

In initial leaching tests, samples were exposed at room temperature (27 °C), 40 °C, and 60 °C for a duration of 64 days. Samples of 1 mL were collected at the specified time interval and the equivalent amount of water was added to the test solution to maintain the identical leachant volume. Collected samples were stored under refrigerated conditions until analyzed. The results represent an average of two replicates. Leaching under various pH conditions was not evaluated since the stability profile of the organic compound tested is sensitive to pH and will prevent monitoring of DF leached over time due to degradation.

The leaching levels were significantly lower than the solubility limit of DF at the temperature and pH conditions of the test [51] [52]. Therefore, the low accumulated levels of DF in the leachant have a minimal effect on the concentration gradient and subsequently the diffusion process.

3.3.3. Sample analysis

The concentration of DF in solution was determined using HPLC (Agilent 1100 Series), equipped with a quaternary pump, ALS auto sampler, diode array detector (DAD) and supported by an analytical work station (LC solutions chromatographic software) (Agilent Technologies, California USA). The chromatographic separation method was based on the method by Ghauch et al. [53] and was achieved on a reversed phase column (Discovery C18, 5 μm, 25 cm × 4.6 mm ID) connected to a security guard column (Discovery HS C18, 5 μm, 2 cm × 4.0 mm ID), both sourced from Supelco, Bellefonte, Pennsylvania, USA.

The HPLC method consists of an isocratic elution using methanol (Riedel de Haen, Germany) / 0.1% formic acid in water (80/20, v/v), at a flow rate of 0.9 mL/min. The injection volume was 10 µl, the column temperature was set to 30°C, and DF (Sigma, USA) was detected at a wavelength of 276 nm with a retention time of 9.0 min.

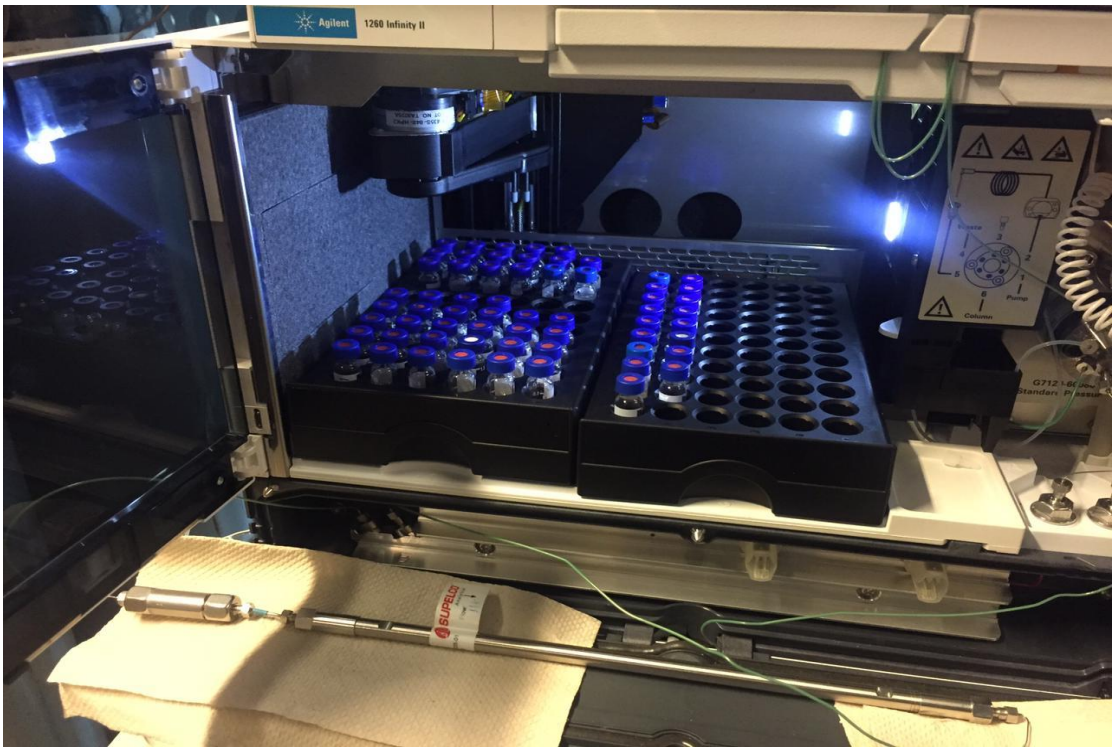

Figure 20. Vials, column and HPLC used to determine the concentration of DF.

3.4 Results

3.4.1. Leaching of Df from hardened concrete

Diclofenac was integrated with concrete mix in the form of powder in order to boost leaching and allow for the estimation of the leaching ratios. The initial leaching conducted after two hours of introducing the cubic samples into the beaker containing water. After that, the samples have been taken after 1, 2, 4, 8, 16, 32 and 64days at different temperatures in order to predict the effect of increasing temperature on the leaching ability of Df.

The leaching amount of Df is directly proportional to the temperature which means as the temperature increased from room to 60℃ the amount of Df leached increased in all samples regardless percentage of Df existed in the mixture.

At room temperature, for Mix 2 which contains 1% diclofenac as a partial replacement of cement, the leached amount was 1.32 ppm after 2 hours and that of Mix 3 (2% Df) was 6.78 ppm while that of Mix 4 (4% Df) increased till 23 ppm, this value reached 50 ppm in Mix 5 (8% Df). After 1 day, the amount of Df leached in all Mix increased sharply to reach 11.3, 25.42, 61 and 161.2 ppm in Mix 1, 2, 4 and 8 respectively. At day 2, the amount leached reached 16.94 ppm for Mix 2, 33.9 ppm for Mix 3, 71.5 ppm for Mix 4 and 250 ppm for Mix 5. This amount started to increase slowly after 4 days, mix 2, 3, 4, and 5 recorded 24.77, 42.14, 88.6 and 302.9 ppm respectively as shown in table 4. The leached values of Df became 30.54, 52, 106.5 and 370.5 ppm after 8 days for Mix 2, 3, 4, and 5 correspondingly. These values gradually inclined to 35, 59, 117.4, and 410 ppm for Mix 2, 3, 4 and 5 subsequently at day 16. After 32 days, the leached amount slightly raised to 39.6, 64.08, 122.7 and 415.6 ppm for Mix 2, 3, 4 and 5 respectively. The final stage was after 64 days, where the values were marginally increased to 40.95, 65.65, 123.88 and 417.305 ppm for Mix 2, 3, 4 and 5 respectively as shown in figure 21.

At 40℃, the initial leached value was different where it recorded 3.86, 9.27, 27.52, 103.97 ppm for mixes 2,3,4 and 5 respectively. These values increased gradually till it reached 63.35, 122.77, 201.43 and 421.06 ppm after 64 days as shown in figure 22.

At 60℃, the initial leached value was huge with respect to the room temperature as it recorded 5, 11.05, 37.08 and 116.24 ppm for mixes 2,3,4 and 5 respectively. These

values increased gradually till it reached 71.83, 140.1, 261.3 and 506.31 ppm after 64 days as shown in figure 23.

Percentage of Diclofenac (%)	Time (DAYS)	PH	Area	Amount Leached (ppm)
1%	0	10.51	17.75155	1.31321
	1	11.01	157.233545	11.631655
	2	11.04	229.02868	16.94285
	4	10.57	334.88564	24.77382
	8	10.48	412.85524	30.54177
	16	11.02	472.85733	34.98054
	32	11.06	536.12119	39.66061
	64	11.23	553.59131	40.95299
2%	0	11.19	91.656355	6.78046
	1	11.05	343.62097	25.42003
	2	10.92	458.37711	33.90934
	4	10.6	569.56824	42.13492
	8	11.14	704.04602	52.08317
	16	11.1	800.14155	59.19203
	32	11.18	866.23209	64.0812
	64	11.33	878.07492	65.6573
4%	0	10.83	311.96048	23.077885
	1	11.34	824.78308	61.014925
	2	11.41	966.96552	71.53315
	4	11.4	1197.24298	88.57106
	8	10.87	1439.21802	106.46895
	16	11.09	1587.07166	117.40671
	32	11.08	1659.97656	122.79999
	64	11.34	1674..58832	123.881
8%	0	11.06	676.29309	50.03009
	1	11.19	2179.10645	161.20354
	2	11.42	3036.78687	250.6522
	4	11.59	3473.4104	290.95228
	8	11.65	5007.81055	340.46251
	16	11.07	5546.03223	386.2785
	32	11.16	5618.35645	399.356
	64	11.34	5641.09147	401.62882

Table 4. Table shows the leaching behavior of Df of four mixes at room temperature.

Percentage of Diclofenac (%)	Time (DAYS)	PH	Area	Amount Leached (ppm)
	0	10.58	52.19908	3.86153
	1	10.12	313.493485	23.19129
	2	10.14	408.41229	30.2131

1%	4	10.42	544.10135	40.25095
	8	10.52	677.19403	50.09675
	16	10.63	765.24155	56.61023
	32	10.67	839.90488	62.1336
	64	10.75	856.46715	63.358835
2%	0	10.61	125.34318	9.272505
	1	10.16	553.346495	40.93488
	2	10.08	782.66245	57.89898
	4	10.46	1070.46082	79.18942
	8	10.67	1334.176695	98.69831
	16	10.62	1513.10871	111.93515
	32	10.97	1619.57148	119.81095
	64	11.06	1659.70111	122.77961
4%	0	10.7	372.024615	27.521245
	1	10.34	1180.368345	87.32004
	2	10.15	1480.04291	109.48905
	4	10.47	1851.31531	136.95464
	8	10.67	2186.33716	161.73854
	16	10.64	2499.18226	184.88186
	32	10.82	2694.18372	199.30747
	64	11.12	2722.935	201.43429
8%	0	11.09	1405.52332	103.97632
	1	11.23	2983.59448	220.71719
	2	11.32	3594.94409	265.94297
	4	11.33	3999.15894	321.84555
	8	11.47	5084.87549	376.16354
	16	11.45	5547.38623	410.37867
	32	11.09	5670.54639	419.48968
	64	11.44	5691.8976	421.06894

Table 5. Table shows the leaching behavior of Df of four mixes at 40℃

Percentage of Diclofenac (%)	Time (DAYS)	PH	Area	Amount Leached (ppm)
1%	0	10.2	67.320305	4.98015
	1	9.81	590.469235	43.6811
	2	10.11	713.27023	52.76555
	4	10.37	841.33799	62.23961
	8	10.83	896.40656	66.31342
	16	10.83	925.50144	68.46577
	32	10.99	959.1647	70.95607
	64	11.14	971.05343	71.8356
	0	10.24	149.287405	11.04383
	1	9.99	803.144075	59.41415
	2	10.19	1019.66999	75.43207
	4	10.39	1346.67359	99.6228

2%	8	10.83	1544.13147	114.23012
	16	10.81	1736.9989	128.49787
	32	10.95	1874.03327	138.63525
	64	11.1	1894.091	140.10401
4%	0	10.39	501.27595	37.08286
	1	9.89	1678.13483	124.14328
	2	10.03	2005.74726	148.37905
	4	10.29	2564.46045	189.71094
	8	10.76	2950.63	218.27859
	16	10.78	3175.8595	234.94037
	32	11.32	3455.53931	255.6302
	64	11.16	3532.6626	261.30752
8%	0	10.35	1571.37146	116.24525
	1	10.89	3486.26953	257.90356
	2	10.64	4561.38232	337.43711
	4	11.05	5524.51514	408.68673
	8	11.28	6315.1167	467.17302
	16	11.32	6663.35986	492.93498
	32	11.25	6818.39404	504.40394
	64	11.34	6845.01277	506.31875

Table 6. Table shows the leaching behavior of Df of four mixes at 60°C

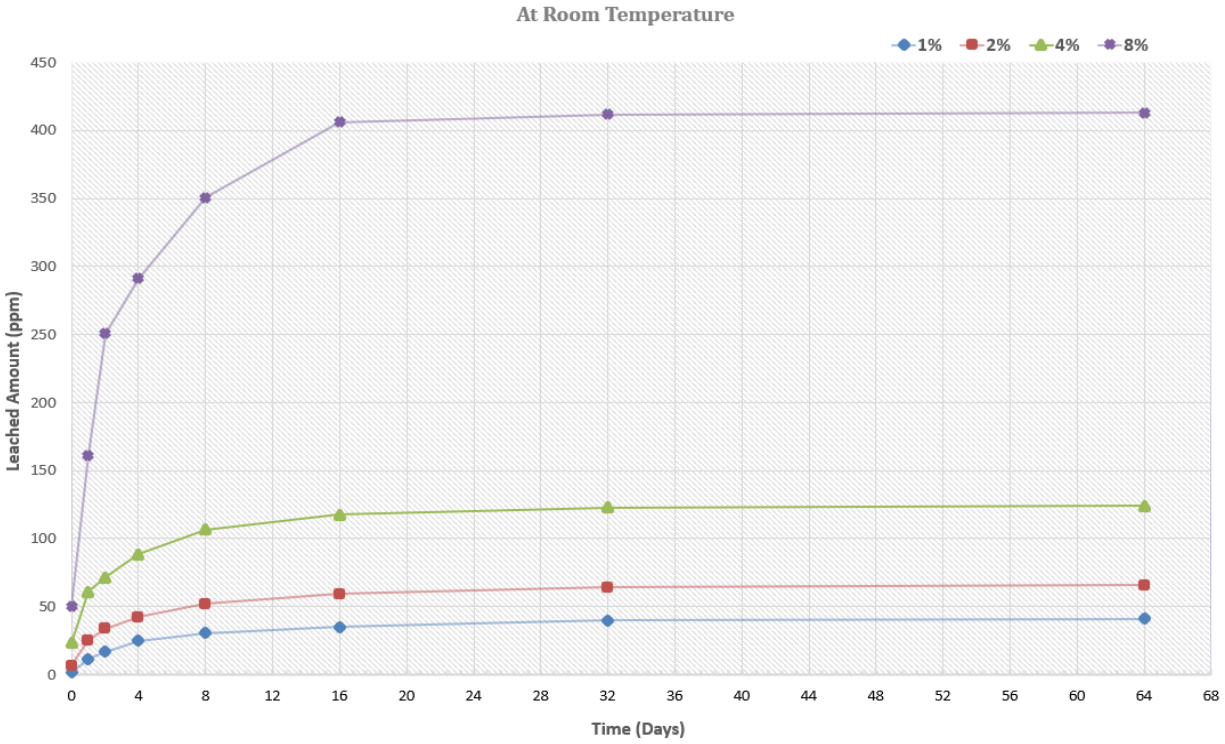

Figure 21. Graph shows the leaching behavior of Df of Mix 2, 3, 4 and 5 at room Temperature

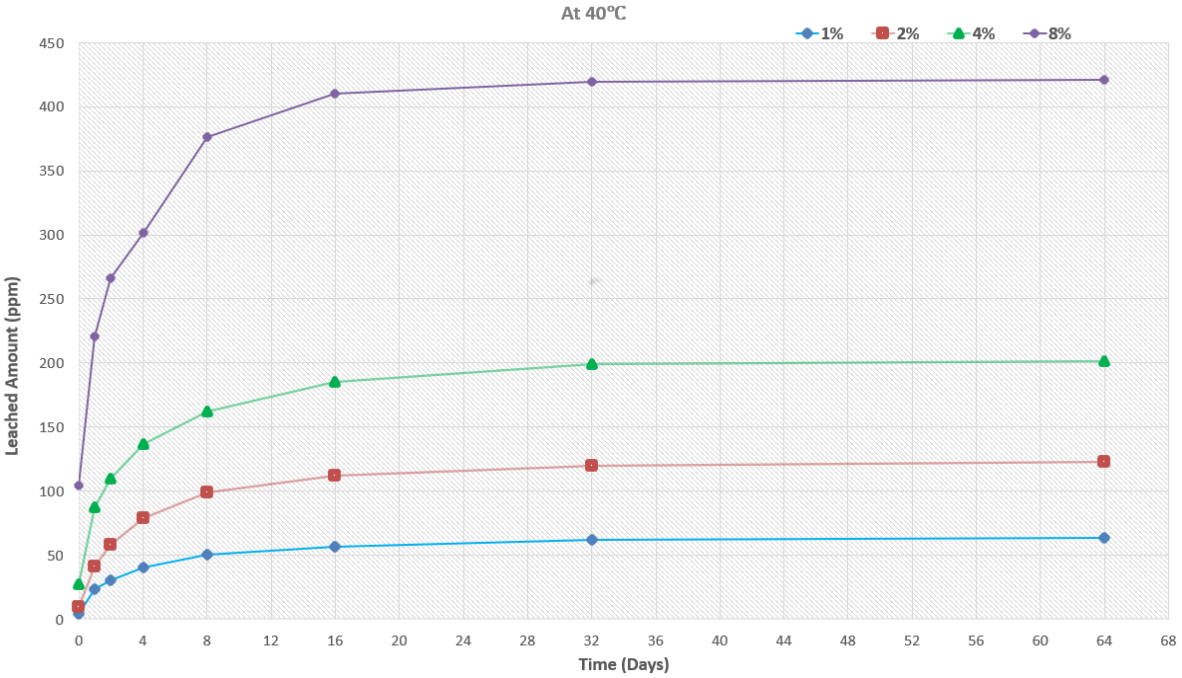

Figure 22.Graph shows the leaching behavior of Df of Mix 2, 3, 4 and 5 at 40 ℃.

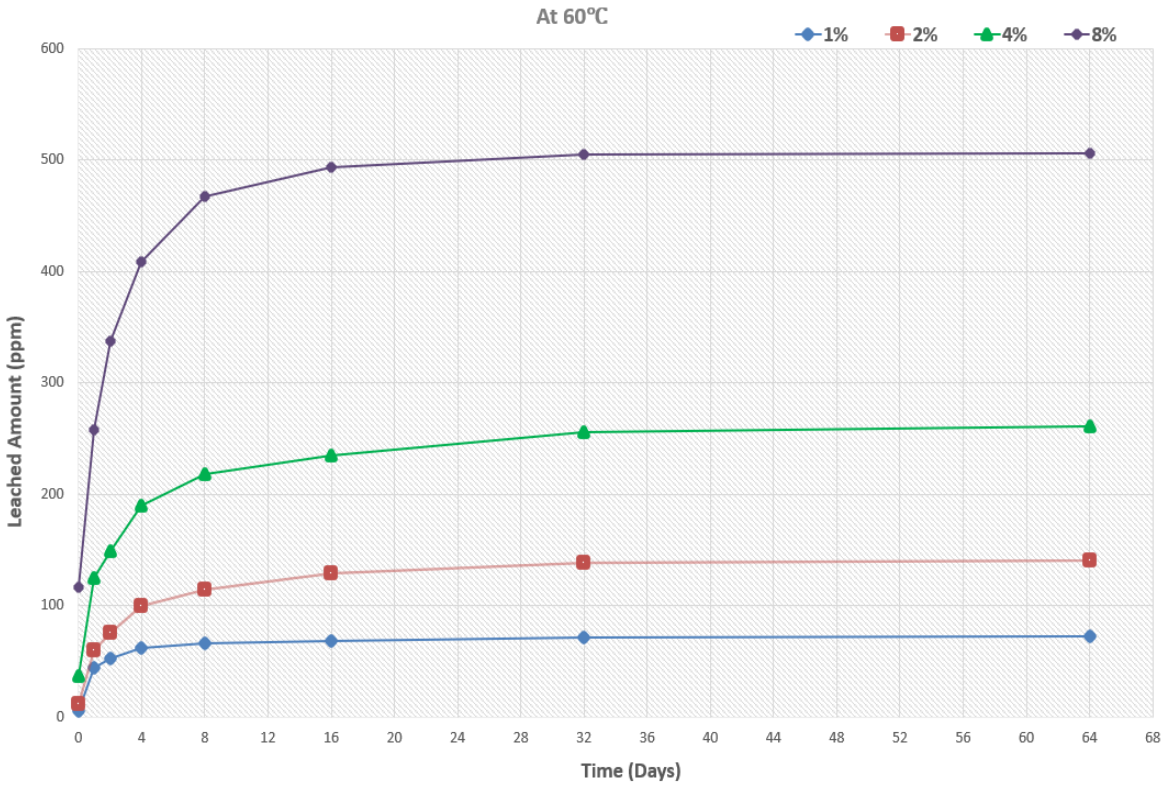

Figure 23.Graph shows the leaching behavior of Df of Mix 2, 3, 4 and 5 at 60 ℃.

CHAPTER 4

CONCLUSION AND RECOMMENDATION

4.1. Introduction

In this Chapter, the conclusions and recommendations that resulted from this research are presented. The work presented in this thesis aimed at assessing the ability of concrete in immobilizing the active pharmaceutical ingredient (API's) by doing Tank leaching test (TNT) in water at various temperatures 20,40 and 60°C and compare it with the literature set limits. In addition, it studied the influence of Df as partial replacement of cement on the mechanical properties of the concrete. The objective was to find a suitable route for the disposal of pharmaceutical wastes by integration these wastes with concrete.

4.2 Summary of the results

Here I am trying to find a correlation between the influence of Df as partial replacement of cement on the mechanical properties of concrete and the ability of concrete at decreasing the leachability of this API.

Mix 2: 1% of DF			
Time (Days)	**Room**	**40**	**60**
0	**1.3132**	**3.861**	**4.980**
1	**11.631**	**23.191**	**43.681**
2	**16.943**	**30.213**	**52.765**
4	**24.773**	**40.251**	**62.239**
8	**30.541**	**50.096**	**66.313**
16	**34.980**	**56.610**	**68.465**
32	**39.66**	**62.133**	**70.956**
64	**40.95**	**63.359**	**71.835**

Mix 3: 2% of DF			
Time (Days)	**Room**	**40**	**60**
0	**6.780**	**9.2725**	**11.043**
1	**25.42**	**40.934**	**59.414**
2	**33.91**	**57.898**	**75.432**
4	**42.134**	**79.189**	**99.623**
8	**52.083**	**98.698**	**114.230**
16	**59.192**	**111.935**	**128.497**
32	**64.081**	**119.810**	**138.635**
64	**65.657**	**122.779**	**140.104**

Mix4: 4% of Df			
Time (Days)	Room	40	60
0	23.078	27.521	37.082
1	61.015	87.320	124.143
2	71.533	109.489	148.379
4	88.571	136.954	189.710
8	106.469	161.738	218.278
16	117.407	184.881	234.940
32	122.8	199.307	255.630
64	123.881	201.434	261.307

Mix 5: 8% of DF			
Time (Days)	Room	40	60
0	50.0301	103.976	116.245
1	161.203	220.717	257.903
2	250.652	265.943	337.437
4	290.952	321.845	408.686
8	340.462	376.163	467.173
16	386.278	410.378	492.935
32	399.356	419.489	504.404
64	401.628	421.069	506.318

Table 7. Tables show the amount of Df leached from each mixture at different temperatures.

Mix number	Percentage of DF	Time (Days)	Average Compressive Strength (Mpa)
Mix 1	0	7	14.28
		28	20.78
Mix 2	1	7	12.55
		28	17.39
Mix 3	2	7	12.92
		28	17.47
Mix 4	4	7	12.91
		28	17.25
Mix 5	8	7	8.62
		28	12.64

Table 8. Average compressive strength of each mixture after 7 and 28 days.

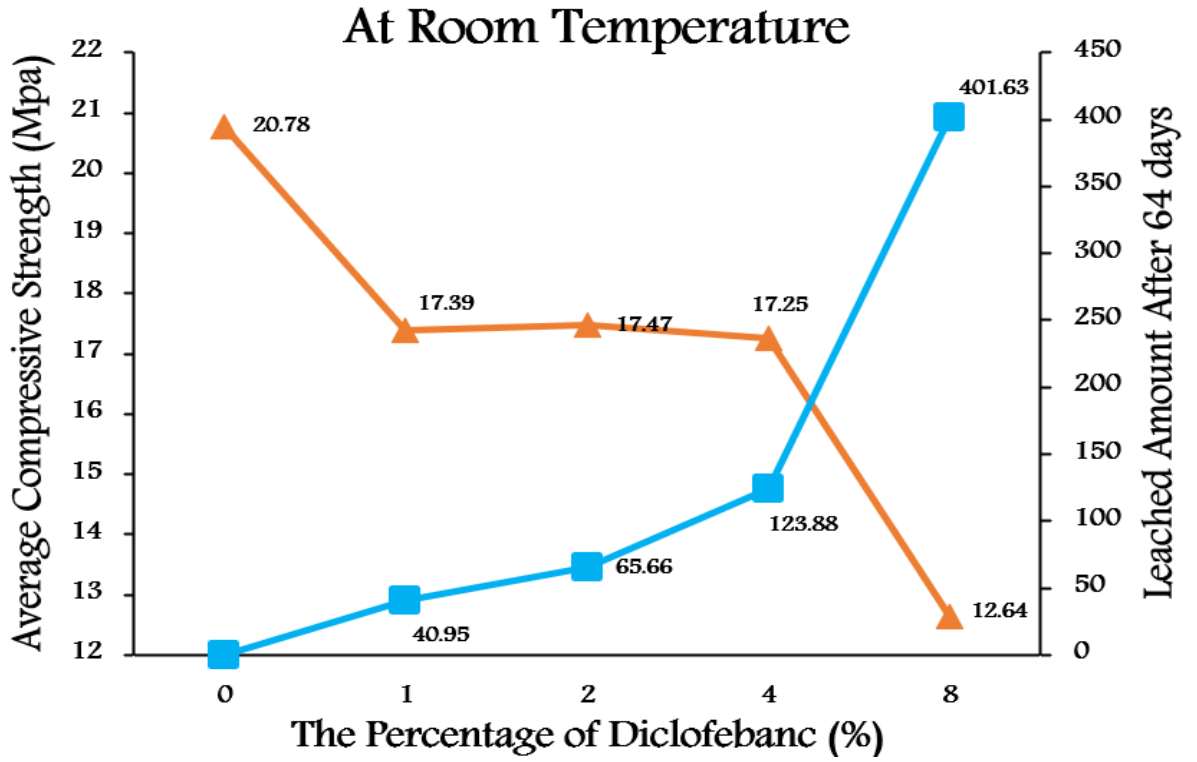

Figure 24.Graph showing the variation of compressive strengths and leached amount of Df as a function of the percentage of Df existing in each mixture at room temperature.

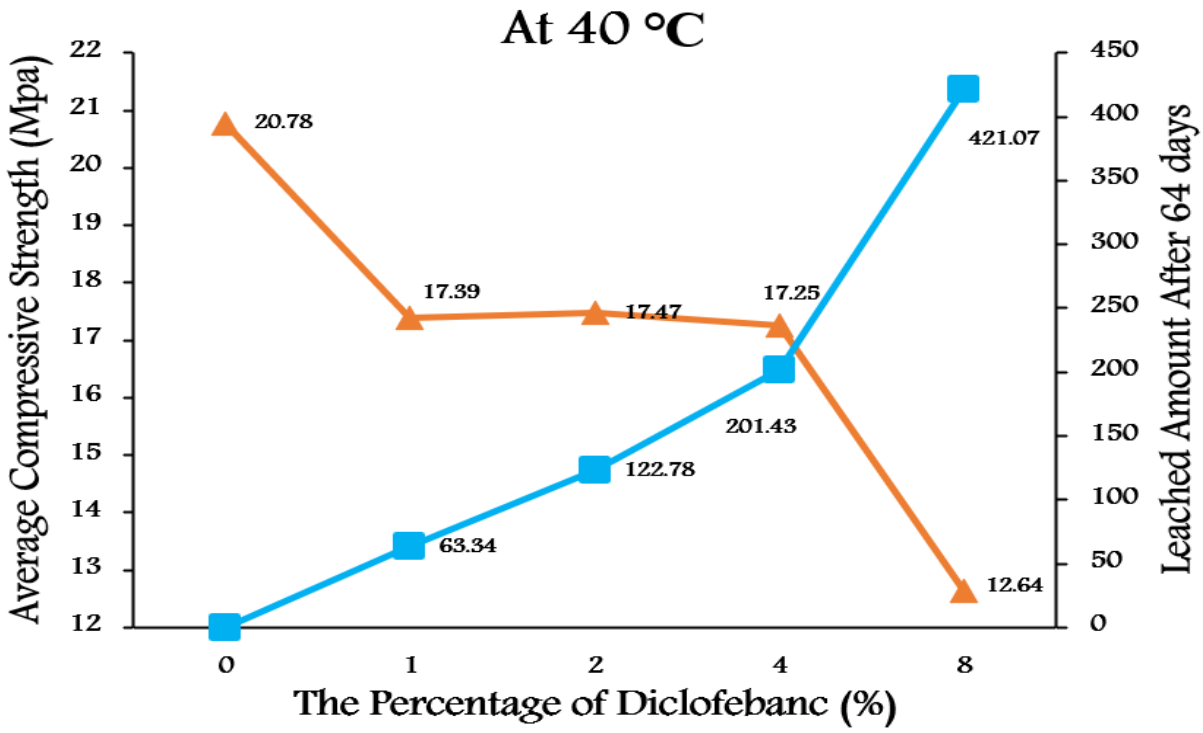

Figure 25. Graph showing the variation of compressive strengths and leached amount of Df as a function of the percentage of Df existing in each mixture at 40 °C.

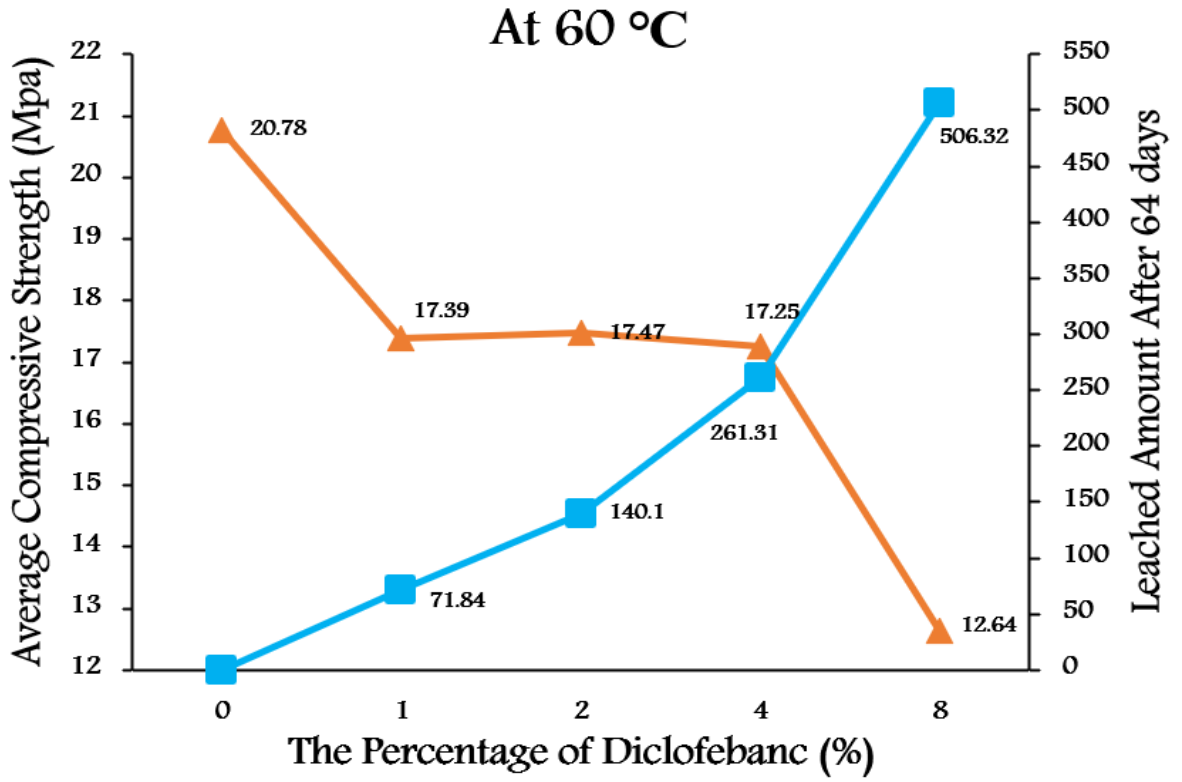

Figure 26. Graph showing the variation of compressive strengths and leached amount of Df as a function of the percentage of Df existing in each mixture at 60 °C.

4.3 Summary of the findings

The following conclusions are drawn from the test results and analysis presented in this paper:

i. The compressive strengths of mixtures 2, 3and 4 are decreased by 16% while that of mixture 5 decreased by 40% from the control mixture (0% Df), which shows that Diclofenac could be used as partial replacement of Portland cement up to 4% in composite cement while incurring a loss about 16% of its strength.

ii. Presence of Diclofenac as a partial replacement of cement in the concrete mixture causes the degradation of mechanical properties of based concretes (f'c decreased by 16%)

iii. The leached amounts of Diclofenac are mostly produced at the early age of 32 days, and subsequently decrease sharply to be undetected between 32 to 64 days.

iv. The higher the percentage of Diclofenac in the mixture, the higher the amount leached of Df in water, also as the temperature increased the leached amount of Df increased in the beaker.

4.4 Comparison with other literature reviews

- Talah et al showed in their experiment that the compressive strength of High-Performance Concrete (HPC) increased from 49 to 65 Mpa after they partially replaced cement (10%) by ash produced from incinerated hospital wastes [27]. On the other hand, in my experiment the results showed that the compressive strength decreased when the cement was partially replaced by Df where the compressive strength dropped from 20.8 to 17.48 Mpa. This difference between the two results is due to the composition of the concrete mixture; HPC needs more fine materials than that of Normal Concrete (NC) which means more cement that may help in gaining strength, also more fine particles mean less porosity and more durability which may rise the strength of the specimen.

- Saad et al proved in their study that the eco-board composed of recycled polyethylene / polypropylene reclaimed from municipal solid wastes was effective at immobilizing DF and reducing its leachability [15].The maximum leachable amount was 4% under accelerated conditions of 70°C, and less than 0.3% following 39 days at 20°C (21ppm at 70°C and less than 2ppm at 20°C). On the contrary, in my experiment the optimal percentage of Df that should be added to the concrete mixture as a partial replacement of cement is 2% which

gave the highest compressive strength comparing to other mixes; the leaching test done showed that it leached 65ppm at room temperature, 122 ppm at 40°C and 140 ppm at 60°C, while that of mix 2 which contains only 1% of Df is only 41 ppm at room temperature, 63 ppm at 40°C and 71 at 60°C. We know that plastic has less porosity than concrete, this means that Df has higher tendency to be leached from concrete than that from plastic. In addition, the concrete used in this experiment has a middle compressive strength which means it has a lot of porosity especially the amount of course aggregates are higher than that of fine aggregates (sand & cement), this means that the specimens contain a lot of voids that Df can seep through which leads to huge amount of leached Df.

4.5 Future work

This section includes the future work that can be done on the integration between pharmaceutical wastes and concrete. As this thesis is divided to chemical and structural analysis.

i. A study can be conducted on the influence of pharmaceutical wastes as partial replacement of cement on the mechanical properties and durability of the concrete. In this Part, I recommend to increase the compressive strength of the concrete in order to investigate the effects of these wastes as the percentage of fine particles increases in the mixture.

ii. Applying the leaching test in order to investigate the ability of concrete at immobilizing the leaching of these waste in water. Also, I recommend to use

High-Performance concrete which has a low porosity compared to that used in my experiment, this means it will have less voids which will decrease the leached amount of Diclofenac.

iii. The leaching test done over 64 days: In order to investigate the ability of concrete in preventing the leach-ability of Df with time, I recommend to extend the life time of the experiment to 128 days or more in order to find out if Df still succeeds in the seepage from concrete even at very low quantity.

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