PROGRAMA DE DOCTORADO EN TECNOLOGÍA Y MODELIZACIÓN EN INGENIERÍA CIVIL, MINERA Y AMBIENTAL

TESIS DOCTORAL

DISEÑO Y OPTIMIZACIÓN DE LOS HUMEDALES ARTIFICIALES PARA EL TRATAMIENTO DE AGUAS RESIDUALES: PURINES DE CERDOS

Presentada por Oumaima El bied para optar al grado de Doctora por la Universidad Politécnica de Cartagena

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PhD THESIS

DESIGN AND OPTIMIZATION OF THE CONSTRUCTED WETLANDS FOR WASTEWATER TREATMENT: PIG SLURRY

Presented to the Technical University of Cartagena in fulfilment of the thesis requirement for the award of

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Acknowledgment

To my **father,**

To my **mother,**

My beloved sisters **Salma** and **Khaoula**,

To my **husband,**

To all the people I hold in my heart, thank you for your help and support.

I am grateful to my family for always being there for me.

Consejería de Agua, Agricultura y Medio Ambiente

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This thesis has originated the following scientific productions:

El bied, Oumaima, Amalia García-Valero, Taoufiq Fechtali, Ángel Faz, and José A. Acosta, 'Purification Performance of Filtration Process for Pig Slurry Using Marine Sands, Silty Loam Soils, Fly Ash and Zeolite', *Agronomy*, 11.8 (2021), 1608 https://doi.org/10.3390/agronomy11081608.

Oumaima El bied , Mathieu Kessler , Martire Angélica Terrero , Taoufiq Fechtali , Angel Faz , Jose A. Acosta . Turbidity and chemical oxygen demand reduction from pig slurry through coagulation flocculation process : under review.

Abstract

The last few years, pig farming have seen a great transformation, which is now considered as an agro-industry made up of some major players on the world scale. In several regions within the world, the management of pig manure has become a real environmental problem which needs a solution from the agricultural sector. Many environmental problems concern such as impacts on surface and groundwater, effects on air and soil quality are notably increasing.

Most of the environmental problems of the pig production sector is the pig slurry (PS) production and it´s management. Only Spain generates a volume of pig slurry around 71 million m3 per year (2018) and it's the first country in Europe with a high number of pig production, this large volume of production needs an adequate treatment and management to minimize the environmental problems. Most common problematics of the pig slurry are:

- Excess of N and salts which are transferred to soils and superficial and groundwater when slurry is used as soil amendment. This affects soils and water quality and contributes to water eutrophication and salinization processes.

- Lack of control of pollutants in the slurry which is applied to the soil, with transfer of metals (mainly Cu and Zn) to the soil and water, with negative effect on environmental health.

- Emissions of ammonia and greenhouse gases (GHG), contributing to climate change. Livestock are responsible for 37% of anthropogenic CH_4 and 65% of anthropogenic N_2O.

-Generation of smells which is the main barriers for the community acceptance of pig farms.

Recently the pig slurry concept is changing, and it is not considered as a waste, nevertheless a by-product that can be used as a natural fertilizer that contain the main nutrients a plant needs to thrive. It´s a source of nutrients that can be valorized in agronomic sector as a valuable economic resource.

To reuse this by product, PS should be treated and disposed properly in order to reduce negative impacts caused by agricultural valorization. The importance of the proper management of PS as a by-product is well reflected in the recent Best Available Techniques (BAT). However, most of the existing state-of-the-art solutions are not technologically and economically viable.

A proper management such as constructed wetlands present a very efficient and economical solution for the pig slurry management, furthermore, an eco-friendly technology that can generate a by-product promoting circular economy, It can remove a high amount of pollutants from the pig slurry and can greatly reduce the environmental impact of the PS and produce useful resources for agriculture, nevertheless, this treatment process has some inconvenient that can limit its use such as clogging and low efficiency in reducing salts content and heavy metals.

The integrated purification system using the constructed wetlands for the pig slurry treatment allows establishing a convergence point for livestock and agricultural farms unlinked by inorganics fertilizers influencing in the sustainability of these sectors.

The aim of this thesis consists of designing and optimization of the constructed wetland treatment process in order to increase its efficiency by proposing an effective pre-treatment by coagulation flocculation, and also to find a new layer that can be added to the constructed

wetland (CW) to improve its efficiency and to study how the slurry reacts to these natural materials.

White and Iberian pigs farm from the southeast of Spain treat their slurry in situ using separation, double filtration, decantation, and constructed wetland treatment. The pretreatment can´t achieve to reduce solids which provokes clogging in the constructed wetlands (CWs). The main objective of this pretreatment is to reduce the turbidity and chemical oxygen demand (COD) from the effluent to make it appropriate for CW treatment. Optimization of the coagulation-flocculation (CF) process using iron chloride and a cationic flocculent DKFLOCC-1598 was investigated by central composite design method (CCD). The effect of coagulant concentration, pH, and flocculent on the COD and turbidity removal were evaluated. The best results were found using 0.024 mol L^{-1} of iron chloride, 0.164 ml L^{-1} of flocculent at pH=7.5, where COD was reduced by 96% and the turbidity removal by 97%. Therefore, the results indicated the high efficiency of the treatment method in removing the COD and suspended solids.

This thesis examined the physicochemical properties of micronutrients, macronutrients, and heavy metals (HM) removed after the slow filtration of pig slurry (PS) through multiple media: sands, silt loam soils, fly ash and zeolite. The objective was to find a new layer that can be added to our constructed wetland (CW) to improve its efficiency and to study how the slurry reacts to these natural materials. The filtration achieved an approximate removal rate of 99.99% for total suspended solids (TSS) and nitrogen and 61, 94, 72, and 97%, respectively, for electrical conductivity (EC), turbidity, chemical oxygen demand (COD) and five-day biological oxygen demand (BOD5). The two sands, soil 1, and zeolite, had a macronutrient reduction median of 60%, whereas soil 2, 3, 4 and fly ash released macronutrients such as Na, Ca, and Mg. All the media achieved nearly 99.99% micronutrient removal for Fe and Zn. The Cu removal rate was over 86% except for sand 1 and 2 and soil 1, which reduced it to only 46%; the overall Mn removal rate was more than 80% except for soil 3 and soil 4, where it was only 9%. Zeolite had a 99.99% removal capacity for HM as opposed to sand 2, soil 4 and fly ash, which released some HMs (Ni, Cu). The use of this inexpensive and abundant media filtration process is sound both technically and financially and seems to be an ideal cost-efficient treatment for pig slurry.

Both experiment pilot, coagulation flocculation and filtration using other materials proved to be suitable to improve the CW efficiency. With coagulation flocculation pretreatment, more than 90% of total suspended solids (TSS) could be removed which can absolutely minimize the clogging risk of the CWs also increase its lifespan. Zeolite can be perfectly added to the constructed wetland to improve the heavy metals and salts contents absorbance, nevertheless, the nitrogen and phosphorus will also decrease which make the treated effluent not suitable to use as an organic fertilizer, in order to implement a circular economy approach and to minimize environmental impacts associated to pig slurry.

Resumen

En los últimos años la cría de cerdos ha experimentado una gran transformación, que ahora se considera una agroindustria compuesta por algunos de los principales actores a nivel mundial. En varias regiones del mundo, la gestión del estiércol de cerdo se ha convertido en un problema medioambiental real que necesita una solución del sector agrícola. Muchos de los problemas ambientales que preocupan son los impactos en las aguas superficiales y subterráneas, los efectos en la calidad del aire y el suelo están aumentando notablemente.

La mayor parte de los problemas ambientales del sector porcino es la producción de purines (PS) y su gestión. Solo España genera un volumen de purines de alrededor de 71 millones de m^3/año (MAPAMA, 2018) y es el primer país de Europa con un elevado número de producción porcina, este gran volumen de producción necesita un tratamiento y gestión adecuados para minimizar los problemas ambientales. Las características del purín de cerdo son:

- Exceso de N y sales que se transfieren a suelos y aguas superficiales y subterráneas cuando se utilizan purines como enmienda del suelo. Esto afecta los suelos y la calidad del agua y contribuye a los procesos de eutrofización y salinización del agua.

- Falta de control de contaminantes en el purín que se aplica al suelo, con transferencia de metales (principalmente Cu y Zn) al suelo y al agua, con efecto negativo en la salud ambiental.

- Emisiones de amoniaco y gases de efecto invernadero (GEI), que contribuyen al cambio climático. El ganado es responsable del 37% del CH_4 antropogénico y del 65% del N_2O antropogénico.

-Generación de olores que son las principales barreras para la aceptación comunitaria de las granjas porcinas.

Recientemente, el concepto de purines de cerdo está cambiando y no se considera un residuo, sino un subproducto que puede usarse como fertilizante natural que contiene los principales nutrientes que una planta necesita para prosperar. Es una fuente de nutrientes que se puede valorizar en el sector agronómico como un valioso recurso económico.

Para reutilizar este subproducto, el PS debe tratarse y disponerse adecuadamente para reducir los impactos negativos causados por la valorización agrícola. La importancia del manejo adecuado del PS como subproducto se refleja bien en las recientes Mejores Técnicas Disponibles (BAT). Sin embargo, la mayoría de las soluciones de vanguardia existentes no son tecnológica ni económicamente viables.

Un manejo adecuado como los humedales artificiales presentan una solución muy eficiente y económica para el manejo del purín porcino, además, una tecnología ecológica que puede generar un subproducto que promueve la economía circular, puede eliminar una gran cantidad de contaminantes del purín porcino y puede reducir en gran medida el impacto ambiental del PS y producir recursos útiles para la agricultura, sin embargo, este proceso de tratamiento tiene algunos inconvenientes que pueden limitar su uso tales como obstrucción y baja eficiencia en la reducción del contenido de sales y metales pesados.

El sistema de depuración integrado utilizando los humedales artificiales para el tratamiento de purines porcinos permite establecer un punto de convergencia para las explotaciones ganaderas y agrícolas desvinculadas por los fertilizantes inorgánicos que influyen en la sostenibilidad de estos sectores.

El objetivo de esta tesis consiste en diseñar y optimizar el proceso de tratamiento del humedal construido con el fin de incrementar su eficiencia proponiendo un pretratamiento efectivo por coagulación-floculación, y también encontrar una nueva capa de sustrato que se pueda agregar al humedal construido (CWs) para mejorar su eficiencia y estudiar cómo reacciona el purín a estos materiales naturales.

Las explotaciones de cerdos blancos e ibéricos del sureste de España tratan sus purines *in situ* mediante separación, doble filtración, decantación y tratamiento de humedales artificiales. Este pretratamiento no logró reducir los sólidos lo que provoca atascos en los humedales artificiales (AAC). El objetivo principal de este pretratamiento es reducir la turbidez y la demanda química de oxígeno (DQO) del efluente para hacerlo apropiado para el tratamiento de CW. La optimización del proceso de coagulación-floculación (CF) utilizando cloruro de hierro y un floculante catiónico DKFLOCC-1598 se investigó mediante el método de diseño compuesto central (CCD). Se evaluó el efecto de la concentración de coagulante, el pH y el floculante sobre la DQO y la eliminación de la turbidez. Los mejores resultados se obtuvieron utilizando 0.024 mol L^{-1} de cloruro de hierro, 0.164 ml L^{-1} de floculante a pH=7.5, donde la DQO se redujo en un 96% y la remoción de turbidez en un 97%. Por tanto, los resultados indicaron la alta eficiencia del método de tratamiento para eliminar la DQO y los sólidos en suspensión.

Esta tesis examinó las propiedades fisicoquímicas de micronutrientes, macronutrientes y metales pesados (HM) extraídos después de la filtración lenta del PS a través de múltiples medios: arena, suelos franco-limosos, cenizas volantes y zeolita. El objetivo ha sido encontrar una nueva capa que se pudiera agregar a nuestro humedal artificial (CW) para mejorar su eficiencia y estudiar cómo reacciona el purín a estos materiales naturales. La filtración logró una tasa de eliminación aproximada del 99,99% para el total de sólidos suspendidos (SST) y nitrógeno de 61, 94, 72 y 97%, en la arena, suelos franco-limosos, cenizas volantes y zeolita, respectivamente.

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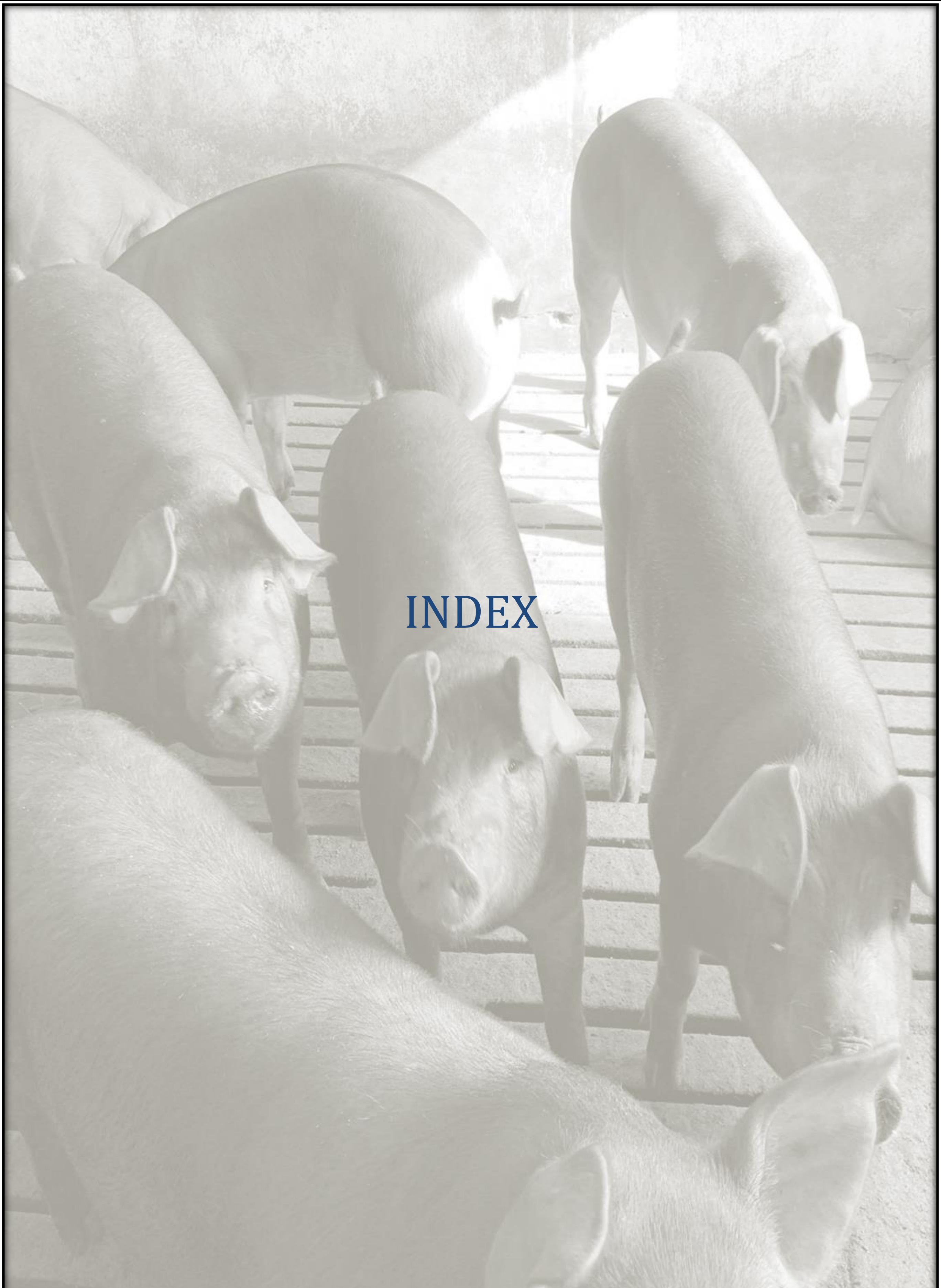
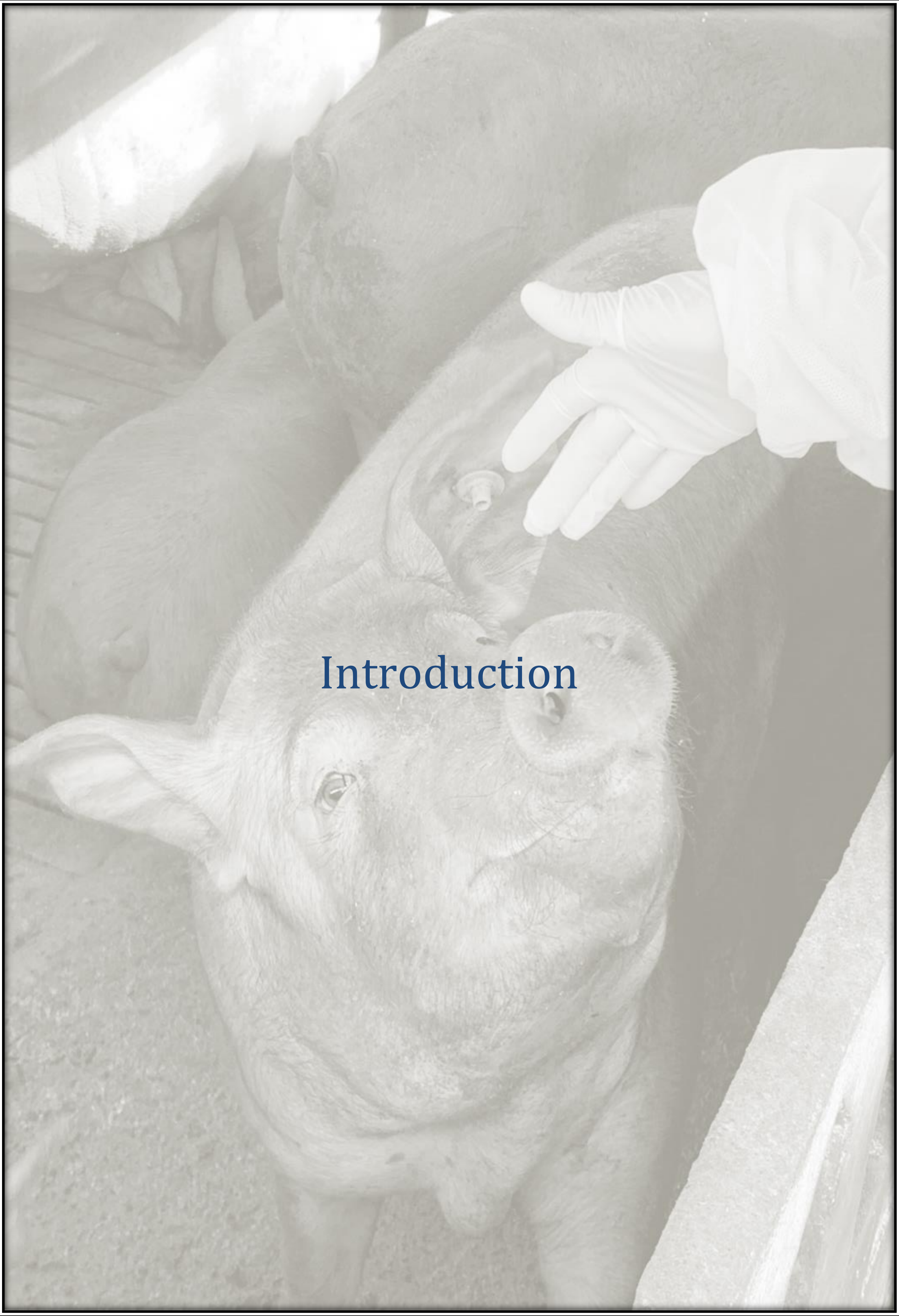


- PS: Pig slurry
- CF: Coagulation Flocculation
- CE: Electrical conductivity
- BOD_5: Biological oxygen demand in 5 days
- COD: Chemical oxygen demand
- NK: Total Kjeldahl Nitrogen
- NO: Organic Nitrogen
- NT: Total Nitrogen
- pH: Potential hydrogen
- PT: Total phosphor
- TSS: total suspended solids
- T: Temperature
- CWs: Constructed wetlands
- HM: Heavy metals
- BAT Best Available Techniques
- GHG: Greenhouse gases



Introduction

I. Introduction

Pork is the most consumed meat in the world (Lowe & Gereffi, 2008) , all regions of the world have pig productions, except a few places where, for religious reasons, pork consumption is not encouraged (Alvarez-Kalverkamp et al., 2014). The consumption of animal products and their production has experienced exponential growth around the world over the past few years and this trend should increase over the next three decades (Lassaletta et al., 2019).

Globally, the European union is the second largest producer of pork meat, after China. Individually, Spain is the fourth producer (after China, USA, and Germany), while, at European level, Spain is the second producer with 17.5% of the tons produced (data 2016, Source: SG Statistics), behind Germany, and is the first EU country in census, with more than 19% of the community census (data 2016, Source: SG Statistics).

The Spanish pig production sector has an importance in the country´s economy while it represents 12.7% of the Final Agricultural production. Among the animal production which represents around 38% of the final agricultural production, the pig sector occupies the first place in terms of its economic importance reaching 36.4% of the final animal production.

Pig slurry originate from the farming sector contains a high soluble organic matter and macro elements (mainly N) and micronutrients (Bernal et al., 1991) which make it useful as a soil fertilizer, however it´s high electrical conductivity and NH_4^+ levels can limit its application (Moral et al., 2008),also the N,P and K contents should be taking in account, it may contain other compounds like phenols (Loureiro et al., 2006) ammonia (Tiquia, Tam, & Hodgkiss, 1996), nitrite and *surfactants* (Warren-Hicks, 1992), present in any sewage with high organic matter content (Wågman et al., 1999) .

The pig's production sector accounts 15% of ammonia emissions from in the agricultural sector in Europe, accounting for 83% of global emissions; the sector is confronted with neighborhood conflicts and olfactory nuisances (Degré, Verhève, & Debouche, 2001) both Ammonia and Methane are largely emitted during the storage of slurry and also during composting the solid fraction of the slurry, while the ammonia is the most important supporter to acidification and eutrophication, although the methane improves climate change. Moreover the pig´s slurry is the responsible of various gaseous emissions (NH_3, N_2O and CH_4) (Degré et al., 2001), while the CH_4 and N_2O are forceful greenhouse gases (Kroeze, 1994, Houghton et al., 2001) and the NH_3 is the bound to acidification of rain and of the environment and for the formation of aerosols (ApSimon et al., 1987, Fangmeier et al., 1994), it also contributes indirectly to N_2O emission by soils (IPCC, 2006).

Natural wetlands generally improve the quality of the water that passes through them, acting as natural filters for the ecosystem. In comparison, most constructed wetlands are used to treat water contaminated by different sources, in a way that they have the purpose of eliminating bacteria, viruses, SS, STS, BOD, nitrogen (mainly ammonium and nitrate), metals …

Each water treatment technology has advantages and disadvantages. The constructed wetlands are undoubtedly a very interesting option. For this reason, they are currently being implemented in various country to purify different type of waste waters with a minimum cost.

Advantage

- Zero energy consumption, because the purification process is carried out by filtration materials and plants.
- Excellent environmental integration, because it replaces buildings and machines with a macrophyte plantation.
- Reduction of odors. It emphasizes that in subsurface flow wetlands the water is not in contact with the atmosphere and drastically reduces the generation of odors.
- Easy operation: Suspended solids are reduced by the lack of mechanical equipment, and the operation is less complicated, less dangerous, and requires fewer means to keep it at its optimum.
- Simpler and easier to follow maintenance schedule.

Disadvantages

- It takes longer to achieve the optimal operating regime. Since it is based on a natural system, it requires the plants to acquire a degree of maturity.
- Insufficient maintenance in subsurface flow wetlands leads to substrate clogging problems.
- It requires a larger surface than conventional purification systems.
- It requires great knowledge in the design, because afterwards it has few possibilities of regulation in the operation of the treatment plant.
- Plants can be food for certain animals, so it must be controlled that they do not access the interior of the plot.
- It´s enable to reduce salts contains.

This thesis will propose two solutions for two different problematics that the CWs which are:

- Clogging: By proposing an adequate pretreatment.
- Reducing salts contents: by adding a new layer to the other materials of the CWs.

1. Pig production

1.1 Word pig production

Global population growth means increment in food production, due to this, the consumption of animal products and their production has experienced exponential growth around the world over the past few years and this trend should increase over the next three decades.

In recent years, the pig sector has grown notably, both in production, in censuses and in the number of farms, thanks to the push from foreign markets supported, in turn, by the competitiveness of the sector in the world market.

In April 2021, China has the biggest number of pigs of any country with 406 million heads. In the same year, the EU and US were in the second and third positions in the list, with over 150 and 77 million heads, respectively *(Shahbandeh, 2021)*.

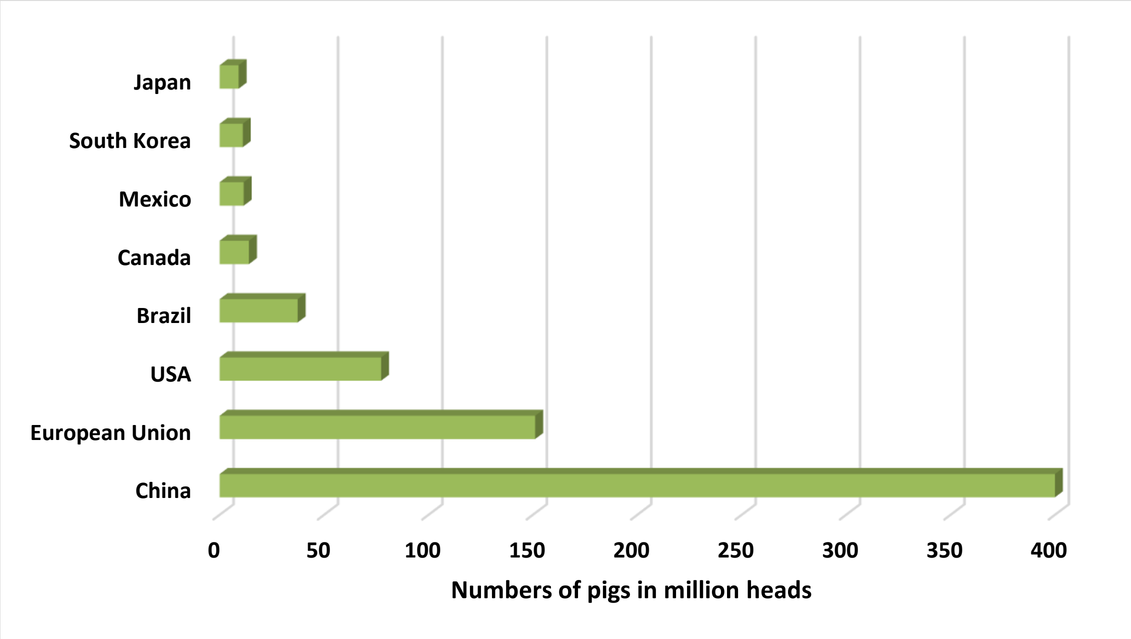


Figure 1. Number of pigs worldwide by country (April 2021).
Source: Statista 2021, Published by M. Shahbandeh, April 20, 2021.

1.2 Production in Europe

Pigs represent the largest livestock category in the EU as shown in *(Figure 2)*, before bovines. The EU countries with the highest EU livestock is Spain accounted for 22% of the EU's pigs, then Germany accounted for 18% of the EU's pigs, and France accounted for 9% of the EU's pigs *(EUROSTAT, 2021)*.

Overall, the European union is the second largest producer of pork, after China as shown in *(Figure 2)*. Spain is the third producing power (after China, the US) while, at a European level, its classified as the first producer regarding to *(EUROSTAT, 2021)* annual data of pig population 2021.

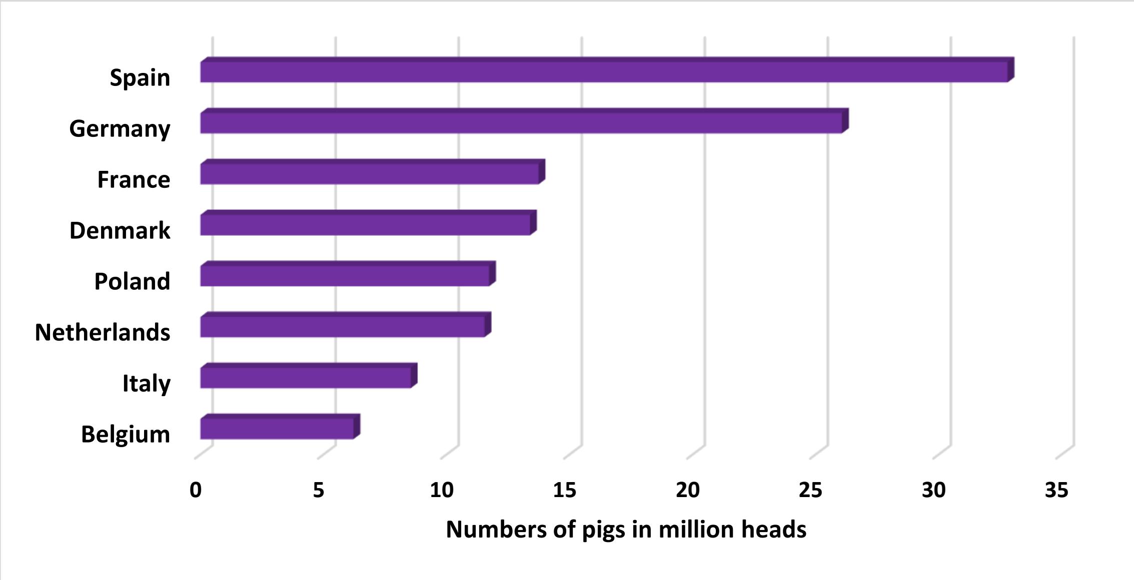


Figure 2. Number of pigs in EU 2020, by country.
Source: Eurostat, Pig population, annual data (2021).

1.3 Production in Spain and autonomous communities

The Spanish pig sector is of key importance in the economy of Spain since it accounts for around 14% of the final agricultural production. Within livestock productions, the pig sector ranks first in terms of its economic importance, reaching about 39% of Final Livestock Production.

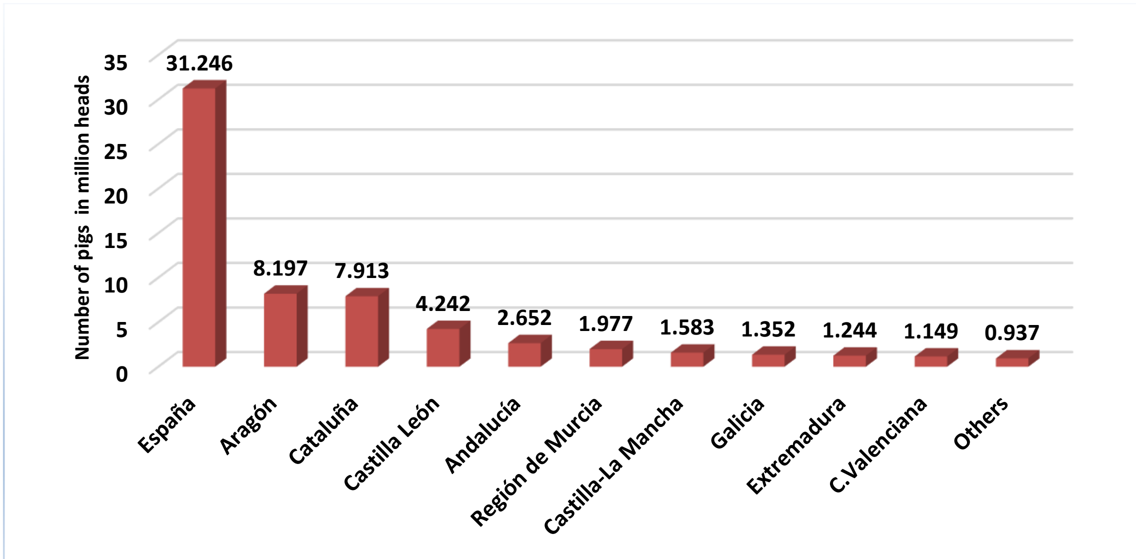


Figure 3. Number of pigs by autonomous community 2019
Source: SG Análisis, Coordinación y Estadística (MAPA). Elaboración: SG Producciones Ganaderas y Cinegéticas MAPA.

In the report issued by MAPAMA (2019) (Ministry of Agriculture and Fisheries, Food and Environment) it was reported the total pig production was concentrated in 6 regions (, Aragon, Catalonia, Castilla y León, Andalusia, Region of Murcia and Castilla La Mancha). The Region of Murcia, as one of the most important livestock regions in the national census, is in fifth place as an autonomous community, contributing 1977 million heads which presents 6,32% of the total number of heads of the Spanish territory.

Taking into consideration the recommendations of RD 324/2000 of March 3 and its Annex I, an approximate volume of 18 856.04 kg of susceptible nitrogen generated should be managed.

1.4 Production in Murcia region

Murcia is the second region has a very high pig production, it has 5,000 cattle farms, 1,500 of which are pig farms, with 2.2 million head of pigs in 2020, compared to almost 1.5 million inhabitants.

The Region of Murcia has produced 384,000 tons of meat in the last year, 12 percent more than the previous year and 28 percent in the last four years according to *(CARM, 2021).*

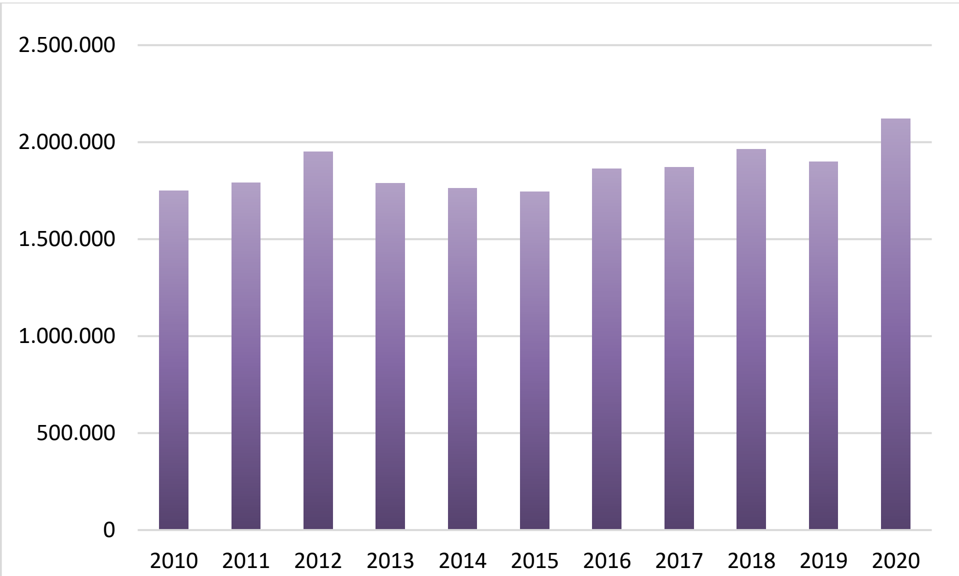


Figure 4. Evolution of the number of pig heads in Murcia region.
Source: Centro regional de estadística de Murcia 29/04/2021.

2. Pig slurry and environment

The environment is still a major issue for pig production, therefore, it´s very interesting to us to control the recent developments in this issue. The development of pig production quickly derives the appearance of environmental problems, resulting from the high numbers of farms and the leak of the waste management.

Pig slurry originate from the farming sector contains a high soluble organic matter and macro (mainly N) and micronutrients *(M.P.Bernal, 1991)* which make it useful as a soil fertilizer. However, its high electrical conductivity and NH4+ levels limit its application *(Moral et al., 2008)*, also the N, P and K contents should be taking in account. In addition, it may contain other compounds like phenols *(Loureiro et al., 2006)*, ammonia *(Tiquia et al., 1996)*, nitrite and surfactants *(Warren-Hicks, 1992)*, present in any sewage with high organic matter content, and Polychlorinated Biphenyls (PCBs), which also appear in a great number of effluents *(Wågman et al., 1999)* .

The pig's production sector accounts 15% of ammonia emissions from the agricultural sector in Europe, accounting for 83% of global emissions. The sector is confronted with neighborhood conflicts and olfactory nuisances *(Degré et al., 2001)*. Ammonia, nitrogen dioxide and methane (NH_3, N_2O and CH_4) are forceful greenhouse gases *(Degré et al., 2001; J.T. Houghton, 2001)*. They are largely emitted during the storage of slurry and during composting the solid fraction of the slurry, the ammonia is the most important supporter to acidification and eutrophication, and the methane and nitrogen dioxide contributes to climate change *(Dennehy et al., 2017).*

Particularly, some treatments applied to effluents can control or on the contrary promote gaseous emissions of CH_4, ammonia (NH_3), nitrous oxide (N_2O) or dinitrogen (N_2) (Nascimento, Andrade, & Fonseca, 2015) .Some measures can be easy, economic and help to reduce the amount of greenhouse gases emission, for example adequate storage *(Dennehy et al., 2017)*, as well as the reduction of proteins in the feed source of pigs can also collaborate in optimizing the natural resources used in the pig production cycle *(FAO, 2020)*.

Using pig manure as an organic fertilizer can be also considered as an easy and simple management. It allows the reduction of synthetic fertilizers and it has a positive effects on agricultural soil *(Antoneli et al., 2019),* unless, the excess in using can provoke several environmental issues that it should be taking into consideration.

The current environmental directives, as the waste Directive (91/156/EEC) *(EUR-Lex, 1991)*, consider the need of performing a global environmental evaluation to assure "the protection of the environment and human health" this legislation concerns the protection of waters against pollution produced by nitrates from agricultural sources, which is still in force since 1991. The national legislation has been adjusted to these regulations since then, through the creation of ordinances, laws and recommendations that contribute to the proper management of everything related to the pig farming sector. Thus, the environmental evaluation of pig slurry implies the assessment of its toxicity, knowledge of the fate, behavior and bioavailability of its components and the prediction of potential ways of contamination *(De la Torre et al., 2000).*

Manure is one of the anthropogenic sources of greenhouse gas GHG and ammonia NH_3 emission *(Olivier & Peters, 2020)*. The greater part of GHG and NH_3 emissions in agricultural activities come from livestock waste streams like housing, storage and lands preading of manures; (Amon, Kryvoruchko, Amon, & Zechmeister-Boltenstern, 2006; Kavanagh et al., 2019; Misselbrook, Powell, Broderick, & Grabber, 2005; Webb & Misselbrook, 2004).

For reducing the environmental negative impacts of the pig slurry, at the moment, there is no unique and precise solution. Every livestock farming has a different management and strategy for the pig slurry. One of the most popular is the direct application to the soil as a fertilizer, which can generate a numerous negative effects in the environment, including salinization in semi-arid areas, toxic concentrations of heavy metals, decreased soil aeration, risk of leaching and runoff of nutrients that can pollute ground and surface waters (M. Hjorth, Christensen, Christensen, & Sommer, 2010). These authors also explain that the large amounts of slurry produced could lead to odor and ammonia emissions from farms and storage locations. In case of intensive livestock farming, there is a surpluses of pig manure, and there is not enough surface area to value it in accordance with the code of good agricultural practices in the vicinity of livestock farms, especially in vulnerable areas. Therefore, a greater energy will be used to be able to transport the manure from the places where it is produced to an available land for its application *(Sahlström, 2003)*.

According to regulations in each country, animal farms must have more or less developed in-situ wastewater treatment facilities. The treatment plant uses different methods and technologies, depending on the slurry concentration, volume production, facilities, etc. Those technologies can be physical, biological, chemical or combination of several techniques. The most popular techniques used for the pig slurry is the two phases separation (liquid and solid), the nitrification-denitrification, and composting, transformation to fertilizers *(Lecomte et al., 2017; Levasseur, 2004)*. Some plants only treat the pig slurry and store it, while others transform it into biogas (Flotats, Campos, & Bonmatí, 2001).One of the new techniques for pig slurry treatment is using constructed wetlands *(Lecomte et al., 2017)*. However, the main problem of this system is the clogging of granular media by presence of solid particles in the pig slurry (Caselles-Osorio et al., 2007; Maibritt Hjorth, Christensen, & Christensen, 2008; Knowles, Dotro, Nivala, & García, 2011; De la Varga, Díaz, Ruiz, & Soto, 2013; Anna Pedescoll, Corzo, Álvarez, García, & Puigagut, 2011),therefore, a pretreatment to remove the solid is highly required by previous authors *(Lecomte et al., 2017)*.

3. Pigs slurry management techniques

The selection of the adequate management technique for pig manure has to be based on the Implementing Decision (EU)2017/302 of the Commission, of February 15, 2017, which establishes the conclusions on the BAT (best available techniques) within the framework of Directive 2010/75 / EU of the European Parliament and of the Council regarding the intensive rearing of poultry or pigs. While these BATs are intended for this type of production, they also they can serve as a reference to meet environmental requirements in other livestock productions and farms *(FAOLEX, 2017).*

They are two possibilities to manage the pig slurry, apply it directly to agricultural soil without any type of treatment, which the most representative among livestock farms, or treat the slurry before reusing it by different types of treatment (physical-chemical, biological ..).

3.1 In small farms

Two types of manure management are usually used in small farms, direct application or storage ponds. Storage ponds in which the slurry evaporates naturally to apply the pasty manure directly on the ground. This option is the most economical, but it does not eliminate the problem of odors or excess nutrients. It is sustainable if the link between livestock and agriculture are in balance, that is, if the application of slurry as compost is carried out in the appropriate amounts per unit area and year.

i. Direct application

Direct land application of pig manure is the largely used management method due to its easy operation and low cost. Almost all the guidelines and regulations concerning reduction of the impact of livestock manure use suggest limits that are close to the amount of N and P that is actually required by crops *(Provolo et al., 2018)* . The improper application of pig manure such as the application of a surplus doses that exceed the needs of crops may cause serious environmental problems such as an increase in the direct emission of ammonia and greenhouse gases (GHG), nutrient leaching, and pathogen contamination (Dennehy et al., 2017; Roubík, Mazancová, Phung, & Banout, 2018) .Therefore , finding suitable management strategies is highly needed. Planning of the use of slurry as organic fertilizer, with agronomic criteria, adjusting the dose to the demand of crops, applying it at the right time and using the right equipment is the key factor that can determine the emission reduction, *(Image 1)* presents examples of application systems that can reduce the emission of GHG.

Image 1. Application systems of Pig manure with hoses and discs

ii. Pig slurry Storage

The slurry produced in livestock's is collected and stored outside in tanks, storage pond or lagoons which is the most common in Spain.

A first aspect to consider for the prevention of environmental risks is to define and maintain a useful storage capacity that should allow retain the slurry produced when the application to the agricultural soil is not recommended from an agronomic or environmental view, also they should complying with the basic requirements that guarantee waterproofing, so as to avoid leaks that could contaminate groundwater sources and reduction of emissions into the atmosphere that produce bad odors and ammonia emission…

Image 2. *Slurry storage tank*

Image 3. *Slurry storage pond*

3.2 Big farms

Intensive livestock production may lead to a surplus of plant nutrients on farms that contribute to environmental problems *(M. Hjorth et al., 2010)*, For reducing the environmental negative impacts of the pig slurry, at the moment, there is no unique and precise solution. Every treatment plant uses different methods and technologies, depending on the slurry concentration, volume production, facilities, etc. Those technologies can be physical, biological, chemical or combination of several techniques. The most popular techniques used for the pig slurry is the two phases separation (liquid and solid), the liquid can be used directly as a fertilizer, and the solid is destined to a composting stage to produce an organic fertilizer), the nitrification-denitrification, and composting, transformation to fertilizers *(Lecomte et al., 2017; Levasseur, 2004)*. Some plants only treat the pig slurry and store it, while others transform it into biogas *(Flotats et al., 2001).* One of the new techniques for pig slurry treatment is using constructed wetlands *(Lecomte et al., 2017).* The alternatives currently available on the market are:

- Solid-liquid separation
- Coagulation-flocculation
- Evaporation and drying
- Stripping and absorption
- Membrane filtration
- Composting
- Nitrification-denitrification
- Anaerobic digestion
- Anaerobic digestion

To choose the adequate treatment, several criteria must be considered:

- Capital costs
- Operating costs
- Maintenance
- The labor time to manage a processing unit
- Nitrogen and phosphorus reduction rates

i. Solid-liquid separation

The market offers many liquid / solid separators using essentially physical mechanisms such as filtration, centrifugation, settling, flotation … and physical chemical treatment such as coagulation / flocculation. In the next part, we will only present the main devices that have made their proof, or which may be of interest in the treatment of pig manure which are:

- Decantation (with gravity)
- Mechanic separators (filter press, screw press, roller press.)
- Evaporation and drying
- Coagulation-flocculation
- Precipitation

ii. Mechanic separation

The process of solid-liquid separation can be classified into two broad categories: sedimentation and mechanical separation. Mechanical separators can take different forms depending on their mode of operation and manufacture, the three main types of mechanical separators are filter press, screw press, and roller press.

The mechanical separation equipment uses porous elements such as membranes to retain the thickest elements of the slurry. Some equipment is designed to not exert any mechanical press while others apply pressure on the slurry.

Image 4. Filter Press, Screw press, Roller press

iii. Decantation

The mechanisms of gravity settling, or sedimentation involve the size and specific weight of suspended matter. So that the sedimentation of the particles is not disturbed by the inflow of effluent, the settling must have specific dimensions. Speed rise of the liquid to be decanted (= flow rate / surface of decanter) must be less than the rate of descent of the particles in suspension.

There are different types of decanters:

- STATIC DECANTERS: In this type, sedimentation or settling occurs, usually in free fall of the particles. There are horizontal, vertical, and helical flow.

Image 5. Horizontal static decanter

Image 6. Vertical static decanter

- DYNAMIC DECANTERS: They are applied to the treatment of liquids that requires a high concentration of particles to increase the possibilities of contact. They are classified according to the characteristics of the sludge formation zone, in units of hydraulic or mechanical type.

Image 7. Hydraulic decanter

Image 8. Mechanical Decanter

iv. Coagulation flocculation

Coagulation-flocculation is based on the addition of organic or inorganic products to achieve a larger particle volume and concentrate insoluble particles present in the slurry and improve solid-liquid separation processes *(M. Hjorth et al., 2010)*, it considered as one of the most effective chemical process to reduce solid in an wastewater is the *(Lecomte et al., 2017)*. Coagulation-flocculation phenomena is extensively important process in a various discipline, including biochemistry, oil and cheese manufacturing in water and wastewater treatment, it is a simple process to operate, but many parameters can influence it efficacy, pH, type and concentration of the coagulant, agitation speed and time (S. H. Kim, Moon, & Lee, 2001; Lecomte et al., 2017; Tawakkoly, Alizadehdakhel, & Dorosti, 2019). Besides, coagulation-flocculation is the suited pretreatment mode for removal colloidal particles *(Maibritt Hjorth et al., 2008)* and reducing the COD, being recommended for pig slurry COD *removal (Dosta, Rovira, Galí, Macé, & Mata-Álvarez, 2008)*. Inorganic salts and iron salts are generally used as coagulant but iron salts usually are more efficient than the aluminum *ones (Amokrane, Comel, & Veron, 1997; Maibritt Hjorth et al., 2008; Samadi et al., 2010)*.

v. Stripping

The main objective of this treatment is to recover the N-ammonia from the liquid fraction of the pig slurry. Stripping can be done with hot air or steam

This process has been used efficiently in wastewater treatment to remove NH_4^+.

Once NH_4^+ is extracted from the wastewater by means of the air stream, it can be recovered by absorption in a H_2SO_4 solution, forming $(NH_4)_2SO_4$.

Image 9. Stripping treatment plant

vi. Aerobic digestion

This treatment consists of the degradation of the organic matter of the slurry in the presence of oxygen provided through bubbling in the slurry pond through microperforated membranes. The Advantages of this treatment are the reduction of organic load and ammonia nitrogen, improve the separation process and reduce the pathogenic microorganisms.

vii. Nitrification / Denitrification

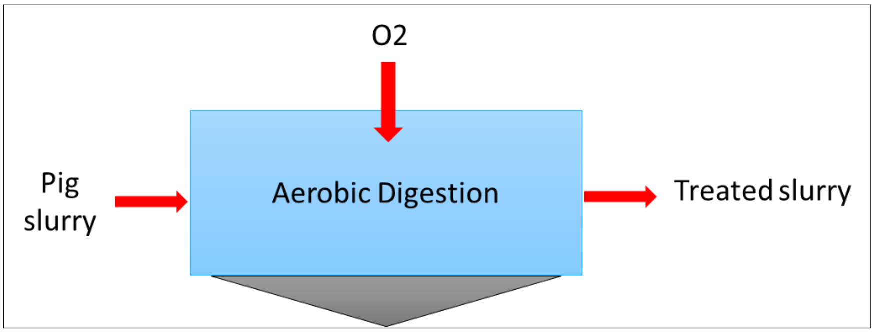


Figure 5. General scheme of aerobic digestion

Nitrification/denitrification is a classic biological technique for the elimination of nitrogen, the process combines aerobic and anoxic stages, where the microorganisms transform the nitrogenous compounds present in the slurry. The advantages of this treatment process are nitrogen and organic matter removal, reduction of greenhouse gas emissions and bad odors.

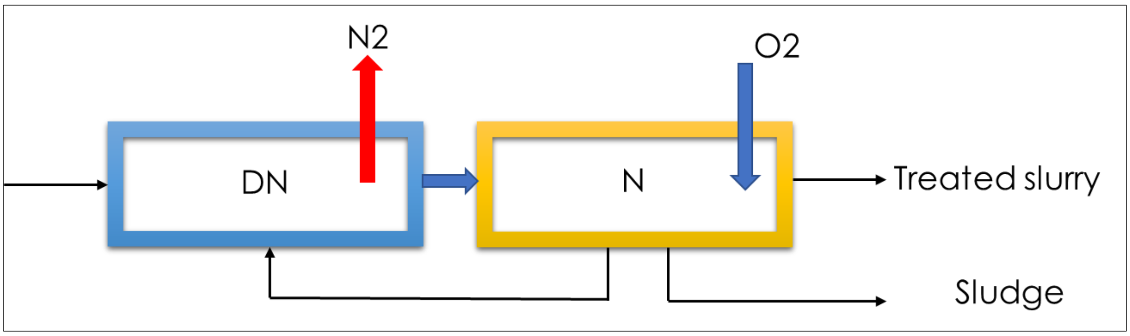


Figure 6. General scheme of nitrification/desnitrification treatment

During nitrification, ammonia is aerobically oxidized to nitrite Equation 1 by ammonium oxidizing autotrophic bacteria (for their growth they use an inorganic carbon source such as CO2 or bicarbonate) and, subsequently, nitrite is oxidized to nitrate by nitrite oxidizing bacteria

Equation 2.

Equation 1 Nitrification

$$NH_4^+ + 1{,}5\,O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

Equation 2 Nitrification

$$NO_2^- + 0{,}5\,O_2 \rightarrow NO_3^-$$

During denitrification, nitrate is reduced to nitrogen gas under the presence of biodegradable organic carbon by the action of heterotrophic bacteria, resulting as by-products of this reaction nitrite and nitrogen oxides.

Equation 3 Denitrification

$$0{,}20\,NO_3^- + 1{,}20\,H^+ + e^- => 0{,}10\,N_2 + 0{,}60\,H_2O$$

viii. Composting

Composting is an aerobic biological process applicable on the solid fraction resulted from a pretreatment of pig manure. It is also applicable in slurry when it contains a high content of dry matter. The main objective of composting is to obtain a stabilized final product, with a low humidity percentage, preserving the maximum percentage of nutrients from the initial untreated product, but free of pathogens and seeds.

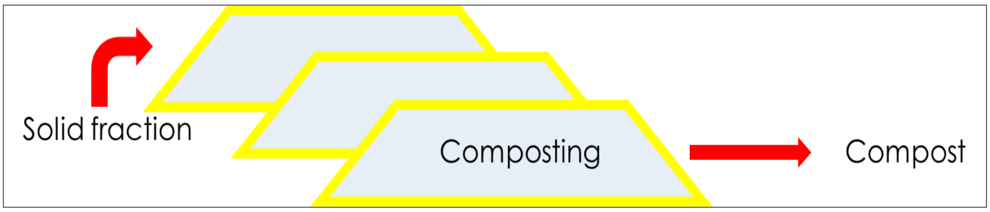


Figure 7. General scheme of composting system

Composting methods:

- ✓ Static batteries with passive aeration
- ✓ Static batteries with forced aeration
- ✓ Rows with mechanical agitation
- ✓ Reactors or silos

In the Guide to the Best Available Techniques for the pig sector *(MARM, 2010)* it is recommended to take into account a series of premises for the effective composting of the solid fraction of the slurry such as Frequent aeration to provides oxygen regulates humidity, compost should contain 25-30% of dry matter , application of high temperatures to eliminate pathogens, the mass should be porose and had achieve an adequate C/N ratio of around 30.

Image 10. Windrow composting, In-vessel composting, Aerated static pile

ix. Anaerobic digestion

It consists of the organic matter degradation in absence of oxygen. Treated slurry and biogas are the two co-products generated with the application of this process. The treated slurry contains essentially the same amount of fertilizers (nitrogen, phosphorus, potassium, etc.) as the raw slurry and has an almost equivalent volume. On the other hand, anaerobic digestion leads to a reduction organic load (COD) and total solids (TS) of the order of 80% and 70% respectively as well as a significant reduction in the odors of slurry and pathogenic microorganisms, in particular coliforms totals, E. Coli, salmonella, Cryptosporidium and Giardia *(Côté, Massé, & Quessy, 2006).*

Anaerobic digestion uses low energy and produces very low solids. In addition, it is possible to use the CH_4 produced to heat the digester, which usually works at 35 °C.

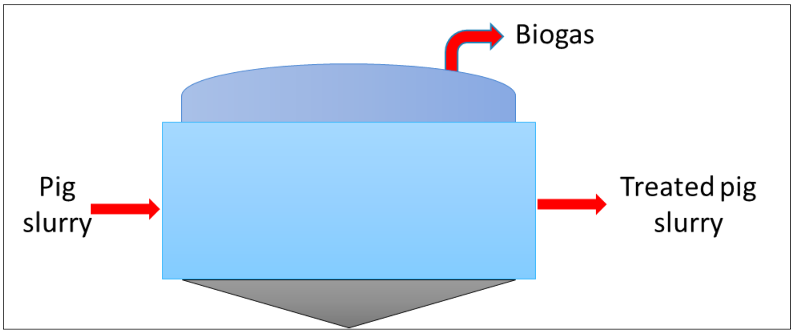


Figure 8. General scheme of anaerobic digestion

4. Constructed wetlands

Constructed wetlands are systems designed to exploit the natural processes of wetlands, which combine hydrology, soils, microorganisms and plants, to treat wastewater. Many studies (Bayo, Gómez-López, Faz, & Caballero, 2012; Liang et al., 2017; Terrero, Muñoz, Faz, Gómez-López, & Acosta, 2020; Vymazal, 2014) have shown that constructed wetlands are highly effective in reducing contaminants and improving water quality.

The use of wetlands in the treatment of urban wastewater has developed rapidly since the mid-1980s. Indeed, these technologies have many advantages which make them an attractive alternative to conventional means of treatment. In particular, these biological treatment systems are economical, simple to use and to maintain. Thus, artificial wetlands can operate without external energy input and can be operated by personnel without special skills. In addition, they show a high level of reliability and efficiency. They are therefore of particular interest to small isolated communities lacking the means and qualified personnel to operate traditional wastewater treatment plants, as well as for developing countries.

Many of these systems have been designed and operated for treating wastewaters, while others have been implemented with multiple uses, such as the use of treated wastewater for the creation and restoration of wetland habitat to increase wildlife or in agriculture or to improve and protect the environment *(Vymazal, 2014).*

Indeed, artificial wetlands can be optimized to achieve a given level of treatment for a specific parameter (carbon pollution, nitrogen, phosphorus, etc.). They will therefore be able to perform better than natural wetlands for water purification. In addition, the wastewater flow must be distributed over the entire surface of the wetland for it to be 100% efficient. This condition can be satisfied in constructed wetlands by controlling the water level and using suitable ways for water supply and discharge (Akratos, Papaspyros, & Tsihrintzis, 2008).

Treatment systems through constructed wetlands are designed mainly using three basic criteria according to *(Vymazal, 2011)* :

- Hydrology: Surface flow of open systems and subsurface flow.
- The type of macrophytes: Emerging, submerged and floating.
- Flow path. Horizontal and vertical.

The system devised in this thesis is already being applicated directly in various in CEFUSA copany with the Research Group of the UPCT GARSA (Management, Use and Recovery of Soils and Water) through the project 'Sustainable environmental management of pig production'. In addition, the same constructed wetlands were used in various projects such as 'Comprehensive water management in pig production', of the AGROPOR-UPCT group and in 'Environmental management for the sustainability of intensive pig farming', of the Fuente Álamo-UPCT City Council.

The research group methodology is validated by the MAPA *(MAPA, 2020) and* the European Union as a 'slurry purification methodology' and is suitable for treatment at source, on the farm itself, thus optimizing the management of these by-products, allowing the implementation of the water footprint. and ecological and the recycling of nutrients present in the slurry. These aspects are basic together with their "traceability", according to the new regulation in force from 2020 on basic rules for the management of intensive pig farms and the Mar Menor Recovery and Protection Law.

GARSA research group participate in various project and realized man investigation about the constructed wetlands purification system for pig slurry, and it was demonstrated that it can minimizes the consumption of irrigation water and reduces the water footprint by minimizing environmental risks contamination of the atmosphere, groundwater and soils. Among the results obtained by the research group, the constructed wetlands showed a high efficiency in reducing nitrogen, phosphorus and total suspended solids but it in various types of pig slurry, there were some inconvenient and limits for using the CWs such as the clogging problem, besides, the CWs doesn´t show big efficacy in reducing the EC and heavy metals.

5. Legislation

In this section, European and Spanish legislation reference is made to the current legislation that directly affects the aspects that influence the management of pig slurry, from its production in pig farms to its recovery in agricultural operations, both at the European, National and Regional level.

- European union legislation

-Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.

-Council Directive of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC).

-COUNCIL DIRECTIVE 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control.

-Commission Regulation (EC) *Nº* 1576/2007, of December 21, 2007, regarding disposal methods or the use of animal by-products.

- Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control.

- Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC (Text with EEA relevance)

-Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control).

-Directive (EU) 2016/2284 of the European Parliament and of the Council of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC and repealing Directive 2001/81/EC.

-Commission Implementing Decision (EU) 2017/302 of 15 February 2017 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the intensive rearing of poultry or pigs (notified under document C (2017) 688).

- Best Available Techniques (BAT) Reference document, means the available techniques which are the best for preventing and minimizing the impacts on the environment.

The BREFs are a series of reference documents covering, the industrial activities listed in Annex 1 to the EU's IPPC Directive. This document provides a description of a wide range of industrial processes, their respective operating conditions and emission rates. The states members are required to take these documents into account when determining best available techniques generally or in specific cases under the Directive.

In chapter 4, section 4.15.2.2 refers to the treatment of livestock wastewater with the different techniques process that can be applied. This section mentioned the research work carried out by the GARSA group, which is the pig slurry treatment with constructed wetlands.

- Spain legislation

-*Real Decreto 1310/1990,* de 29 de octubre, que regula la utilización de lodos de depuradora; desarrollada por la Orden de 26 de octubre de 1993 sobre utilización de lodos de depuradora en agricultura.

-*Real Decreto 261/1996,* de 16 de febrero, publicado en el BOE nº 61 de 11 de marzo de 1996, que trata sobre la protección de las aguas contra la contaminación producida por los nitratos procedentes de fuentes agrarias y que además establece las áreas más sensibles, denominadas zonas vulnerables. Así mismo contempla los códigos de Buenas Prácticas Agrarias, dosis máxima de aplicación para estas zonas y programas de actuación.

-*Orden MAM/304/2002,* de 8 de febrero*,* por la que se publican las operaciones de valorización y eliminación de residuos y la lista europea de residuos.

-*Real Decreto 1429/2003,* de 21 de noviembre, por el que se regulan las condiciones de aplicación del Reglamento CE 1774/2002, en materia de subproductos de origen animal no destinados al consumo humano; de conformidad con el Real Decreto 1131/2010, de 10 de septiembre, por el que se establecen los criterios para el establecimiento de las zonas remotas a efectos de eliminación de ciertos subproductos animales no destinados a consumo humano generados en las explotaciones ganaderas.

- *Real Decreto 824/2005*, de 8 de julio, sobre productos fertilizantes.

- *Real Decreto 1514/2009*, de 2 de octubre, por el que se regula la protección de las aguas subterráneas contra la contaminación y el deterioro.

-*Real Decreto 949/2009*, de 5 de junio, por el que se establecen las bases reguladoras de las subvenciones estatales para fomentar la aplicación de los procesos técnicos del Plan de biodigestión de purines; modificado por el RD 1255/2010 y complementado por la Orden ARM/1840/2010.

-*Ley 22/2011*, de 28 de julio, de residuos y suelos contaminados.

-*Real Decreto 1528/2012*, de 8 de noviembre, por el que se establecen las normas aplicables a los subproductos animales y los productos derivados no destinados al consumo humano.

-*Ley 21/2013*, de 9 de diciembre, de evaluación ambiental.

-*Real Decreto Legislativo 1/2016,* de 16 de diciembre, por el que se aprueba el texto refundido de la Ley de prevención y control integrados de la contaminación.

-*Real Decreto 980/2017*, de 10 de noviembre, por el que se modifican los Reales Decretos 1075/2014, 1076/2014, 1077/2014 y 1078/2014, todos ellos de 19 de diciembre, dictados para la aplicación en España de la Política Agrícola Común.

-*Real Decreto 306/2020*, de 11 de febrero, por el que se establecen normas básicas de ordenación de las granjas porcinas intensivas y se modifica la normativa básica de ordenación de las explotaciones de ganado porcino extensivo. Este RD que deroga el RD 324/2000, de 3 de marzo, dispone de una serie de exigencias en la utilización de deyecciones y estiércoles, recogiendo los procedimientos para su gestión a fin de ofrecer unas garantías medioambientales adecuadas. Por otra parte, en el Anexo I de dicho RD se ofrece una tabla para el cálculo del volumen de estiércol teórico producido por plaza, que a su vez nos permite calcular la cantidad de nitrógeno contenido en dicho volumen referido a las bases zootécnicas para el cálculo del balance alimentario de nitrógeno y fósforo (MAPAMA, 2017).

- Murcia Region legislation

-*Orden de 31 de marzo de 1998,* de la Consejería de Medio Ambiente, Agricultura y Agua por el que se aprueba el Código de Buenas Prácticas Agrarias de la Región de Murcia; complementado por la Orden de 3 de diciembre de 2003, de la Consejería de Agricultura, Agua y Medio Ambiente, por la que se aprueba el Código de Buenas Prácticas Agrarias de la Región de Murcia.

-*Orden de 20 de diciembre de 2001*, por la que se designan las zonas vulnerables (Campo de Cartagena) a la contaminación por nitratos procedentes de fuentes agrarias en la Comunidad Autónoma de la Región de Murcia; complementada por la Orden de la Consejería de Agricultura de 3 de marzo de 2009, por la que se establece el programa de actuación sobre la zona vulnerable correspondiente a los acuíferos cuaternario y plioceno en el área definida por zona regable oriental del trasvase Tajo-Segura y el sector litoral del Mar Menor; modificada por la Orden de 27 de junio de 2011, de la Consejería de Agricultura y Agua.

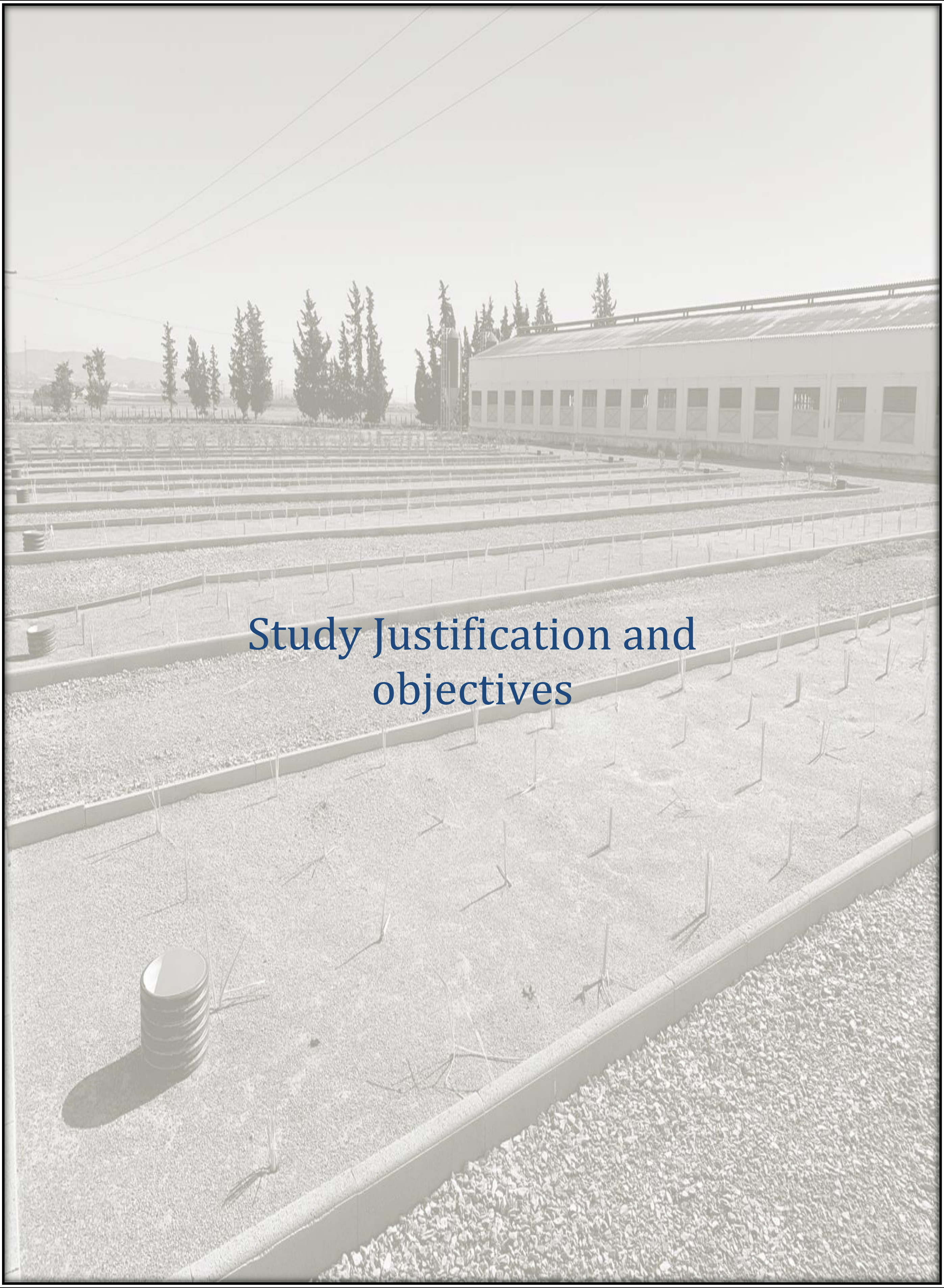
-*Orden de 3 de diciembre de 2003*, de la Consejería de Agricultura, Agua y Medio Ambiente, por la que se aprueba el Código de Buenas Prácticas Agrarias de la Región de Murcia.

-*Orden de 22 de diciembre de 2003*, por la que se designan las zonas vulnerables (Vega Alta y Media del Río Segura) a la contaminación por nitratos procedentes de fuentes agrarias en la Comunidad Autónoma de la Región de Murcia; complementada por la Orden de la Consejería de Agricultura de 19 de noviembre de 2008, por la que se establece el programa de actuación sobre la zona vulnerable correspondiente a los acuíferos de las Vegas Alta y Media de la cuenca de Río Segura; modificada por la Orden de 27 de junio de 2011, de la Consejería de Agricultura y Agua.

-*Orden de 26 de junio de 2009*, de la Consejería de Agricultura y Agua por la que se designa la zona vulnerable a la contaminación por nitratos de Valle del Guadalentín, en el término municipal de Lorca; complementada por el programa de actuación desarrollado por la Orden de 27 de junio de 2011.

-*Orden de 16 de junio de 2016*, de la Consejería de Agua, Agricultura y medio ambiente, por la que se modifican las Órdenes de 19 de noviembre de 2008, 3 de marzo de 2009 y 27 de junio de 2011, de la Consejería de Agricultura y Agua, por las que se establecen los programas de actuación sobre las zonas vulnerables a la contaminación por nitratos de origen agrario en la Región de Murcia.

Study Justification and objectives



II. Study Justification and objectives

1. Study justification

The current Common Agriculture Policy (CAP) motivate destructive industrial scale farming which deteriorates the water, soil and air quality of Europe due to the increasement in the concentration of nitrates in surface and groundwater, as well as the eutrophication of reservoirs, estuaries and coastal waters, besides, the direct application of pig slurry without any treatment or management that effect the soil quality and provoke air pollution with GHG and ammoniac.

According to *(CAP, 2018)* 60% of European rivers, lakes, and wetlands are effected by the industrial scale farming, and among the diffuse sources that cause this pollution and the most important currently is the excessive or inappropriate application of nitrogen fertilizers in agriculture.

To solve this problem, many legislations were made at European, national and regional level which are described previously. Directive 91/676 / EEC, of 12 December, on the protection of waters against pollution produced by nitrates of agricultural origin, is making pressure on the Member States to identify the waters that are affected due to contamination by nitrates from agricultural sources.

The Mar Menor is an inland sea separated from the Mediterranean Sea by a narrow 22 km long strip of sand (La Manga), crossed by various gullies, which determines the semi-confinement of its waters and gives them unique salinity and temperature characteristics. It also has five islands of volcanic origin and several wetlands on its margins, as well as two salt systems.

Image 11. Mar Menor localization

The Mar Menor is one of the destroyed waters by the agricultural activities, it has been absorbing the nitrates and phosphates from agricultural activities for a long time, which causes the 80% of the pollution that led to the total collapse of the lagoon in 2016. The Ley 3/2020, de 27 of July propose the protection, recovery, development and revaluation of the biological, environmental, economic, social and cultural wealth of the Mar Menor, and the articulation of the different public policies attributed to the Autonomous Community of the Region of Murcia that effect on the Mar Menor, so that its exercise is carried out in a comprehensive and sustainable way.

The Mar Menor has suffered serious deterioration in recent decades, mainly due to excessive urban development and the run-off of nitrates from agriculture. In 2021, the situation became very desperate, thousands of fish and other marine life washed up dead on the shores due to the lack of oxygen *(Image 12).*

Image 12. Actual situation of the Mar Menor (Source: El PAIS)

In order to minimize the pollution produced by nitrates of agricultural origin, a practical guide "The Code of Good Agricultural Practices" was published to help farmers, growers and land managers to protect the environment. Among the key actions described in this Code of Good Agricultural Practices are:

- Periods in which the application of fertilizers to the land is not convenient.
- Fertilizer application conditions to lands near watercourses.
- Capacity and design of manure storage tanks.
- Procedures for the application of chemical fertilizers and manure in order to avoid losses of nutritive elements to surface or underground waters.

The Best Available Techniques (BAT) published in 2017 about pig production, a series of technologies that can be easily applied in order to reduce and control the environmental impact of livestock. This guide makes a compilation of the BATs recognized by international organizations based on the Commission's Implementing Decision (EU) 2017/302, of February 15, 2017, which establishes the conclusions on BAT in the framework of Directive 2010/75/EU of the European Parliament and of the Council regarding the intensive rearing of poultry or pigs.

There is a big need to find solution for pig slurry produced in agricultural sector by research and modernization taking into consideration the available technologies based on compliance with the European and Spanish regulations, therefore, it is essential to implant studies that serve as a reference to encourage the management of slurry to reduce the environmental impact generated by the sector.

Constructed wetlands is one of the technology with a low operating and maintenance costs, does not use electrical energy and the flow is driven by gravity compared to conventional systems such as activated sludge treatment, membrane bioreactors, sequential batch reactors, photocatalysis, electrocoagulation … which require a significant input of energy (Borin, Politeo, & De Stefani, 2013; Saeed & Sun, 2012; Vymazal, 2011). Nevertheless, this conventional technology has some disadvantages explained below.

Problematic of the constructed wetlands and study justification

Constructed wetlands are a very good technology for water treatment and it combines water treatment with the eco-environment in an adequate way.

The constructed wetlands have attracted intensive attention since developed and now they are widely used as a treatment process for different waste waters such as industrial wastewater, agricultural waste water, mining and petroleum production waste water ... However, many problems are found in the practical application of constructed wetland, the most common problem are:

- Clogging
- Occupy large areas
- They had a non-standard design.
- Low efficiency in salts content removal.

Clogging

The main operational problem of the constructed wetlands is clogging of granular medium which can be detected by the appearance of water on the surface of the granular medium. Clogging is a blockage a of the pore space which alters the water movement and pollutants and it 'is considered as a high significant concern in the development of constructed wetlands and it 'is one of the most common problem that has a big influence on wastewater purification processes. The major contributing factors are the accumulation of suspended solids on top of the wetland which provokes a clogging as shown in *(Photo 2).*

the contracted wetland substrates are easily saturated and plugged with the high solids content, besides, the growth of microorganisms within the filter media *(Pucher & Langergraber, 2019),*both processes lead to changing the constructed wetlands hydraulic properties which effect on the water flow and result gradual clogging of the porous medium of the system. Those problems result to a short lifespan of the constructed wetland.

Photo 1. Constructed wetlands

The treated effluent characteristics is an important factor that has a direct relationship with the CW clogging, which can be caused by physical, chemical and biological factors (Wang, Sheng, & Xu, 2021). The physical factor is initially the suspended solids that enters to the CW system and provoke reducing the filtration materials porosity. The chemical factor also provoke pore clogging by the formation of insoluble organic salts that precipitates between the CWs materials, additionally the biological factor can also provoke clogging due to extracellular polymers secreted by the accumulated bacteria in the CW *(A. Pedescoll et al., 2009).*

Photo 2. Clogging of the constructed wetland

It is generally accepted that the application of a good wastewater pretreatment is essential for the long-term operation of CW, therefore, this thesis will propose and demonstrate an efficient pretreatment for the constructed wetlands that can remove suspended solids besides other parameters.

Low efficiency in salts content removal

Various studies *(Huang et al., 2019; Liang et al., 2017)* proved that it could successfully treat wastewater from agriculture, aquaculture, and industry. Angelica Terrero *(Terrero et al., 2020)* showed that a CW reduced 85% of total suspended solids (TSS), and the total Kjeldahl removal of nitrogen and phosphorus was 33% of the manure's chemical oxygen demand (COD). However, the CW could not reduce electrical conductivity or water hardness, two factors that can limit the reuse of treated pig slurry, especially as a fertilizer because the electrical conductivity measures the concentration of salts in the water, which is a parameter that strongly affects plant growth. Other researchers such as *(De La Mora-Orozco et al., 2018)* also confirms the low efficacy of the constructed wetland in reducing the electrical conductivity, while the study show a decrease in electrical conductivity was between 12% and 23% depending on time retention, Nevertheless other studies as *(Kelvin & Tole, 2011)* demonstrate that CW can increase the electrical conductivity by up to 23% that may can be attributed to more additional ions being dissolved from the filtration materials.

These problems to a certain extent influence the efficiency of constructed wetlands in wastewater treatment. The review presents correlation analysis and countermeasures for these problems, in order to improve the efficiency of constructed wetland in wastewater treatment, and provide reference for the application and promotion of artificial wetland.

Pig slurry management does not normally comprise a single technique, but rather a sequence of different actions is necessary. Constructed wetland seems to be a low-energy technology, non-mechanical, chemical free and environmentally friendly option for the PS treatment, but it can be limited by:

- *Clogging*
- *Incapacity in reducing salts contents and heavy metals (for agricultural use).*

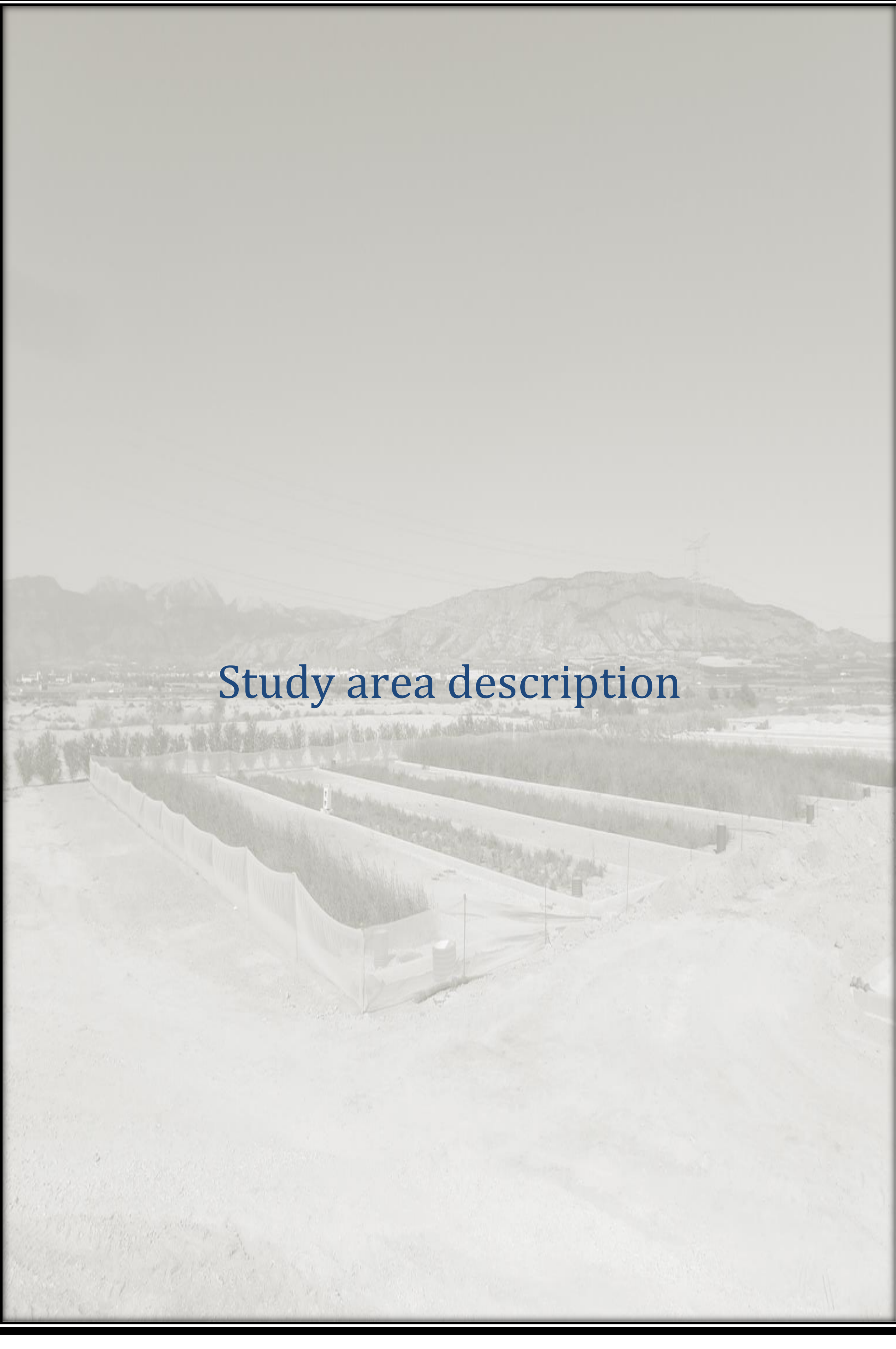
2. General objectives

The main objective is to implement, demonstrate and disseminate a sustainable, replicable and transferable system for the integrated management of pig manure to produce valuable resources that can be safely reused. We propose low cost, and easy to implement and transfer treatment techniques in accordance with the Best Available Techniques (BAT, Reference Document for the Intensive Rearing of Poultry or Pigs). The project will contribute to identify the most efficient techniques (or combination) for the treatment of pig manure. We aim to ensure that both solid and liquid fractions undergo adequate treatment to produce resources (water for irrigation, inorganic fertilizers and compost) to be used by other industries or processes. The use of fertilizers and organic resources in agriculture represents an opportunity to recycle valuable nutrients and improve soil condition and management. At the same time, we aim to reduce environmental impacts associated to pig manure such as odors, emission of NH3 and greenhouse gases, and contamination of water and soil by excess of nutrients.

As specific objectives of this project, the following are proposed:

1. Characterize the slurry, both raw and purified by different treatment process.
2. Proposing a pretreatment that can eliminate the totals suspended solids of the pig slurry to avoid clogging of the CWS.
3. Optimizing the Coagulant and flocculent doses for pig slurry treatment.
4. Showing the efficiency of the coagulation flocculation in removing TSS besides the COD and other parameters.
5. Study the slurry comportment with different filtration materials.
6. Study the filtration material composition (chemical and mineral composition).
7. Chose a new layer that can be added to the constructed wetlands in order to improve its efficiency.

Study area description



III. Study area description:

1. Geographical location of study area

Cefusa is a livestock company of Grupo Fuertes, it has many livestock in all Spain. The studied pig slurry was collected from CEFUSA company that is located in Alhama de Murcia, in Murcia Region. Murcia has a land area of 881.9 km² , with 459,403 (2020) inhabitants *(INE, 2020).*

Figure 9. Study area localization

2. Climatology of Murcia Region

The Region of Murcia is, by its latitude, on the edge of the Mediterranean climate and the dry subtropical climate. Thus, the polar front affects the region on rare occasions, long into winter. In winter, thermal anticyclones appear over La Mancha that reach the region and give a dry and cold weather.

In Murcia, summers are very hot, humid, and mostly clear; winters are long, cold, and partly cloudy and it is dry all year round. During the year, the temperature generally ranges from 4 ° C to 33 ° C and rarely drops below -0 ° C or rises above 36 ° C.

In the long warm season, from June to October, heat waves frequently appear (Saharan tropical air), prevailing haze, with a whitish sky and very high temperatures.

The rainfall presents very weak annual records; related to the shelter offered by the Levantine sector of the Betic Cordilleras. The entire Region is below 700 m *(Climate data, 2020).*

Wind is one of the most important climatic factors in the region, due to the movement of the atmospheric action centers that govern the weather and climate throughout the year in the Peninsula. The barrier effect of the Betic Cordilleras favors the course of the South West.

The North and North East component winds appear with a high frequency because the tectonic porthole that forms the Cartagena field and the Mar Menor channels their flows.

3. Geology of Murcia Region

The geography of Murcia region is defined by its multiple contrasts: dry land and irrigated land, plains and mountainous areas, littoral and interior, vineyards and plateaus, as a result of its status as a transition zone between the sub-plateau north and the subbetic system. Morphologically, the relief of the regional territory is frames within the domain of the Betic Cordilleras and presents an alternation between mountainous sectors, valleys and depressions, creating, in confined spaces, high contrasts in height.

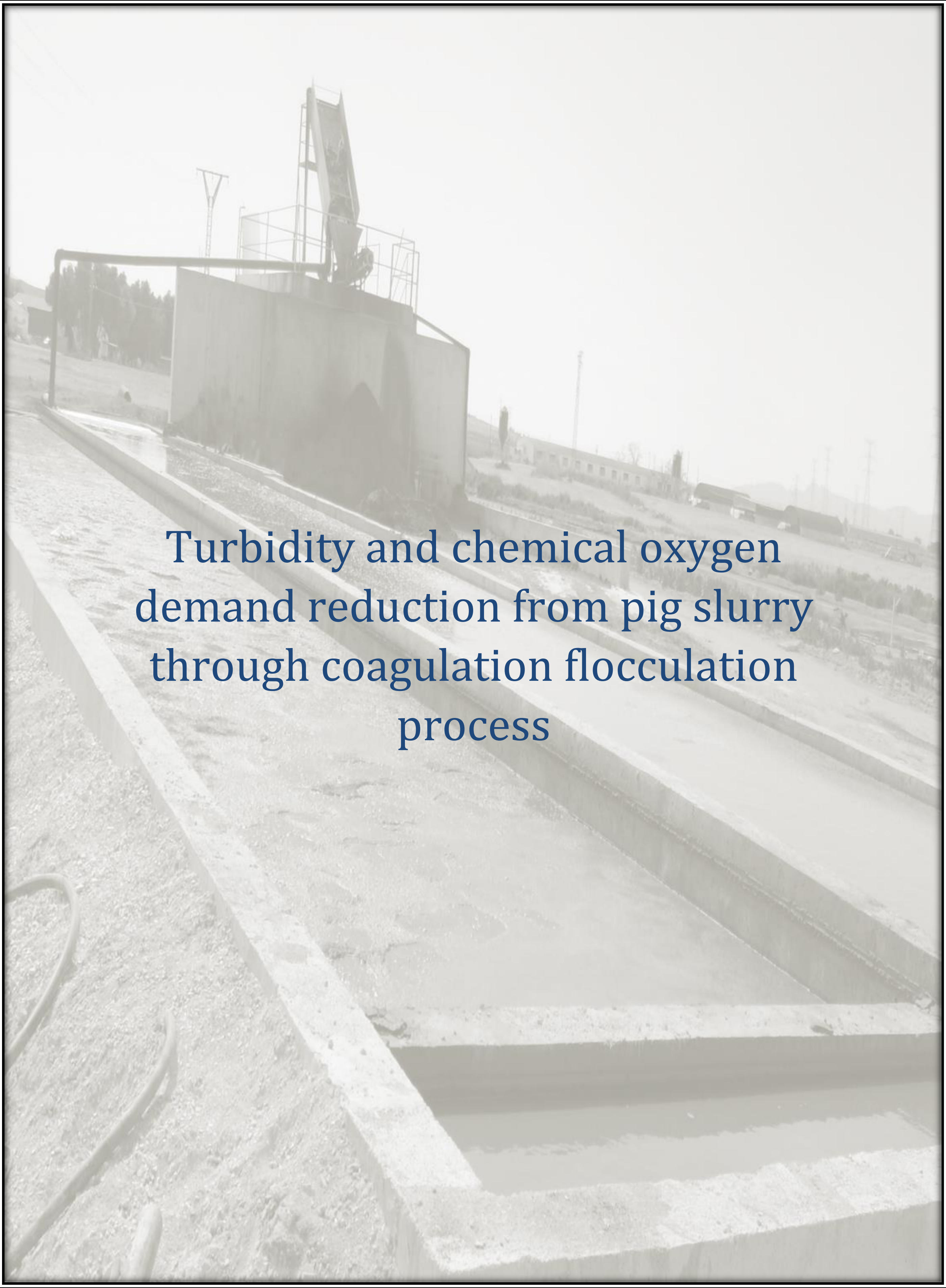
4. Economical aspects

In Murcia region, agriculture, livestock, forestry, and fishing, in 2018 contributed 5.66% to the regional gross value added and 2.89% at the national level. The agriculture constitutes the great vital and vigorous sector of the regional and local economic sector. Intensive crops such as artichoke, broccoli, lettuce, and watermelon make up the main productions in this area. On the other hand, pig farming is the main species produced in this region *(Digital, 2020).*

To give us an idea of the importance of agriculture in the Region of Murcia, we only have to look at the total area for agricultural uses: 567 thousand hectares which presents the 50% of the total of its territory. Murcia's agricultural sector is among the most prosperous in Europe. The Region of Murcia is considered one of the most fertile and prosperous lands in all of Spain, giving rise to an agricultural industry based on quality, environmental balance, with a high percentage of drip irrigation, and investment in I+D+I to guarantee the viability of the new crops implanted and the profitability of the traditional ones.

The Region of Murcia is the community in which the employment of Agriculture, Livestock and Fishing occupies a greater space 11.5% of the total. In addition, during COVID-19 pandemic, the employment has fallen in all autonomous communities except in Murcia region, where the annual number of employees in 2020 grew by 0.1%, thanks to the creation of 500 new jobs, according to *(MURCIA, 2021).*

In addition to the wide variety and richness of the agricultural products, Murcia has a large presence of agro-industries that contribute to increasing the value of the final production. Some of the products of the Murcian garden are highly valued in the national and international markets.



Turbidity and chemical oxygen demand reduction from pig slurry through coagulation flocculation process

IV. Turbidity and chemical oxygen demand reduction from pig slurry through coagulation flocculation process

1. Introduction

In Spain the pig sector has grown remarkably, both in production and number of farms *(MAPA, 2020)*. Due to this growth trend, tons of pig slurry are produced annually which is considered a risky effluent for the environment when the generated pig slurry is not adequately treated Pig slurry can provoke several serious environmental problems on water, soil and air *(CORDIS, 2018)*, including eutrophication of water bodies (Lopez-ridaura, Werf, Marie, & Le, 2009a), groundwater contamination *(Krapac et al., 2002)*, emission of greenhouse gases (Lopez-ridaura, Werf, Marie, & Le, 2009b), soil degradation and pollution *(Hoeve, M.T., 2014).*

Every treatment plant uses different methods and technologies to reduce the environmental negative impacts of the pig slurry. Constructed wetlands is one of the newest treatment techniques *(Lecomte et al., 2017)*. However, the main problem of this system is the clogging of granular media by presence of solid particles in the pig slurry *(Caselles-Osorio et al., 2007; Maibritt Hjorth et al., 2008; Knowles et al., 2011; Anna Pedescoll et al., 2011)*, the need to find a pretreatment to remove solids in order to avoid clogging of the wetlands is very needed *(De la Varga et al., 2013).*

One of the most effective chemical process to reduce solid in an wastewater is the coagulation-flocculation process *(Lecomte et al., 2017)*. Besides, it is a suited pretreatment mode for removal colloidal particles regarding to *(Maibritt Hjorth et al., 2008)* and reducing the chemical oxygen demand (COD) (Azimi, Shirini, & Pendashteh, 2021; Ndegwa, ZhuJun, & Luo, 2001; Zhu, Gamal El-Din, Moawad, & Bromley, 2004). Comparing to other studies, *(Dosta et al., 2008)* reported that total COD and total suspended solids reduction yields higher than 66% and 74%, respectively, using chloride ferric, *(Zhu et al., 2004)* also confirm that using chloride ferric can reduce up to 76% of total suspended solids in the pig slurry.

Inorganic salts and iron salts are generally used as coagulant but iron salts usually are more efficient than the aluminum ones *(Amokrane et al., 1997; Maibritt Hjorth et al., 2008; Samadi et al., 2010)*. Some research study demonstrate that colloidal particles of the manure swine are generally negatively charged (Christensen, Hjorth, & Keiding, 2009). Other authors demonstrate that pig manure requires the use of cationic polymers also admit that organic particles suspended in neutral or alkaline wastewater, which confirms the results of those studies (Maibritt Hjorth & Jørgensen, 2012; Liu, Carroll, Long, Gunasekaran, & Runge, 2016),while *(M. Hjorth et al., 2010)* concluded that medium charge density and high molecular weight polymer is the most effective at removing solids from pig slurry prior, for this reason, a cationic DKFLOCC-1598 flocculent has been chosen to treat our slurry.

Coagulation-flocculation process is highly recommended in removing solids from liquid solutions (Kurniawan, Hung, Chan, & Gilbert, 2006; Lecomte et al., 2017). According to *(APHA, n.d.)*, the turbidity represents the suspended solids of a solution, being the main indicator parameter of the solids removal in a wastewater or pig slurry. In addition, the COD generally used to indirectly determine the amount of organic compounds in water (Islam, Shafi, Bandh, & Shameem, 2019), high COD indicates presence of all forms of organic matter, both biodegradable and nonbiodegradable *(Islam et al., 2019)*. Therefore, these parameters *(turbidity and COD)* are the most important to evaluate the effective of a coagulation-flocculation process.

The most common pretreatments for the CW are the two phases separator, double filtration and decantation, nevertheless, it does not give a good separation of the solid liquid phases, which provide a clogging of the constructed wetland and a diminution of their lifespan (Licciardello et al., 2019) .This study proposes a suitable pretreatment for the CW and will demonstrate how the coagulation flocculation pretreatment can present an excellent solution for CW clogging by reaching a very high solids removal rate as well as for COD removal.

To overcome the limitations and the disadvantages of the coagulation-flocculation (CF) process it´s necessary to apply a central composite design method (CCD), in this study we used the R statistical software to optimize the affecting factors. In this paper the effect of three factors, coagulant concentration, pH, and flocculent was investigated on the two responses COD and turbidity removal. The optimal operating conditions to achieve the maximum COD and turbidity removal were validated experimentally.

2. Specific objectives of the study

The objectives of this study are: (i) investigate whether the coagulation/flocculation process utilizing the chloride ferric as a coagulant and first use of DKFLOCC-1598 as a flocculent, were effective and applicable processes for the treatment of this type of pig slurry, and (ii) make the effluent suitable for the next treatment step (wetlands) to avoid its clogging and extend its lifespan. (iii) optimizing the operating conditions, whether maximizing the reduction of turbidity and COD removal efficiencies by a central composite design method (CCD) using the R statistical software.

3. Material y methods

3.1 Location of the pig slurry farm

The studied slurry is collected from an intensive pig farm located in Alhama de Murcia (Murcia Region) Southeast of Spain, where the constructed wetland pilot plant was constructed under Mediterranean climate, the mean annual temperature was 17,6 ºC and for rainfall was 312 mm (Climate data, 2020). The pig slurry for the experiment came from a farm of 2900 heads of breed mother pigs with piglets and growing pigs, with an average weight of 300 kg.

3.2 Pig slurry sampling collection

The pig slurry that will be treated in this study was pretreated with a scenario that consist of five processes *(Figure 10):* (a) separation phase, (b) vertical decantation, (c)1st filtration 1000 µm, and (d) 2nd filtration 250 µm, then (e) horizontal decantation.

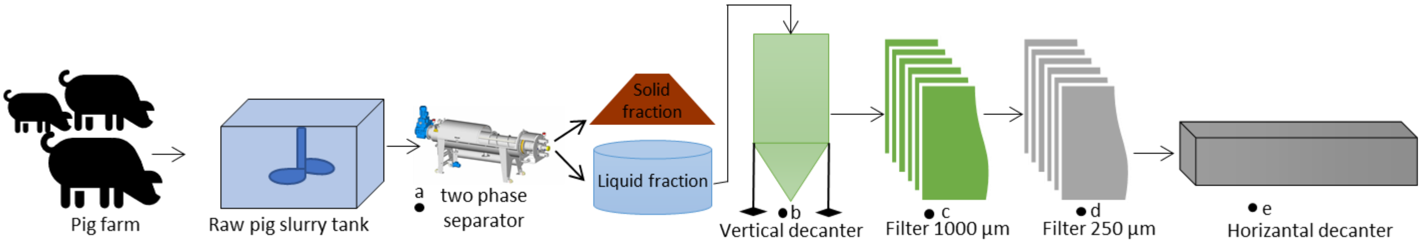


Figure 10. Scheme of the pretreatment system

The pig farm has a raw pig slurry tank, phase separator, two filters (1000 µm and 250 µm), horizontal decanter of 40 m of length, 3.20 m of width and 0.5m of depth, subsurface flow constructed wetland is used as the main treatment, and the treated slurry is finally stored in an impermeable pond. In this research the PS was sampled from two different points, the first one is the raw pig slurry tank, and the second point is the input of the CWs, which is the pretreated pig slurry. The coagulation flocculation treatment will be applied in the pretreated slurry from the second point.

i. Raw pig slurry pond

The pig farm has a raw pig slurry pong, where the raw slurry produced on the farm is stored and homogenized by a mechanical agitator, 24 hours a day and intermittently, shaking for 1 hour and stopping for 2 hours. This mechanical stirrer is driven by a 380 V / 50Hz three-phase motor with a power of 5.5 Kw h^{-1} and IP68 protection.

Photo 3. Raw pig slurry pond

ii. Two phase separators

A phase separator (SF), which receives the slurry that is driven by a submersible pumping equipment of the AT series (Westfalia-Separador, Eisele, Germany), which has a 380V / 50Hz three-phase motor, with a power of 7.5 Kw h^{-1}, operating at 1500 rpm and an IP68 protection system. The performance of this equipment ranges from 3900 to 5700 L min^{-1}. The phase separator installed is a "worm screw separator", this type is highly recommended for farms with a large volume of slurry.

Photo 4. Worm screw separator

iii. Filters

Filtration is a separation process in which a solid-liquid mixture is percolated through a porous media (filter) which ideally retains solid particles and allows liquid to pass (filtrate). In this farm two type of filters with different pores dimension were installed, first the 1000 µm and then 250 µm. Those filters were mounted on respective rotating drums, driven by a motor-reducer and supported by a stainless-steel structure. It also had a frequent self-cleaning system for system maintenance.

Photo 5. 1000 µm and 250 µm filters

iv. Horizontal decanter

The pig farm uses a horizontal decanter of 40 m of length, 3.20 m of width and 0.5m of depth. The pig slurry from the horizontal decanter is destined to the constructed wetland.

Photo 6. Horizontal decanters

3.3 Physical chemical analytical methods and equipment

Pig slurry samples were transported to the laboratory and conserved at 4ºC to minimize biological and chemical reactions. Therefore, only the soluble fraction of the wastewater was used for the physical chemical characterization, which included pH, electrical conductivity (EC), turbidity, the total suspended solids (TSS), chemical oxygen demand (COD), and biological oxygen demand in 5 days (BOD5). The parameters were determined according to *(APHA (2005) Standard Methods for the Examination of Water and Wastewater., 2005).*

The pH and EC were measured by HANNA equipment. Total suspended solids (TSS) were filtered through a weighed standard glass–fiber filter and the residue retained in the filter was dried to a constant weight at 105 °C (2440-D method, APHA–AWWAWEF 2012). Biochemical oxygen demand in five days (BOD5) was determined by manometer OXITOP WTW equipment. Chemical oxygen demand (COD) was determined by photometric determination of the chromium (III) concentration after 2 h of oxidation with potassium dichromate/sulfuric acid and silver sulphate at 148 °C (Macherey–Nagel GmbH & Co. KG. Nano color Test, Ref 985 028/29), (DIN 38 409-H41-1, DIN ISO 15 705-H45).

The experimental equipment used for the coagulation–flocculation experiments at laboratory is a Jar-test device (FC4S reference 18011) in which six stirring blades were connected to a motor that operated under adjustable conditions such as string time and speed.

The coagulant and flocculent used in this research were chloride ferric and DKFLOCC-1598 (cationic flocculent).

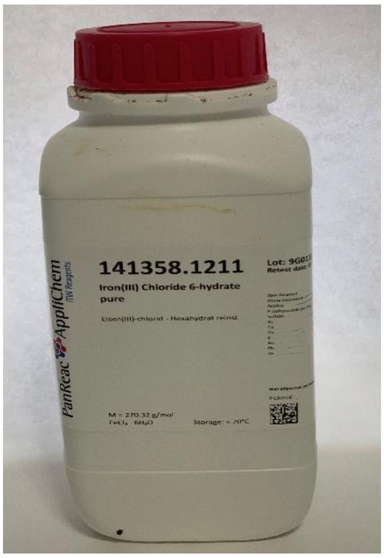


Photo 7. Chloride ferric coagulant

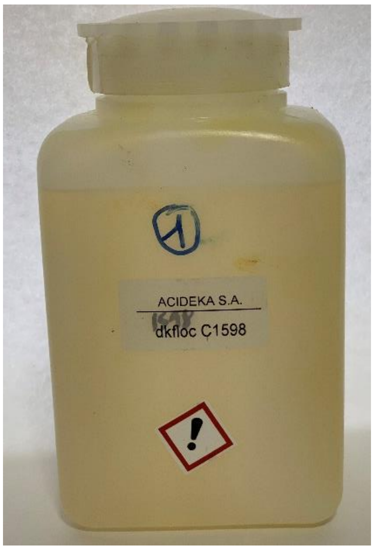


Photo 8. Cationic flocculent (DKFLOCC-1598)

The parameters to be determined the following:

i. Temperature (T):

The temperature measurement is a direct measurement that was taken during the sample collection and it´s expressed in ºC. HANNA Instrument model HI 9025 portable electronic thermometer shown in photo X was used.

Temperature measurement of wastewater provides an important back up to various parameters measurements such as pH, Dissolved Oxygen, Suspended Solids and Turbidity. ... for example, the more the oxygen is less soluble in hot water than in cold water. also, wastewater temperature directly effects on the chemical reactions and reaction rates.

Photo 9. HANNA Thermometer (Reference 11708)

ii. Potential Hydrogen pH

In this research the pH measurement was obtained using HANNA Instrument with reference HI5222-02 Photo 10. The equipment is firstly calibrated with 3 standard solutions of known pH starting from pH=4, then pH=7 then finally pH=9, then place the electrode in the sample and begin reading, when the result is stabilized with temperature compensation the results shown in the equipment screen.

PH (hydrogen potential) refers to the measurement of the concentration of hydrogen ions in water. The concentration of the hydrogen ion determines the alkalinity or acidity of the water. An increase in acidity results in a lower pH while an increase in alkalinity indicates a high pH.

pH measurement has a major role in the wastewater treatment process also gave an idea of the presence of particulate matters, accumulation of toxic chemicals and increasing alkalinity levels are common problems in wastewater.

Photo 10. HANNA pH METER (reference: HI5222-02)

iii. Electrical Conductivity EC

Electrical conductivity characterizes the ability or the power of a material or a solution to allow electrical charges to move freely and therefore allow the passage of an electrical current. This property is depending on the presence of ions, their concentration, mobility, and valence, and on the temperature of the measurement. Solutions of most inorganic compounds are good conductors. Siemens is used as a unit of measurement:

1dS/m = 1 mS/cm = 1 mmhos/cm

In this research, conductivity meter Hanna with reference HI5321CE was used to measure the electrical conductivity.

Photo 11. HANNA conductivity meter (reference HI5321CE)

iv. Total suspended solids TSS

Total suspended solids (TSS) are defined as solids in water that can be trapped by a filter which is reported in milligrams of solids per liter of water mg L^{-1}. The most valid method of determining TSS is by filtering and weighing the effluent sample. The determination in this research was carried out by filtering a 1 ml of the homogenize sample on a glass fiber filter, then dry it at 60 ºC for 24 hours. For filtering the sample, a Vacuum Brand vacuum pump and Watman 0.45 µm filters were used. The TSS are calculated using the formula:

$$\frac{TSS \;=\; [(A-B)\;\times\;1000]}{V}$$

A = Glass weight + filter + dry TSS (g)

B= Glass weight + filter (g)

V= Sample volume (mL)

Photo 12. Measuring Total suspended solids

v. Turbidity

Turbidity is the measure of relative clarity of a liquid and it´s caused by particles suspended or dissolved in water that scatter light making the water appear cloudy or murky. The turbidity is this research is measured with a turbidity meter DINKO Model D-110. Turbidity is reported in units called a Nephelometric Turbidity Unit (NTU).

Photo 13. DINKO Turbidimeter D-110IR

vi. Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is a measure of the amount of oxygen required to oxidize oxidizable organic and inorganic material in a sample. This parameter gives an estimate of the quantity of pollutants present in the liquid solution. In this research COD measurement was performed by NANOCOLOR manufacturing kits test (Kits references used: 985028 and 985029), then measured with a photometer Photometer NANOCOLOR PF-12 (Reference: 919250RM).

Photo 14. COD analysis equipment with Photometer NANOCOLOR PF-12

vii. The five-day biochemical oxygen demand (DBO_5)

The five-day biochemical oxygen demand, or BOD_5 is one of the important parameters of water quality. The BOD_5 measures the amount of biodegradable organic matter contained in water. This biodegradable organic matter is evaluated by the intermediary of the oxygen consumed by the microorganisms involved in the mechanisms of natural purification.

In this research the BOD5 was performed by manometric determination using OxiTop, this Instrumentation is based on pressure measurement in a closed system where the microorganisms in the sample consume the oxygen and form CO2 which is absorbed by NaOH that create a vacuum which can be read directly after 5 days of reaction, as a measured value in mg/l BOD5 (UNE-EN 1899-1, 1998; UNE-EN 1899-2, 1998). This parameter is expressed in milligrams of oxygen required for five days to degrade the organic matter contained in one liter of water.

Photo 15. OXITOP BOD Instrumentation

3.4 Experimental design of coagulation-flocculation assay

As pH is one of the most restrictive parameters in the coagulation step and affects the hydrolysis equilibrium that the coagulant agent can bring out, we decided firstly to carry out the treatment at pH 7.88 as this was the natural pH value determined in the original PS.

At the start, to have knowledge about the closest concentration to the optimum, several coagulant doses from 0.02 mol L^{-1} to 0.032 mol L^{-1} were tested at free pH without adjusting it or adding any flocculant. Using concentrations from 0.03 mol L^{-1} to 0.032 mol L^{-1} gives an orange color which means an excess of iron chloride, while a low concentration of 0.02 mol L^{-1} did not provide any coagulant particles, 0.02 mol L^{-1} gave a dark brown color turned, after sludge separation, to a clear brown, 0.022 mol L^{-1} gave a yellow and became clear for the coagulant dose near 0.026 mol L^{-1}. Therefore, the concentration of 0.026 mol L^{-1} was selected as the center of our statistical study.

The coagulation-flocculation tests, were carried out based on the following operations:

- Coagulation speed 170 rpm.
- Injection of the coagulant.
- Stirring for 3 min.

- Flocculation speed at 40 rpm.
- 15-minute flocculation period.
- Stopping the agitation.
- 30-minute settling period.
- Purge of sampling points.
- Sampling of supernatant water for analyzes.

Turbidity and COD measures were performed to confirm the expectation and it shows that using only the coagulant achieved to reduce 79% of COD with low turbidity reduction of 55%, hence, to improve the turbidity removal it is highly recommended to use a flocculent.

After fixing the coagulant dose, various flocculent doses were added, starting from 0.06 ml L^{-1} to 0.2 ml L^{-1}. First, the minimum and the maximum of the flocculent concentration ranges were added *(Photo 16),* it is clearly observed by a naked eye, that using the minimum concentration of the chosen flocculent range, the water is more turbid, and the solid liquid separation is too slow, which means the lack of flocculent. Around 0.2 ml L^{-1} the particles were perfectly floccule, but the water had white turbid due to the excess of flocculent, so a three other concentration were chosen arbitrary between the maximum and minimum concentration, 0.1 ml L^{-1} 0.14 ml L^{-1} and 0.18 ml L^{-1} *(Photo 17).*

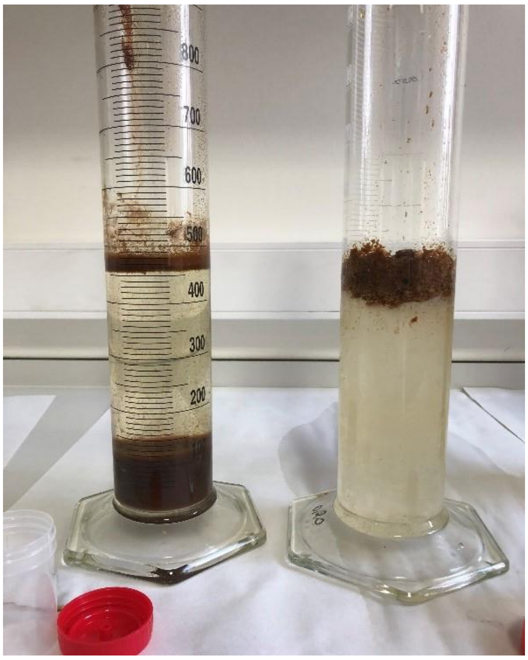


Photo 16. Using 0.06 ml L^{-1} and 0.2-ml L^{-1} of flocculent concentration after 30 min of settling

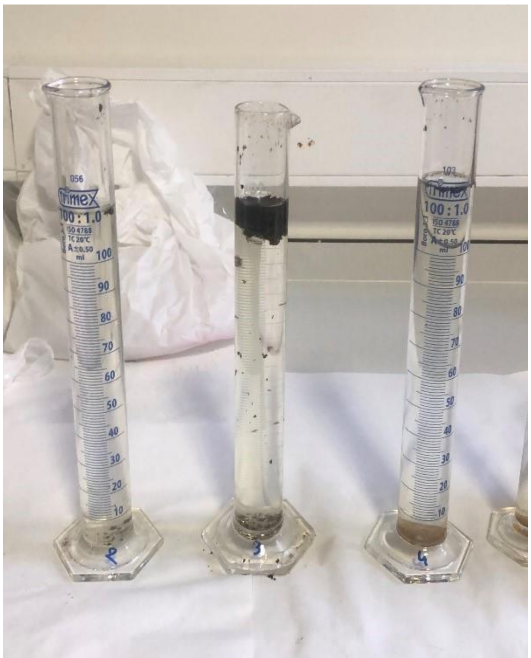


Photo 17. Using 0.1 ml L^{-1}, 0.18 ml L^{-1} and 0.14 ml $L^{-1}$of flocculent concentration after 30 min of settling

On that account, 0.140 ml L^{-1} was chosen as the center of our statistical studies, after measuring the COD and turbidity using the same coagulant dose and different flocculent doses, the COD has a negligible difference, but the turbidity was changeable.

The optimal pH range for coagulation using the iron is 5.5 to 6.5. For high alkalinity water an extra amount of coagulant may be required to lower the pH in order to reach the optimal pH range *(EPA, 2020)*, thus, it will be helpful to adjust the pH with adding an acid before the coagulant to reduce the amount of coagulant needed and effectively lower chemical costs.

The decreasing of pH can be explained by the acidic character of Fe^{3+} (acid of Lewis). By reacting with OH- ions of the pig slurry to iron precipitate in form of Fe (OH)3 according to *(Stumm & O'Melia, 1968)* . The pH of our effluent was 7.74 which make it ideal for the coagulation flocculation treatment, for this reason the free pH of the solution was chosen as the center of our statistical study, and it will help to avoid the maximum adjustment.

Coagulation-flocculation experiments were performed with a bioblock flocculator that comprises six paddle rotors for 1-liter high shape beakers. Tests were carried out at room temperature; pH of each solution was adjusted by adding NaOH 0.5 M or HCl 5.48 M adjustment according to the experimental design. 500 ml of raw pig slurry was put into 1L beakers, the various concentrations of the coagulant were added to the effluent at free pH, that vary between 0.020 mol L^{-1} and 0.032 g L^{-1}, and rapidly mixed (160 rpm) for 3 min. Then slowly mixed (40 rpm) with adding the cationic flocculent, that vary between 0.1 ml L^{-1} to 0.179 ml L^{-1}, for 15 min. Latterly the solution was left to settle for 30 min. the supernatant sample were collected by using a pipette of 10 ml to analyze the COD and turbidity removal percentage, that were calculated according to this equation:

$$\text{Removal (\%)} = ((Ci-Cf)/Ci) * 100 \qquad \text{(Eq. 1)}$$

With Ci is the initial concentration and Cf is the final concentration with the same unit for the COD (mol L^{-1}) and with NTU of the turbidity.

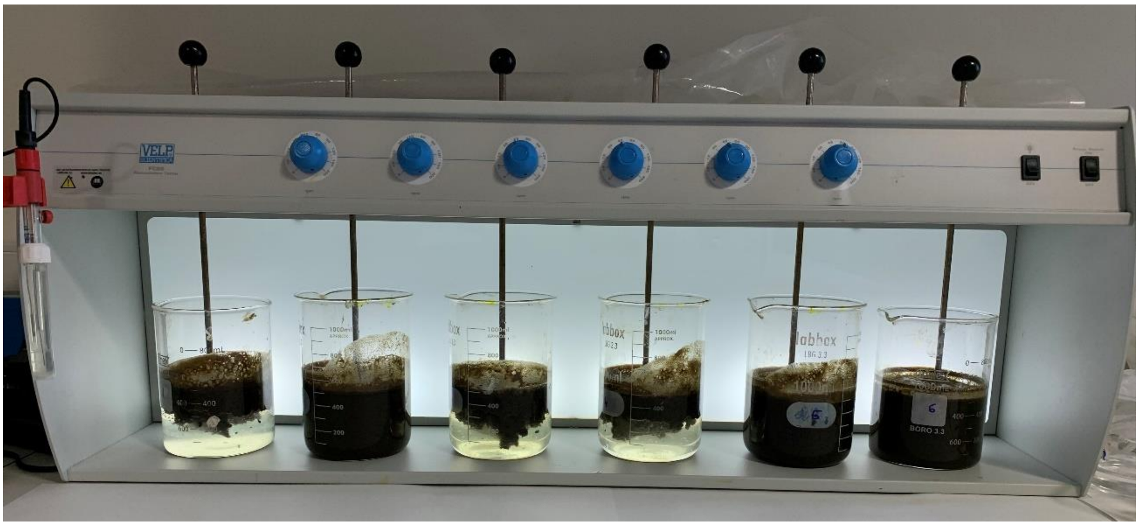


Photo 18. Jar-test device (FC4S reference 18011) with six stirring blades

3.5 Design of the experiments and statistical analysis

The central composite design was used to determine the influence of pH, coagulant, and flocculant dosages on the efficiency of the coagulation–flocculation process. For that purpose, a Central Composite Design (CCD) was prepared to fit a second order response surface *(Montgomery, 2019)*.

Twenty-three experiments were carried out under different pH condition. COD and turbidity removal responses were selected to evaluate wastewater treatment efficiency. The factors chosen were coagulant (chloride ferric) and a cationic flocculant (DKFLOCC-1598) dosage and pH. These factors were selected due to our interest in reducing the operational costs of the wastewater treatment. The center of the design was set to be 0.026 mol L^{-1} for the coagulant concentration, 0.14 ml L^{-1} for the flocculent concentration at the free pH of 7.74. Those values are based on the previous preliminary assay. The R statistical software was used *(RCoreTeam, 2019)* with the RSM library *(Lenth, 2009).*

A blocking factor was introduced to considering three batches of experiments. The design of the experiment is described in *(Table 2)* for each block, three replicates of the central point were used. Two of the blocks included one replicate of each vertex of the cube, while the third block contained one replicate of the star points of the CCD design.

After the experiments were conducted and results obtained for COD and turbidity reduction, a second order response surface was fitted. Following standard practice for statistical model selection, the full model that included interactions and blocking was then sequentially simplified based on the significance of the fitted coefficients.

The experimental matrix for the CCD and the results of COD and turbidity removal are shown in *Table 2*. The experiments were realized at random to minimize errors due to possible systematic trends in the variables. The use of CCD allowed the selected factors to be evaluated in terms of their significance and the optimum values to be determined. This was done to obtain the best COD and turbidity removals from the PS and to study the percentage removal relative to the COD and turbidity removals obtained. The coagulation–flocculation process is the most suitable and effective method for removing solids from different wastewaters including pig slurry which is the aim of this research.

4. Results and discussion

4.1 Physical chemical characteristics of the pig slurry

Table 1 shows the characterization of the raw pig slurry and after the pretreatment with the five processes scenario mentioned in section 3.2.

Table 1. Characterization of raw and treated pig slurry

	Raw pig slurry	After the pretreatment (The 5 processes)	After treatment with CF process in optimum conditions
pH	7.63	7.88	6.4
EC (ms cm $^{-1}$)	9.10	8.76	8
TSS (g L^{-1})	80	30	0
BOD_5 (mg L^{-1})	5300	4200	400
COD (g L^{-1})	11.2	8.94	1.29
Turbidity (NTU)	3500	2110	2.11

Pig excrements include a solid components, feces, and liquid components, urine. The Slurry is a mixture of these two components. It may be added to this mixture the losses drinking water, non-consumed feed, washing water and, in most cases, precipitation water, the pig slurry is therefore a complex effluent with a highly variable composition *(Table 1)*. This variability comes mainly from the following factors: the category of pigs, the type of diet and the management of wash water and precipitation (Boursier, Béline, & Paul, 2005).The pH of animal slurry is normally ranged from 6.3 to 8 in the Spanish commercial farms according to *(Antezana et al., 2015),* based on presented results *(Table 1)* our effluent has a pH of 7.54 which is a normal pH for pig slurry.

The EC of the pig slurry depends on the age and type of the pigs (ProvoloL & Suller, 2007; María R. Yagüe, Bosch-Serra, Antúnez, & Boixadera, 2012). Our Effluent has a low conductivity, according to *(Antezana et al., 2015)* the range of EC in Spanish commercial farms is from 6.59 to 53.5 MS cm $^{-1}$ for growing pigs, *(M & JL, 2005; Omotoso & Olusegun, 2014)* therefore, the studied pig slurry is not considered as a high salinized slurry. The COD is considered low comparing to other farms that can achieve 37 g L^{-1}*(Terrero et al., 2020)*, and other cases till 113 g L^{-1} (Kowalski, Makara, & Fijorek, 2013),DBO_5 also is considered low 4.2 g L^{-1} comparing to other type where the slurry can has a DBO5 of 41 g L^{-1} *(Kowalski et al., 2013).*

The physical separator achieved to eliminate only 62% of the solids, which make the effluent not good enough for the wetland's treatment. The CW is comprised from the surface to the bottom of 0.30 m washed sand, 0.10 m fine gravel, 0.50 m coarse gravel and 0.30 m of fine gravel, therefore the input slurry should contains low solid materials in order to raise the lifespan of the wetlands by avoiding the clogging of granular media (Caselles-Osorio et al., 2007; Maibritt Hjorth et al., 2008; Knowles et al., 2011; De la Varga et al., 2013; Anna Pedescoll et al., 2011), which is the main problem of constructed wetland. Hence physical-chemical pretreatment to remove the maximum solids is greatly appropriate.

4.2 Coagulation-flocculation assay

Results showed that the supernatant pH decreased continually with increasing coagulant dose and gave a value of 5.5 to 6.4, the decreasing of pH can be explained by the acidic character of Fe3+ (acid of Lewis) by reacting with OH- ions of the pig slurry to iron precipitate in form of Fe (OH)3 *(O'Melia.C.R, 1969).*

Some water quality parameters, such as pH and temperature, influence the coagulation process. For example, the pH can affect the effectiveness of the particle destabilization process and the temperature effects on the viscosity of water, which can influence the coagulation procedure *(Bratby, 2006)*.

The optimal pH range for coagulation using the iron is 5.5 to 6.5. For high alkalinity water an extra amount of coagulant may be required to lower the pH in order to reach the optimal pH range *(EPA, 2020),* thus, it will be helpful to adjust the pH with adding an acid before the coagulant to reduce the amount of coagulant needed and effectively lower chemical costs.

4.3 Optimum combination of coagulant-flocculent-pH

As described above, to begin with, a full model with block and second order terms of coded variables coagulant, flocculent and pH with interactions was fitted to COD and turbidity reduction. As described above, to begin with, a full model with block and second order terms of coded variables coagulant, flocculent and pH with interactions was fitted to COD and turbidity reduction. The blocking factor was found to have no significant effect, neither did the flocculent. The model was consequently simplified to a second order model with coagulant and pH with interaction. The interaction term coagulant*pH was discarded as no significant. The first order term coefficients of coagulant and pH were also found to be non-significant but were preserved in the response surface model to add flexibility.

The coded variables x1 and x3 are:

x1 = (Coag - 0.026) / (0.026 - 0.024753)

x3 = (pH – 7.74) / (7.74 - 7.5779)

For COD removal, the final selected model was

```
## Estimate p-value
## (Intercept) 81.20699   < 2e-16 ***
## x1         0.13265    0.87866
## x3         -0.16301   0.85120
## x1^2        1.92674   0.03388 *
## x3^2        2.29649   0.01354
```

A contour plot of the final fitted response surface is to be found in *Figure 14.*

Table 2. Experiment design table results

Run order	Coag mol L^{-1}	Floc µl	pH	Blk
1	0,0248	164,9	7,90	1
2	0,0260	140,0	7,74	1
3	0,0248	115,1	7,58	1
4	0,0260	140,0	7,74	1
5	0,0272	115,1	7,90	1
6	0,0272	164,9	7,58	1
7	0,0260	140,0	7,74	1
1	0,0272	115,1	7,58	2
2	0,0260	140,0	7,74	2
3	0,0260	140,0	7,74	2
4	0,0272	164,9	7,90	2
5	0,0260	140,0	7,74	2
6	0,0248	164,9	7,58	2
7	0,0248	115,1	7,90	2
1	0,0260	180,0	7,74	3
2	0,0240	140,0	7,74	3
3	0,0260	140,0	7,74	3
4	0,0280	140,0	7,74	3
5	0,0260	140,0	7,74	3
6	0,0260	140,0	7,74	3
7	0,0260	140,0	8,00	3
8	0,0260	100,0	7,74	3
9	0,0260	140,0	7,48	3

Table 3. Composition of various experiments of the central composite design, cod reduction and turbidity removal responses for pig slurry treatment

Run.order	Coag mol L^{-1}	Floc µl	pH	%COD removal	% TURB removal
1	0.024	164.94	7.90	85.57	99.76
2	0.026	140	7.74	82.10	98.29
3	0.024	115.06	7.57	85.79	99.15
4	0.026	140	7.74	80.98	99.83
5	0.027	115.06	7.90	88.59	99.07
6	0.027	164.94	7.57	87.13	97.95
7	0.026	140	7.74	77.62	99.78
1	0.027	115.06	7.57	86.01	99.86
2	0.026	140	7.74	83.10	98.57
3	0.026	140	7.74	72.03	99.86
4	0.027	164.94	7.90	84.45	99.82
5	0.026	140	7.74	80.98	98.48
6	0.024	164.94	7.57	88.25	99.90
7	0.024	115.06	7.90	84.11	97.94
1	0.026	179.99	7.74	83.22	99.74
2	0.024	140	7.74	85.12	99.77
3	0.026	140	7.74	85.34	98.13
4	0.028	140	7.74	84.67	99.89
5	0.026	140	7.74	84.00	96.32
6	0.026	140	7.74	78.74	99.88
7	0.026	140	7.99	86.57	99.94
8	0.026	100	7.74	83.66	97.30
9	0.026	140	7.48	85.12	99.88

An appropriate combination of the three factors is desirable to obtain a high efficiency of treatment. To seek the optimal conditions of these factors the central composite design method (CCD) using the R statistical software is not only time and energy consuming, but also is a significant, fast, and economical statistical technique for the determination of the interactive effects of parameters on experimental data. In order to reduce the number of experiments, the CCD methodology was used, and the number of experiments that the statistical were 23 *(Table 2)* this table offers a better alternative to the conventional method because it includes the influences of individual factors as well as the influences of their interaction. Based on *(Table 3)*, COD and turbidity removal obtained after realizing the 23 experiments using the same methodology described in coagulation flocculation experiments. As is shown in *(Table 3)*, the turbidity removal is high for all experiments, it ranges from 96.3% to 99.9% which shows that none of the three factors significantly affect the turbidity removal, while the COD removal varies from 72.0% to 88.6%, which means that it is possibly affected by the three factors which are pH and coagulant and flocculent doses.

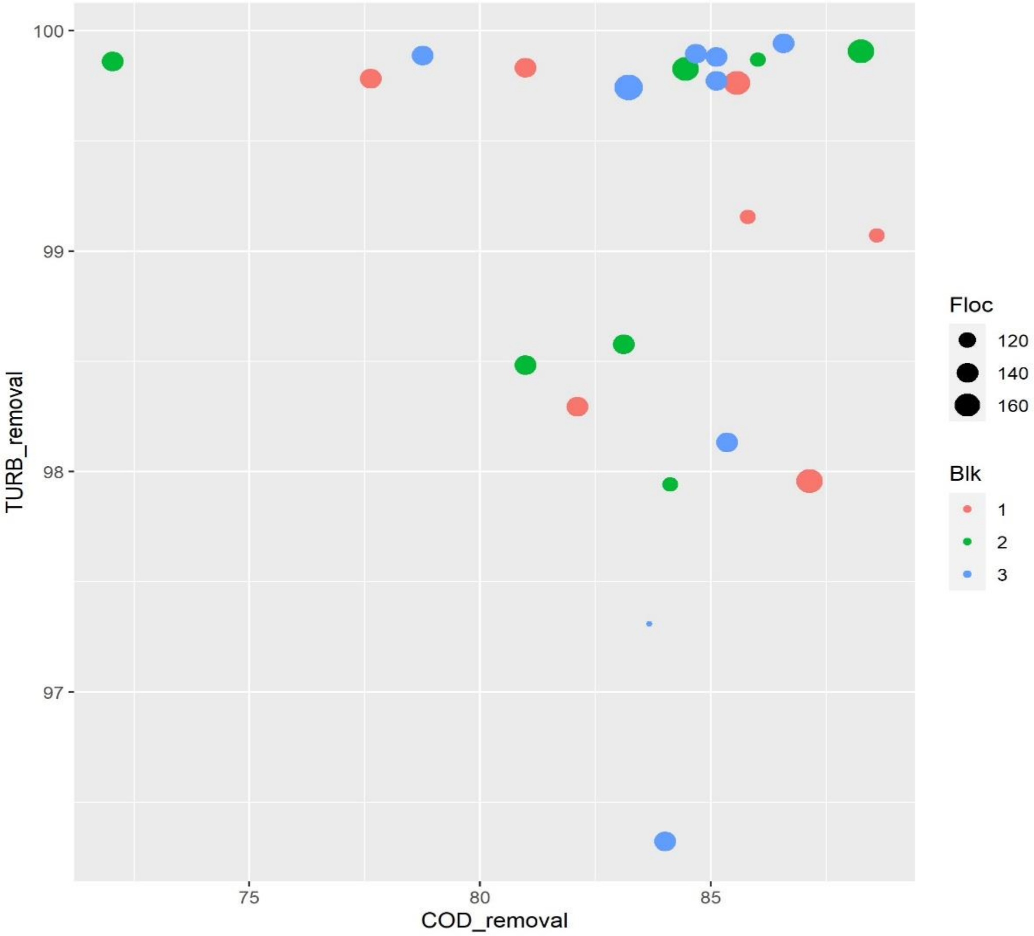


Figure 11. Effect of flocculent concentration on COD and turbidity removal

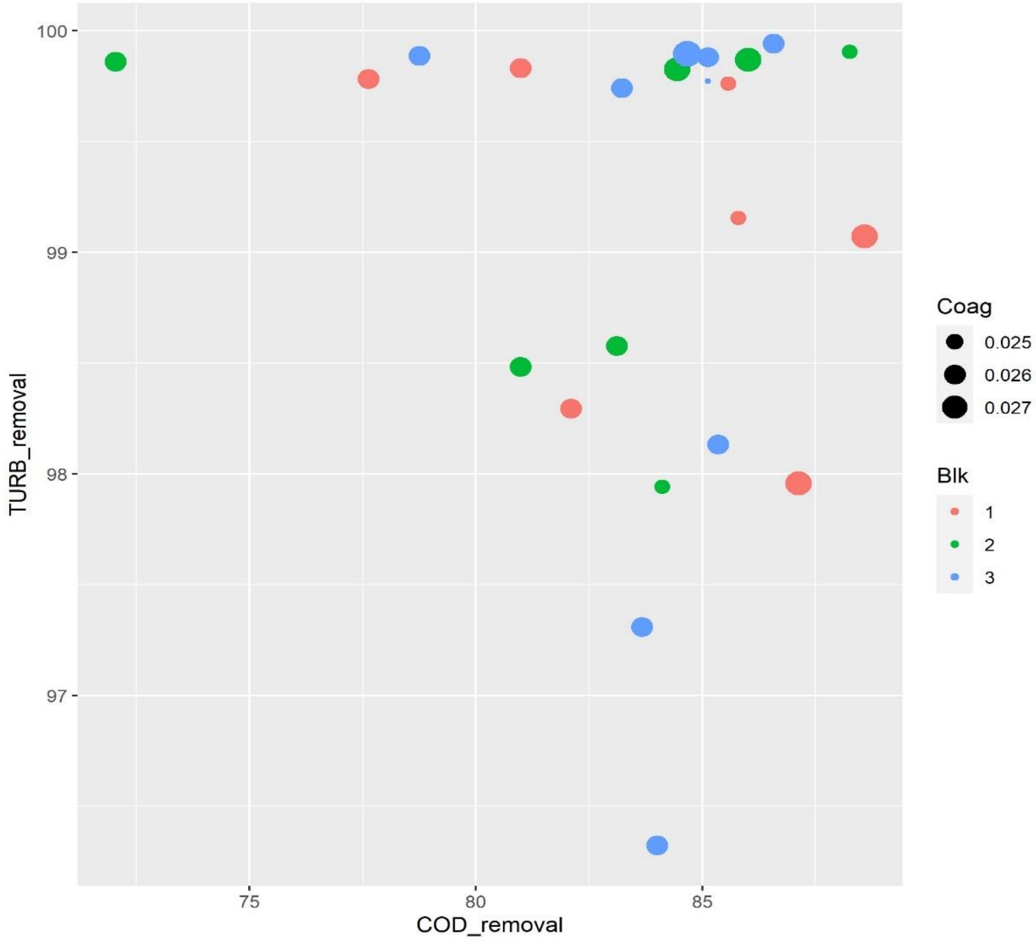


Figure 12. Effect of coagulant concentration on COD and turbidity removal

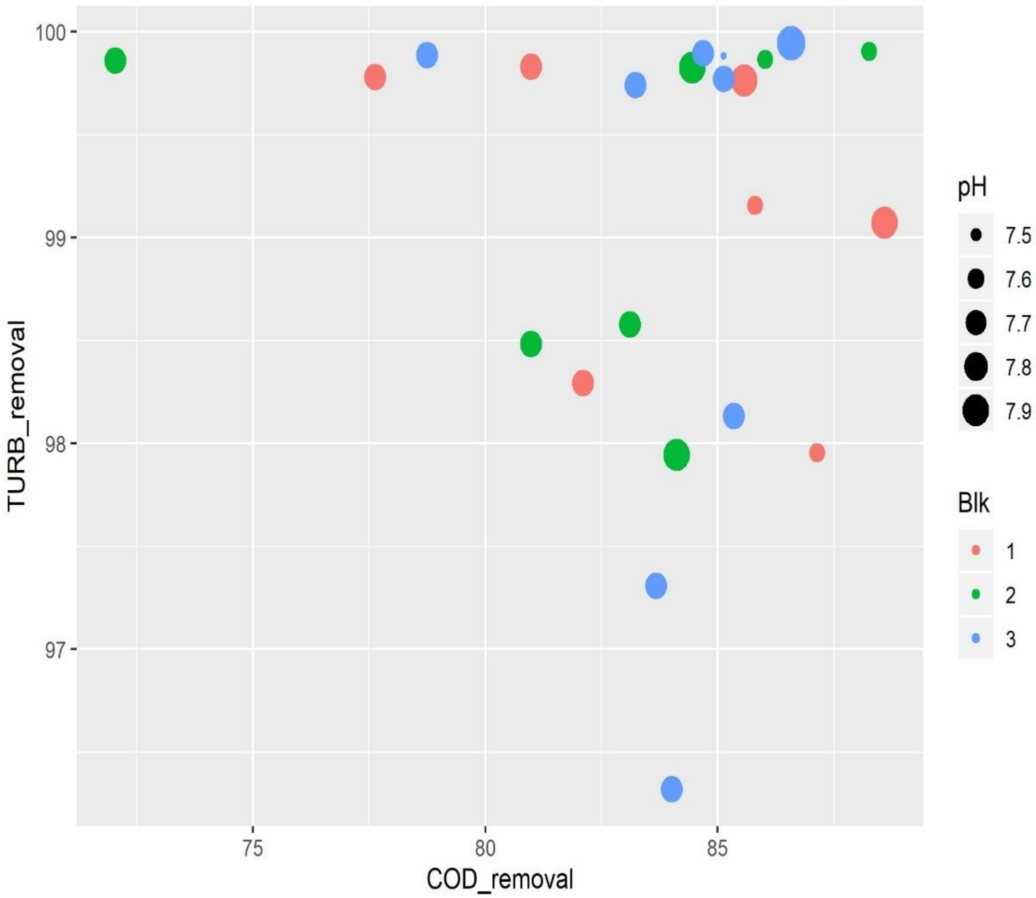


Figure 13. Effect of pH on COD and turbidity removal

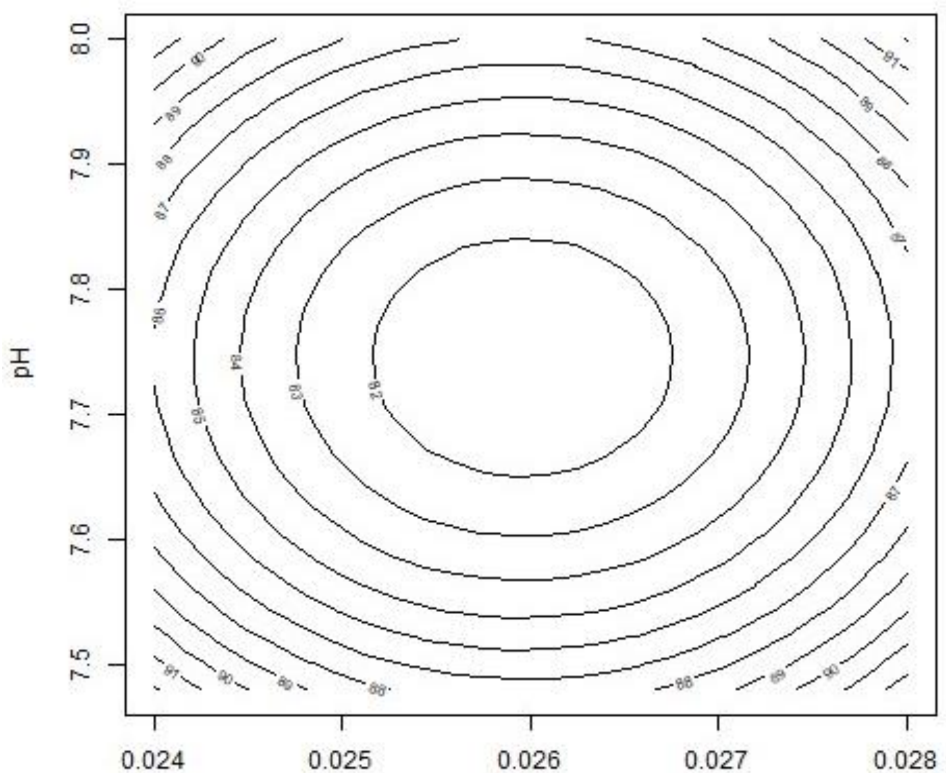


Figure 14. Effect of pH and coagulant concentration on cod removal

The two figures *(Figure 11,Figure 12)* show the joint variation of the two responses COD and turbidity % removal, where the size of the points relates to each of the three factors. The influence of different dosages of flocculent and coagulant on turbidity and COD removal efficiency is shown in *(Figure 11)*. The ''no significant'' message that shows the statistical model indicate that the flocculent concentration has no significant effect on COD and turbidity removal, the two responses maintained a high reduction using all the different flocculent concentrations of the selected range. The minimum percentage of COD removal is more than 70%, and 93 % for the turbidity. Therefore, according to the results showed on *(Figure 11)* and *(Table 3)*, the flocculent concentration range has no significant effect on the two responses. therefore, it can be ignored as a variable.

Many authors (Al-Hamadani, Yusoff, Umar, Bashir, & Adlan, 2011; Rasool, Tavakoli, Chaibakhsh, Pendashteh, & Mirroshandel, 2016) and *(Lecomte et al., 2017)* agree on the changes in the coagulant dosage is an effective factor on the COD reduction. As it can be seen from *(Figure 12)*, COD removal efficiency varies between 72% and 89%, therefore, the coagulant concentration has significant effect on COD reduction. Turbidity reduction percentage retains high on all the coagulant concentration range while the minimum reduction percentage is around 98%, on that account, the range of the coagulant concentration has no significant effect on the turbidity removal, but it effects on the COD % removal.

As a result of *Figure 11* and *Figure 12*, flocculent not significantly effect on COD and turbidity removal, while coagulant dose effect only the COD removal. The flocculent concentration can be ignored as a variable and can be chosen directly from *(Table 3)* which corresponded to the optimal conditions of the coagulant dose and pH.

In addition to coagulant and flocculent parameters, pH also can highly effect on the turbidity and COD removal and it can be an important parameter in the coagulation of the organic matter regarding to (Boughou, Majdy, Cherkaoui, Khamar, & Nounah, 2018). Results presented in show the effect of pH on the turbidity and the COD percentage removal. Many authors *(Al-Hamadani et al., 2011; Irfan et al., 2017)* agree that the pH influences the COD and turbidity reduction.

The pH range proposed by the experience plan was too small to have any significant effects on the turbidity response, while it retains high percentage of 96% to 99% for all the pH range from 7.4 to 8.

In contrast, the pH small range has a significant effect on the COD removal which confirms *(Al-Hamadani et al., 2011; Irfan et al., 2017; Rasool et al., 2016)*, achieving 71% as minimum percentage removal and around 90% as a maximum percentage removal. The best COD reduction yields were observed at two different pH ranges with a significant reduction of almost 90%. this reduction can be interpreted by the removal of the organic matter under the effect of chloride ferric *(Boughou et al., 2018)*.

On that account and basing on Figure 13, the response turbidity can be ignored due to its high percentage in different pH and coagulant and flocculent concentrations values proposed by the statistical model *(Table 3)*. Thus, our focus will be more on the COD reduction that shows a greater variability. Hence, based on *Figure 11, Figure 12 and Figure 13,* choosing the optimum points will depend on only 2 variables: pH, coagulant concentration and on only one response which is COD % removal.

As reported by *(Bratby, 2006)* the pH is one of the most important factors in coagulation process, at the optimum pH, normally the coagulant produces the most efficient hydrolysis species, which is responsible for the pollutant removal. From *(Figure 13)* and *(Figure 14)* it´s clear that pH and coagulant concentrations have a great effect on the COD % removal.

The results showed in *(Figure 14)* indicate that initially the COD % removal increase in two different ranges of pH, first range is below pH 7.6, where the COD % removal reach till 91%, and the second range is pH up to 7.9, where the COD% removal could reach till 91%. In contrast, in the range between 7.6 and 7.9 the COD% removal knows the minimum value, which is between 82% and 85%, therefore this graph perfectly explains the pH range function of the chloride iron coagulant explained previously.

The coagulant doses proposed by the design of experiments is between 0.024 mol L^{-1} and 0.028 mol L^{-1}, using the 0.026 mol L^{-1} as a center of the design, regarding *(Figure 14)*, two coagulant doses ranges yield the same results at pH below 7.5 and above 7.9, the first range is between 0.024-0.025 mol L^{-1} and the second is 0.027-0.028 mol L^{-1}, while between 0.025 and 0.027 mol L^{-1} it couldn't reach more than 87% as the maximum and 82% as minimum COD % removal.

The COD% removal increases with the coagulant doses increment and decreases with a surmount above the optimum dose according to several researcher *(Irfan et al., 2017; Tahereh Zarei et al., 2018; Tawakkoly et al., 2019).* Sometimes the surmount can gives the same results as the optimum but with higher sludge volume and certainly with a higher *cost (Patel & Vashi, 2013; Subramonian & Wu, 2014)*.

Therefore, choosing the smallest concentration as optimum dose can be explained with the objective of reducing the dosing costs and the sludge volume in the treatment process *(Patel & Vashi, 2013; Subramonian & Wu, 2014)* to that end the 0.024 mol L^{-1} will be the optimum concentration for the coagulant.

As it can be seen in *(Figure 14)* COD % removal could reach 82% to 88% in a two different pH ranges, around 7.5 and above 7.9, choosing a unique pH value is necessary. Acidification has been demonstrated as an effective way to reduce GHG and NH3 emissions *(Kavanagh et al., 2019)*, therefore, acidification though adding chemical agents such as ferric chloride (FeCl3) and achieve the pH closest to 5.5 will reduce GHG and NH3 *(Husted & Husted, 1995; Kavanagh et al., 2019)*. Based on this scenario, we will choose the small pH value 7.5 as the optimum pH to treat our pig slurry.

Therefore, based on *Figure 11, Figure 12,Figure 13* and *Figure 14* the optimal coagulant dose of 0.024 mol L^{-1} at pH 7.5 are the optimal conditions to treat our slurry taking into considerations that the flocculent concentration .

5. Conclusions of the coagulation flocculation treatment

In this work, the coagulation–flocculation process with Chloride ferric as coagulant and DKFLOCC-1598 as a cationic flocculant was used for the treatment of pig slurry and it has been found to be a highly effective coagulant, flocculent for this type of the pig slurry. To minimize turbidity and COD, a central composite design method (CCD) using the R statistical software was employed to optimize the levels of coagulant dosage, flocculant dosage and pH.

Results reveal that the optimal conditions for the minimum turbidity and COD were coagulant dosage of 0.024 mol L^{-1}, flocculant dosage of 0.1649 ml L^{-1} at pH 7.5. Regarding to the CCD results, those concentrations can achieve 88.25% of COD removal and 99% of turbidity removal *(Figure 16,Figure 17),* beside the EC that also could be reduced by a percentage of 12% . The verification experiments proved and demonstrated that the CCD approach was appropriate for optimizing the coagulation-flocculation process by getting the same removal rate of COD and Turbidity.

It is also worth mentioning that the high turbidity removal has a positive impact and highly recommended in terms of minimizing clogging risk of the CWs.

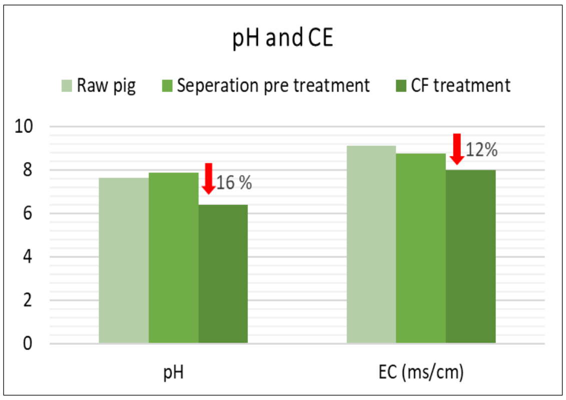


Figure 15. pH and CE before and after the treatment

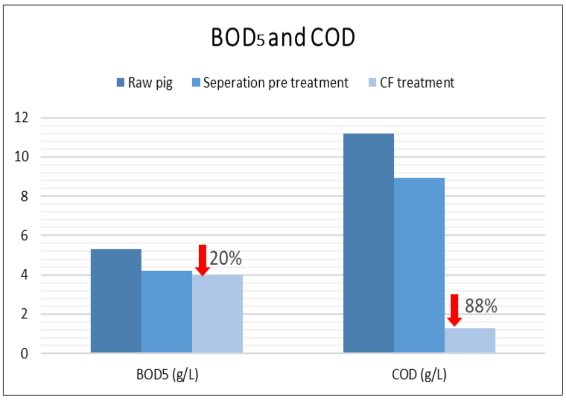


Figure 16. BOD5 and COD % removal

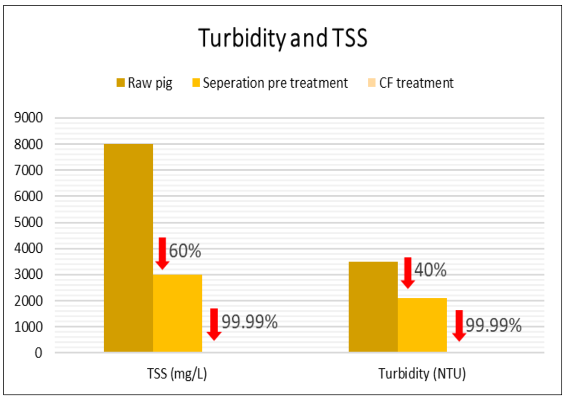
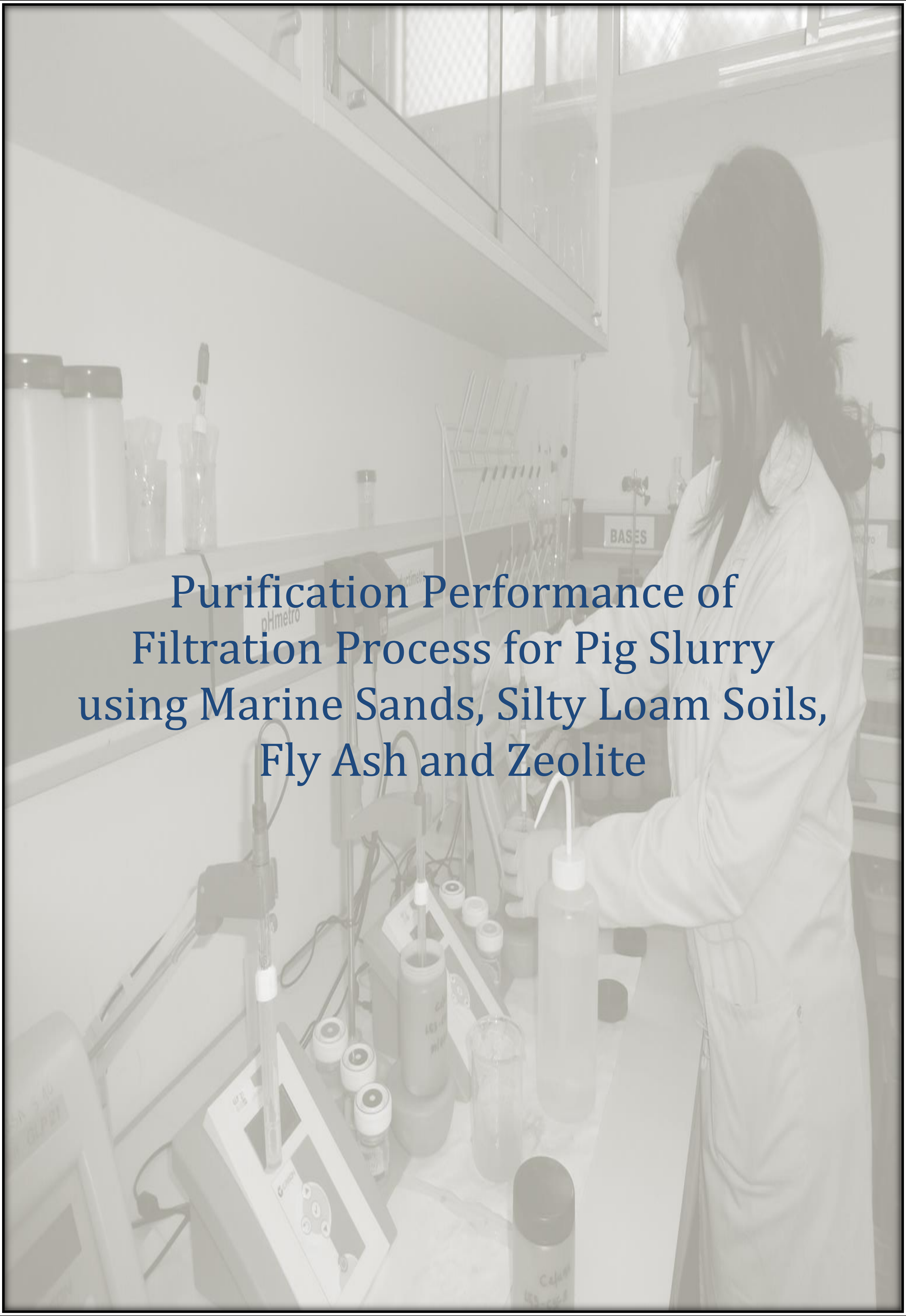


Figure 17. Turbidity and TSS removal



Purification Performance of Filtration Process for Pig Slurry using Marine Sands, Silty Loam Soils, Fly Ash and Zeolite

V. Purification Performance of Filtration Process for Pig Slurry using Marine Sands, Silty Loam Soils, Fly Ash and Zeolite

1. Introduction

Treatment plants have different methods of extracting metallic "micronutrients" from pig slurry that are then turned into fertilizer. These methods employ physicochemical, biological, or activated sludge processes. Choosing the right treatment technique depends on various factors, such as the size of the facility, its installation and maintenance costs, required depuration level, and organic matter and nutrient removal (Petersen et al., 2007). However, one of the newest and most economic techniques is a constructed wetland (CW) (Lecomte et al., 2017). Various studies (Huang et al., 2019; Liang et al., 2017) proved that it can successfully treat wastewater from agriculture, aquaculture, and industry and showed that a CW can reduce 85% of total suspended solids (TSS), and 80 % of the total Kjeldahl removal of nitrogen and phosphorus, and a 33% of the manure's chemical oxygen demand (COD). However, the CW was not able to reduce electrical conductivity or water hardness, two factors that can limit the reuse of treated pig slurry, especially as a fertilizer.

The CW extends from the surface down through 0.30 m of washed sand, 0.10 m of fine gravel, 0.50 m of coarse gravel and 0.30 m of fine gravel *(Figure 18).* A new layer will be added in the third position from the top just after the fine gravel. The aim of this work is to increase the vertical flow efficacy by adding one or more new layers of marine sands, silty loam soils, fly ash or zeolite. A specific study of a pig slurry filtrate will be realized to determine the capacity of each material to reduce pig slurry pollution loads. The selection of the materials was determined by two criteria. First, they had to be low cost to make them technically and financially sustainable and to induce big and small farmers to install an in-situ treatment plant. Second, the richness of the materials in very fine mineral constituents (ferric anion and silica) makes them more active in solution and gives them high adsorbency *(De Gisi, Lofrano, Grassi, & Notarnicola, 2016).*

Fly ash is rich in silica, according to Miricioiu *(Miricioiu & Niculescu, 2020)* so it can be considered a potential raw material for synthesizing nanoporous materials, such as zeolites or mesoporous silica. It also has a high adsorbency potential, making it ideal for wastewater treatment, and its direct use can significantly reduce environmental damage due to its disposal *(Miricioiu, Niculescu, Filote, Raboaca, & Nechifor, 2021).*

Concerning the waste from the concentrated slurry, it was concentrated again using EVACOLD equipment to derive a high-nutrient fertilizer.

2. Specific objectives

Our focus was to find a new layer to add to the flow of our vertically constructed wetland to improve efficiency, to study how the pig slurry reacted to the different natural materials, and to compare the results with the CW. Various authors (de Matos, von Sperling, & de Matos, 2018; Vymazal, 2018) studied clogging, percolation flow rate, long-term clogging and rest period and found that a CW can operate for 15 years. Clogging is inevitable, but it can be resolved by a good pretreatment proposed in the first chapter of this thesis.

3. Materials and methods

3.1 Experimental design

The treatment system consists of the purification process based on a physical separation combined with a modified constructed wetland, in order to produce a purified effluent to be applied to agricultural soil, reducing the consumption of water and inorganic fertilizers and minimizing the emissions of gases and energy consumption.

The experimental device consisted of a glass column 10 cm in diameter and 50 cm in height. The effective height of the filter bed was 30 cm, 70% of which was used for the filter material (H material = 20 cm) and 30% for the raw pig slurry (H effluent = 10 cm). This column was fed from the top by adding around 800 mL of liquid pig slurry which corresponded to the 30% of the effective height of the filter bed at ambient temperature. This volume of pig slurry was left to flow through the filter materials, and the method used was based on slow filtration (Verma, Daverey, & Sharma, 2017). The inflow and outflow rates did not depend on time or any other parameter (Sanft & Walter, 2020), so the slurry passed under a constant load through the filter bed (10 cm diameter and 20 cm in height). The upper part of the column (a) was open to maintain water flow, and the bottom of the column was closed with a porous plate.

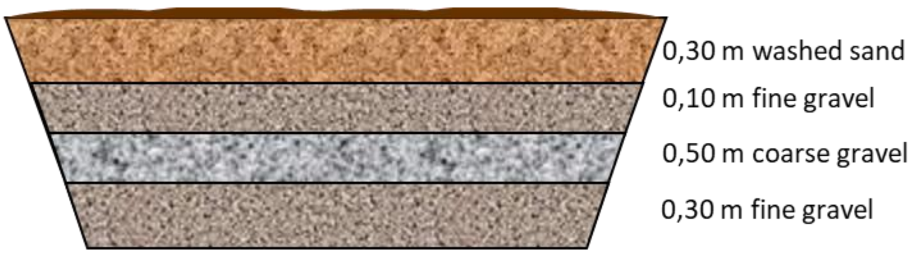


Figure 18. Constructed wetlands composition

Every 24 h we added the same volume of pig slurry under the same conditions for three days. The pig slurry was collected and analyzed after every treatment cycle. The treated slurry was sampled from the filter outlet (b) *(Figure 19).*

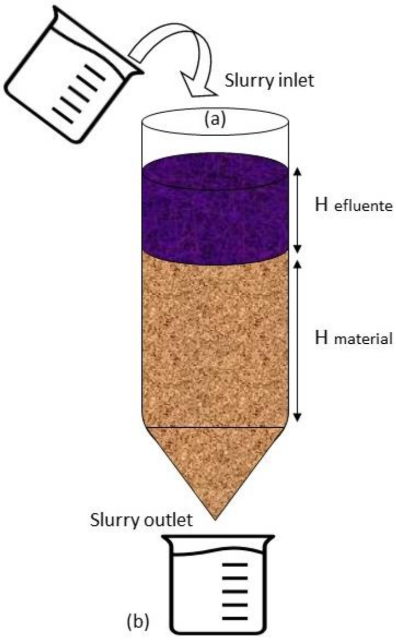


Figure 19. Experimental device

3.2 Pig slurry sample collection and analysis

This sample was transported directly to the laboratory and stored at 4 °C. Later, only the liquid fraction was used for analysis.

i. pH and electrical conductivity

The pH and EC were measured by a laboratory research-grade benchtop pH/mV and EC/TDS/Salinity/Resistivity Meter-HI5521 *(Photo 10, Photo 11).*

ii. Total suspended solids (TSS)

Total suspended solids (TSS) were filtered through a weighed standard glass–fiber filter and the residue retained in the filter was dried to a constant weight at 105 °C (2440-D method, APHA–AWWAWEF 2012) *(Photo 12).*

iii. Chemical and biological oxygen demand (COD and DBO5)

Biochemical oxygen demand in five days (BOD_5) was determined by manometer OXITOP WTW equipment *(Photo 15)*. Chemical oxygen demand (COD) was determined by photometric determination of the chromium (III) concentration after 30 min of oxidation with potassium dichromate/sulfuric acid and silver sulphate at 160 °C (Macherey–Nagel GmbH & Co. KG. Nano color Test, Ref 985 028/29), (DIN 38 409-H41-1, DIN ISO 15 705-H45) *(Photo 14).*

iv. Total Nitrogen

Kjeldahl nitrogen (KN) was determined by a modified Kjeldahl method (Duchaufour, 1970) using 1 mL of pig slurry in the digestion with sulfuric acid and a catalyst mixture during 40 minutes at 400 °C, then leave it to cool down and distilled. Finally, it is titrated with 0.1 N hydrochloric acid to get the final value result.

Ammonium nitrogen (NH^{4+}–N) is obtained following the Kjeldahl method, but without digestion.

Nitrate (NO^{3-}) and Nitrite (NO^{2-}) were determined as soluble anions using the ion exchange chromatography technique.

Total nitrogen (TN) included organic and inorganic forms (Kjeldahl nitrogen plus nitrites and nitrate forms).

Photo 19. BUCHI K-350 Distillation Unit (reference BUCHI 043500)

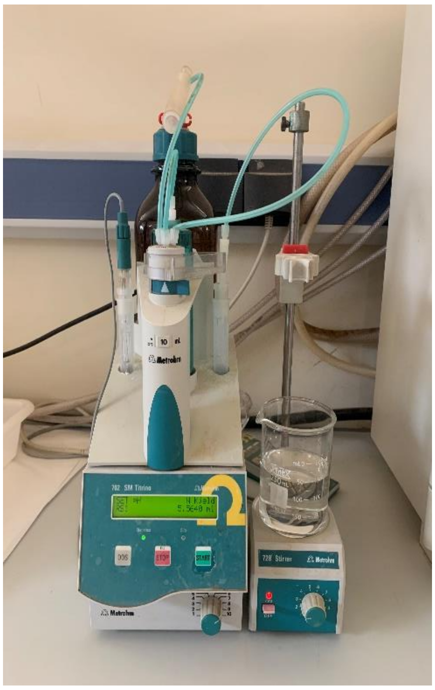


Photo 20. Eco KF Titrator (Reference 2.1027.0010)

i. Anions and cations

Anions were analyzed by high-performance ion chromatography (IC) (Methrom, model 861), and cations were determined using atomic absorption spectrometer (PerkinElmer AA-Analyst, 800).

Photo 22. Advanced Compact IC (Methrom, model 861)

i. Heavy metals

Heavy metals were analyzed using inductively coupled plasma mass spectrometry (ICP–MS), using Agilent 7900 (Perkin Elmer AA-Analyst 800).

Photo 23. Coupled plasma mass spectrometry (ICP–MS), using Agilent 7900 (Perkin Elmer AA-Analyst 800)

i. Filter substrates analysis techniques

For the filter substrates, different analysis techniques were performed: particle size analysis by laser diffraction using MASTERSIZER equipment (reference 2000LF), and mineralogical analysis by X-ray diffraction (XRD), and chemical analysis by X-ray fluorescence.

Photo 25. Bruker S4 Pioneer (XRF) spectrometer

Photo 24.Bruker D8 Advance X-ray Diffractometer (XRD)

3.3 Characterization of the filtration materials

The materials used for filtration were four soils, two marine sands, zeolite, and fly ash.

Two types of soil were collected from a pottery company in the Alicante region. After fabrication, the soils lost their principal characteristics and could not be recycled so returning them to nature was the only way to eliminate soil waste. The choice of this material was justified because of the abundance of these soils in the region. and the fact that it met the selection criteria of being more active in solution, being highly adsorbent power (De Gisi et al., 2016) and containing ferric ions.

The marine sand was collected along the Mediterranean coast of La Manga, washed with distilled water, and dried at 40 °C for 48 hours.

Natural zeolite was purchased from ZeoCat, (reference 1217-10-3), and the fly ash was purchased from a Barcelona cemetery.

i. pH and EC of the filtration materials

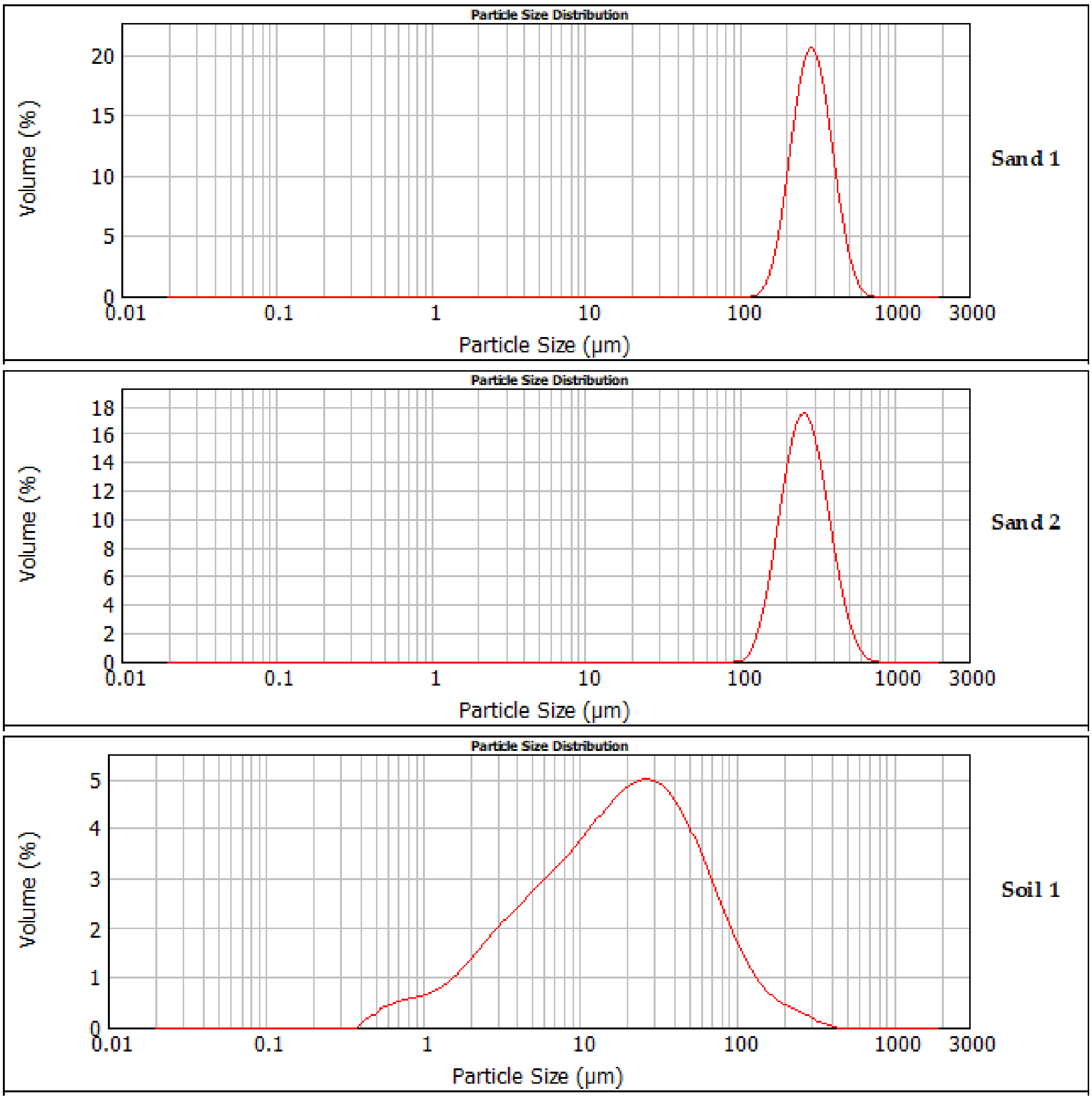
All the materials had a basic pH between 9.02 and 9.96, except fly ash which was considered very basic (12.10) *(Table 4).* The electrical conductivity of the two sands, soil 2, soil 4 and zeolite was very low, varying between 0.1 and 0.3 ms cm^{-1}; soil 1 and soil 3 had high conductivity (1.61 and 2.29 ms cm^{-1}, respectively) while fly ash had the highest EC of 6.30 ms cm $^{-1}$. The pH and EC of the filter material is very important because they directly affect the pH and EC of the filtered effluent (Ncube, Pidou, Stephenson, Jefferson, & Jarvis, 2017).

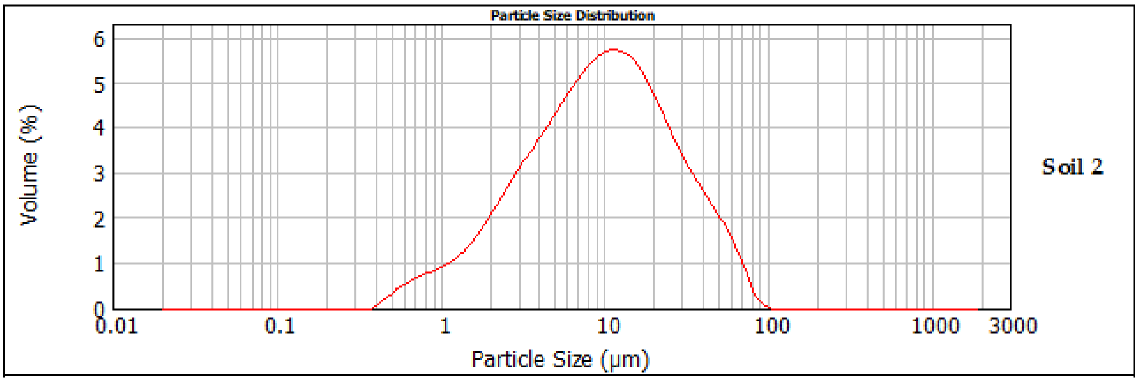
Table 4. The pH and electrical conductivity of the filter materials

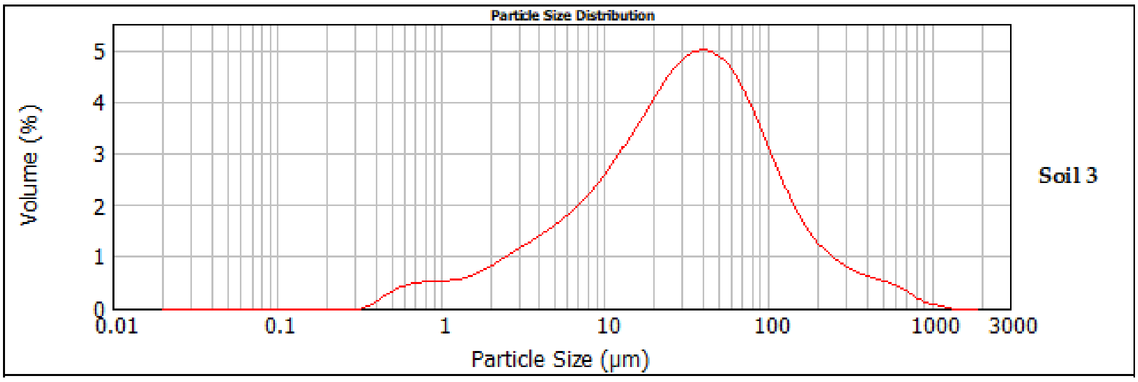
Material	Sand 1	Sand 2	Soil 1	Soil 2	Soil 3	Soil 4	Fly Ash	Zeolite
pH	9.69	9.52	8.60	9.10	8.46	8.42	12.10	9.02
EC (ms cm^{-1})	0.10	0.35	1.61	0.46	2.29	0.39	6.30	0.30

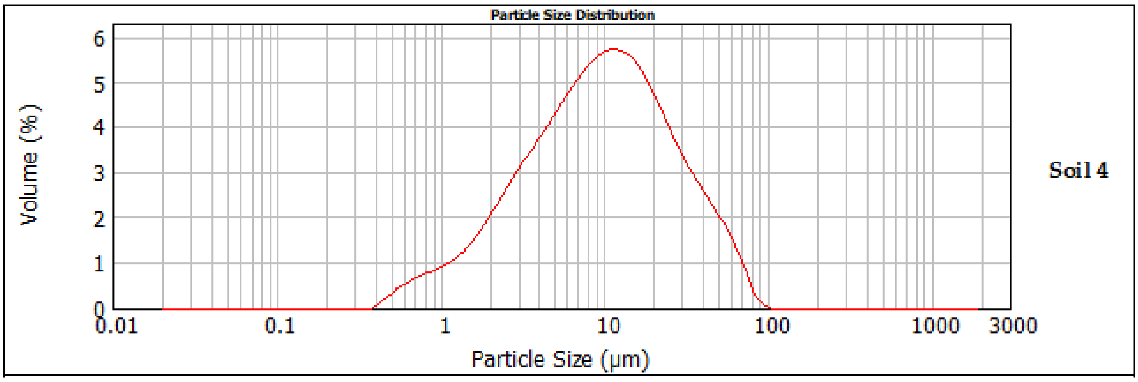
ii. Particle size

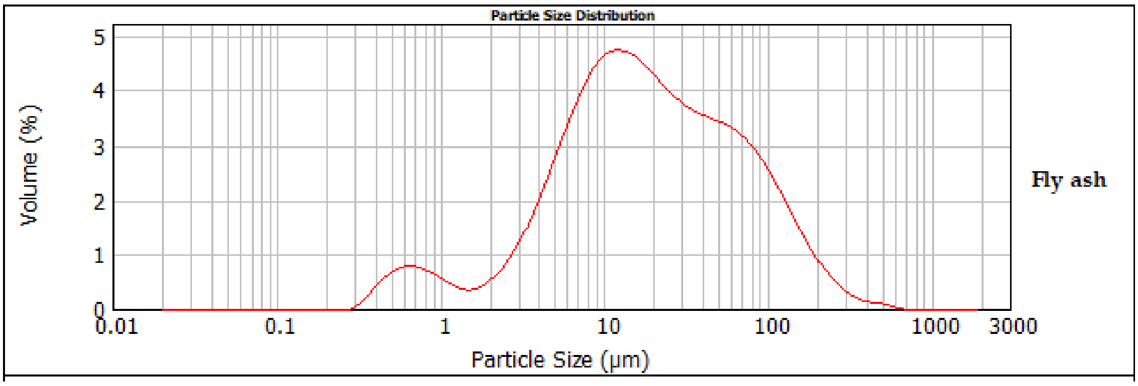
Size distribution curves were established by laser diffraction, representing the particles size of each material. The results indicated that sand 1 and sand 2 had almost the same particle size, 150 µm, with a uniform coefficient of 1.67 and 1.55, respectively. Soil 1, 2 and 3 were silt loam soils while soil 4 was a silt soil. Their particle size varied between 20 and 50 µm.




Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
0.01
0.1
1
10
100
1000
3000
Particle Size (μm)
Soil 2


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
0.01
0.1
1
10
100
1000
3000
Particle Size (μm)
Soil 3


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
0.01
0.1
1
10
100
1000
3000
Particle Size (μm)
Soil 4


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
0.01
0.1
1
10
100
1000
3000
Particle Size (μm)
Fly ash

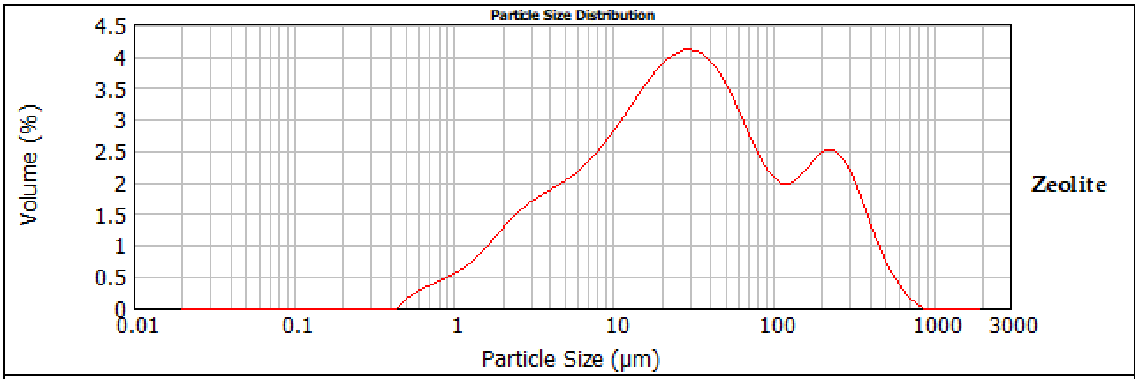


Figure 20. Particle size distribution curves of the filtration materials

iii. Mineralogy of the filter materials

Figure 21 and *Table 5* shows the mineralogy of the filter materials. The two sands contained various chemical compounds, the most significant concentrations of which were silica (SiO_2) and calcite ($CaCO_3$) for both, as described in the mineralogical analysis in Table 2. X-ray spectra analysis showed that the soils were mostly composed of quartz, followed by muscovite. The chemical composition of soils (1-4) consisted principally of silica in quartz and substantial amounts of alumina, calcium oxide, and ferric oxide. The first component of the fly ash, as shown in *Figure 21*, is mullite ($Al_{4.5}Si_{1.5}O_{9.75}$), which presented the highest percentage of 57%. In the second position was quartz (SiO_2) 24%, followed by gypsum ($CaSO_4.2H_2O$) 9%. According to El Fadel and Kim, the two high peaks are explained by the coal mineralogy of the fly ash Fly *ash (K. H. Kim, Yoon, & Park, 2014)* had a total of elements percentages $\Sigma(SiO_2\%+Al_2O_3\%+Fe_2O_3\%)$ = 86.35%, which was classified among the silicon-aluminum ash, Class F, according to Coal Ash *(American Coal Ash Association, 2017)* and ATSM *(ASTM, 2018)* Standards.

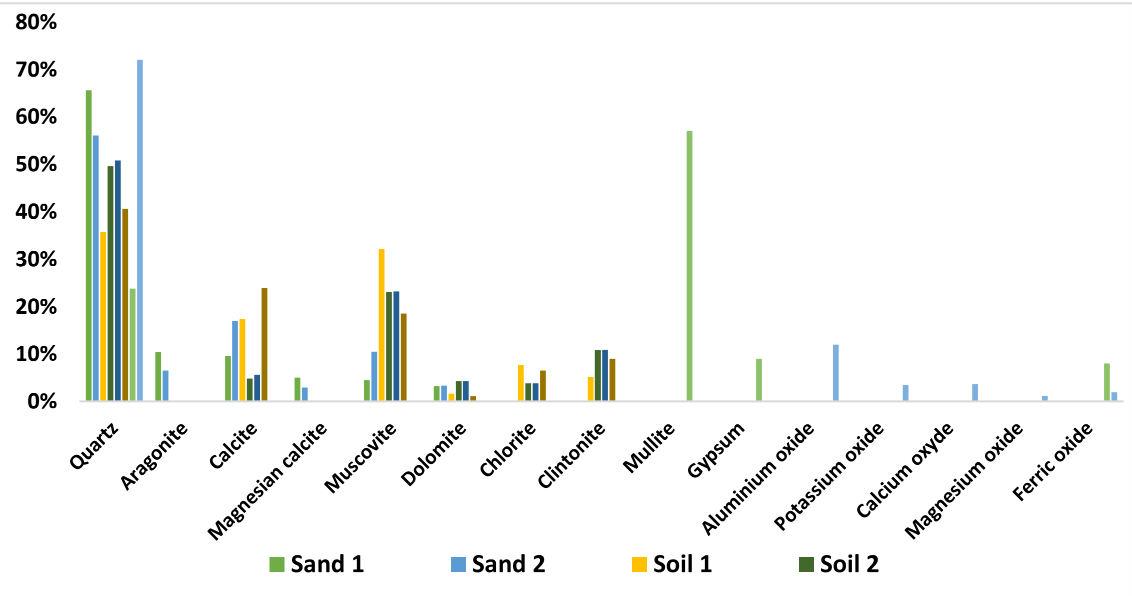


Figure 21. X-ray diffraction pattern of the filter materials

Quartz (SiO2) presented the highest value in zeolite mineralogy (72%), followed by aluminum oxide (Al2O3) (12%), while magnesium oxide (MgO) presented the lowest value (1.20%). The two peaks explained the natural aluminosilicate origin of the zeolite *(Rinaldi, 1983)*. Based on the chemical composition of the zeolite as shown in *Table 5*, the silica-to-aluminaratio was 5.382, making it a Faujasite zeolite. According to Martinez *(Porosity, Or-, & Corma, 2013)* standards, this type has larger zeolitic pores (0.74 nm) *(Wolińska-Grabczyk & Jankowski, 2015).*

Table 5. Geochemical composition of filter materials (%)

Compounds	Sand 1	Sand 2	Soil 1	Soil 2	Soil 3	Soil 4	Fly Ash	Zeolite
SiO2 (%)	34.5	32.9	37.3	48.9	48.6	41.1	40.9	64.7
Al_2O_3 (%)	1.36	2.34	12.5	17.5	18.1	14.9	26.5	12
Fe_2O_3 (%)	2.79	9.18	5.23	8.55	8.27	6.68	18.9	1.43
CaO (%)	34.5	31.2	19.8	5.89	5.69	14.5	6.01	4.12
MgO (%)	1.64	1.27	2.72	2.59	2.81	1.47	0.94	0.94
SO3(%)	0.23	0.22	0.14	0.24	0.40	0.25	1.74	0.04
K_2O (%)	0.30	0.52	2.81	0.06	5.16	3.10	2.04	2.65

4. Results and discussion

4.1 Physical chemical characterization of raw pig slurry

The characteristics of animal manure vary considerably among and within species according to country, farm, production method, feed composition and water consumption *(Boursier et al., 2005)*. *Table 6* presents the physicochemical results of the raw and treated pig slurry by different materials.

Table 6. Physicochemical results of the filtered pig slurry

	pH	EC (ms cm^{-1})		TSS (g L^{-1})		NK (g L^{-1})		N-NH4 + (g L^{-1})		Turbidity (NTU)		COD (g L^{-1})		BOD_5 (g L^{-1})	
PS	7.46–7.65	7.75	±0.14	81	±1.93	0.62	±0.11	0.52	±0.07	2000	±75.5	5.19	±0.47	4.09	±0.38
Sand 1	8.29–9.28	7.18	±0.11	3	±0.14	0.47	±0.02	0.42	±0.02	300	±8.66	1.3	±0.15	0.8	±0.05
% reduction		7%		97%		25%		19%		85%		74%		80%	
Sand 2	8.85–9.10	5.2	±0.25	6	±0.08	0.47	±0.08	0.28	±0.03	350	±22.27	1.09	±0.09	1.04	±0.20
% reduction		33%		93%		25%		46%		83%		80%		75%	
Soil 1	7.60–8.20	3.69	±0.06	2	±0.05	0.07	±0.00	0.05	±0.00	180	±4.63	0.98	±0.05	0.81	±0.03
% reduction		52%		98%		89%		90%		91%		80%		80%	
Soil 2	8.10–8.80	16.09	±0.11	5	±0.14	0.063	±0.01	0.03	±0.00	175	±3.06	1.07	±0.13	0.52	±0.04
% reduction		-108%		94%		90%		94%		91%		80%		88%	
Soil 3	8.11–8.81	6.95	±0.03	7	±0.15	0.05	±0.00	0.04	±0.00	160	±8.62	1.42	±0.08	0.64	±0.05
% reduction		10%		91%		91%		93%		92%		72%		85%	
Soil 4	8.00–8.67	9.44	±0.25	10	±0.15	0.06	±0.01	0.02	±0.00	195	±3.79	1.44	±0.20	0.71	±0.05
% reduction		-22%		88%		90%		96%		90%		72%		82%	
Fly Ash	11.60–12.40	9.44	±0.18	0	±0.00	0.42	±0.02	0.2	±0.01	100	±11.55	1.06	±0.06	0.11	±0.01
% reduction		-22%		99.99%		33%		61%		95%		80%		98%	
Zeolite	7.40–7.80	2.73	±0.07	0	±0.00	0.01	±0.00	0	±0.00	120	±11.02	0.52	±0.05	0.1	±0.00
% reduction		65%		99.99%		98%		99.99%		94%		90%		99.99%	
CW	7.38–7.5	6.65	±0.03	7	±0.12	0.4	±0.06	0.25	±0.03	400	±11.55	1.01	±0.06	1.51	±0.15
% reduction		14%		91%		36%		52%		80%		80%		63%	

**EC, electrical conductivity; TSS, total suspended solids; KN, Kjeldahl nitrogen; COD, chemical oxygen demand; BOD5, biochemical oxygen demand; PS, pig slurry; CW, constructed wetland.*

The effluent had a pH of 7.54, which is normal for pig slurry. According to Antezena, the pH of animal slurry ranges from 6.3 to 8 on Spanish commercial farms *(Antezana et al., 2015).*

The EC of the pig slurry depended on the age and type of the pig (growing pigs and gestating sows had a higher EC than for lactating sows and nursery piglets) and storage time, thus enhancing drying and mineralization of the slurry *(Boursier et al., 2005)*. Differences in the concentration of proteins and minerals in the diet may also have contributed to differences in EC *(ProvoloL & Suller, 2007; M. R. Yagüe & Quílez, 2012).*

Our effluent had a low conductivity of 7.4 ms cm^{-1}. According to Antezena *(Antezana et al., 2015)* the national commercial farm range *(Sánchez & González, 2005; Villamar, Canuta, Belmonte, & Vidal, 2012)* is 6.59–53.5 ms cm^{-1} for growing pigs, which means that the slurry was at the low end, and there was a high possibility that the use of cleaning water diluted our effluent.

The raw PS turbidity was 2000 NTU, signifying solids and the presence of organic matter, which gave a good idea of the pollution level: the TSS, COD and BOD_5 were 80.90, 7 and 4 g L^{-1}, respectively, which signified that the piggery wastewater contained large amounts of organic matter.

The Kjeldahl nitrogen comprised nitrogen in ammonic and organic form, excluding nitrous forms (nitrites) and nitric form (nitrates), and the origin of organic nitrogen (urea).

Table 6 shows the results obtained after the passage of raw pig slurry through the filter materials. As the water passed through the filter, a thin biological film built up on the surface of the materials. Solid particles and natural microorganisms accumulated in it and contributed to the slow-flow filtration. The biofilm made the filter very effective because it extracted tiny particles from the water at the layer where purification occurs *(Sehar & Naz, 2016)*. The increase in pH values of the slurry after different filtration tests was explained by the presence of basic ions. The increase in pH was linked to the alkaline filter media, according to El *Houati (El Haouti et al., 2016).* As shown in *(Table 4),* it came mainly from alkaline aluminosilicates, which corresponded to the release of basic ions in the effluent *(Torres-Carrasco & Puertas, 2017).* Only zeolite and the CW did not have any effect on pH.

The electrical conductivity during filtration highlighted decreasing and increasing values: decreasing values were related to chemical exchanges between the effluent and the filtering materials ,precipitation and adsorption *(Khattabi, Aleya, & Mania, 2005).*

A significant decrease in the electrical conductivity up to 65% was recorded using zeolite, and the decrease in microbiological activity caused a drop in the amount of organic material degraded (BOD_5 and COD) *(Arrizabalaga Philippe, 1997)* thus limiting the mineralization of inorganic substances. Conductivity reduction with zeolite confirmed the pH values. Noyes *(Noyes, Melcher, Cooper, Eastman, & Kato, 2002)* said that basic environment seemed to be less conductive to filtering and less loaded with salts

Electrical conductivity (EC) reduction by the other materials was explained by the retention of dissolved salts (sulphate, calcium, sodium, magnesium, chloride) by sandy and loamy materials and by the low conductivity of the filter materials Sand 1, Sand 2, Soil 1, Soil 3, and Soil 4.

Increasing values were directly related to the electrical conductivity of the filter materials. Referring to *(Table 4),* fly ash had a high conductivity comparing to the other materials 6.30 ms cm^{-1}, which explained the high conductivity of the filtered effluent 9.44 ms cm^{-1}. The same was true for Soil 3 and 4.

Table 6 shows that a constructed wetland reduced EC by only 14%, the material that had a high significant effect on reducing the EC is zeolite (65%). Total suspended solids achieved an elimination rate between of 82 and 99.99%. COD reduction achieved an elimination rate that ranged between 72 and 90%, and BOD_5 reduction was 99.99%.

Reductions in organic loads and TSS are explained by the physical–chemical characteristics of the materials. Because the particle sizes were 150–10 µm, the materials were ideal for capturing and retaining suspended solids. The small particles size increased the exchange surface between the effluent and material, thus easily trapping TSS in the pores of the adsorbent, according to Setyobudiarso *(Hery & Endro, 2014).* As more organic substances from the effluent became trapped in the pores of the adsorbent, the BOD_5 and COD content fell *(Hery & Endro, 2014)* This reduction was due mainly to filtration and sedimentation and to sieving at the filter bed (Achak, Ouazzani, & Mandi, 2010). Moreover, the high concentration of silica (>35%)_was able to absorb solids suspended in water *(Ahmad & EL-Dessouky, 2008)*. Its, strong polarity and mineral elements, in particular ferrous ions (Fe^{2+}), neutralized the negative charges on the organic matter *(EL FADEL, MERZOUKI, BENLEMLIH, LAAMYEM, & MOUNIR, 2011)*.

Compared to filtration with CWs, all the materials achieved equal or better reduction of TSS, COD and BOD_5. Only the zeolite achieved a high elimination rate (around 99.99%) of the three parameters previously mentioned.

This reduction of Kjeldahl nitrogen was explained by the oxidation of organic nitrogen to oxidized nitrogen (NOx). Joint denitrification can occur simultaneously in areas of the filter bed that became anoxic *(Deronzier et al., 2001)* and was further stimulated by lime (CaO) that was present in the filter materials.

The pH of the effluent and filtration materials was very important for nitrifying bacteria, which required a pH between 7.4 and 9 for nitrosomonas, and between 8.5 and 9.1 for Nitrobacter. According to Biod and EPA *(Biod et al., 2006; EPA, 2020)*, this explained the high reduction of nitrogen by the four soils and zeolite.

However, the low reduction of nitrogen by Sand 1, Sand 2 and fly ash was explained by their high pH: 9.69, 9.52, 12.10, respectively *(Table 4)*. Furthermore, the pH of the filtered effluents was 8.92, 8.98 and 12.02. According to CPW *(CPW, 2020)*, the closer the pH was to 9.6 the closer nitrification came to 0.

The maximum nitrogen removal by zeolite was explained by its large specific surface area, which is ideally suited for autotrophic bacterial colonies that convert ammonia to nitrite and nitrite to nitrate through aerobic and anaerobic nitrification. Zeolite allowed a very good optimal nitrification level *(Ahmad & EL-Dessouky, 2008; Deronzier et al., 2001).*

Sand 2 could reduce the same as the CW, while soils (1-4), fly ash and zeolite achieved a high reduction rate. The high reduction of almost 99.99% was obtained by zeolite which is 65% higher comparing to the CW.

5.1 Micronutrient results in raw and filtered pig slurry

Table 7 shows the micronutrients Mn, Cu, Zn, Fe in raw and filtered pig slurry, and the high percentage of their reduction.

Table 7. Micronutrients of raw and filtered pig slurry

	Mn (µg L^{-1})		Cu (µg L^{-1})		Zn (µg L^{-1})		Fe (µg L^{-1})	
PS	190	±0.00	106	±0.01	451	±0.01	783	±0.01
Sand 1	23	±0.00	56	±0.01	BDL*	±0.00	BDL*	±0.00
% reduction	87.74%		46.60%		99.99%		99.99%	
Sand 2	28	±0.00	333	±0.12	BDL*	±0.00	BDL*	±0.00
% reduction	85.11%		-214.15%		99.99%		99.99%	
Soil 1	31	±0.00	63	±0.01	BDL*	±0.00	BDL*	±0.00
% reduction	84.21%		40.28%		99.99%		99.99%	
Soil 2	9	±0.00	BDL*	±0.00	BDL*	±0.00	BDL*	±0.00
% reduction	95.26%		99.99%		99.99%		99.99%	
Soil 3	173	±0.00	13	±0.00	BDL*	±0.00	BDL*	±0.00
% reduction	8.95%		87.45%		99.99%		99.99%	
Soil 4	171	±0.02	BDL*	±0.00	BDL*	±0.00	BDL*	±0.00
% reduction	10.53%		99.99%		99.99%		99.99%	
Fly Ash	11	±0.00	BDL*	±0.00	BDL*	±0.00	213	±0.00
% reduction	94.74%		99.99%		99.99%		72.80%	
Zeolite	BDL*	±0.00	BDL*	±0.00	BDL*	±0.00	9	±0.00
% reduction	99.99%		99.99%		99.99%		98.85%	
CW	601	±0.02	40	±0.00	11	±0.00	11	±0.00
% reduction	-215.79%		62.26%		97.78%		98.72%	

**Below detection limit (BDL)*: Mn: 0.00033 mg L^{-1}, Cu: 0.0003 mg L^{-1}Zn: 0.00126 mg L^{-1}, Fe: 0.00045 mg L^{-1}*

Iron and zinc ions present high values in raw pig slurry, and all materials had a removal rate of 99.99%, except fly ash, which reduced iron ions by only 80%.

Copper and manganese ion concentrations were 106 and 190 µg L^{-1}, respectively, and all materials achieved a high reduction between 50 and 99.99% for cupric ions. Manganese reduction by all materials was 80 to 99.99%, except soil 3 and soil 4, which only reduced 10%.

The CW released a high content of manganese as it reduced copper, zinc, and iron. Compared to the other materials, zeolite was the only material that had a reduction rate of almost 99.99% for all micronutrients.

The ferric oxides and aluminum oxides contained in the filtration materials made them good adsorbents for metallic ions (Thomas, Mostafa, Bruno, Tikou, & Mamert, 2006) .Zeolite has a high ion exchange capacity and ability to remove dissolved heavy metals in an aqueous solution, which explains the high reduction of micronutrients after contact between the pig slurry and filtration materials (Chung, Son, & Ahn, 2000).

5.2 Heavy metal reduction

Table 8 presents the metallic elements (Pb, Co, Ni, Cr and Al) in raw and filtered PS.

In the raw slurry, lead, cobalt, nickel, chromium, and aluminum ions were present in with concentrations of 1, 1, 11, 0.8, and 38 µg L^{-1}, respectively. Aluminum ions recorded the highest concentration and were strongly reduced by all materials with the high reduction rate of 99 %, except for the CW (74%).

Nickel ions had a low concentration of 11 µg L^{-1}. Sand 1, soil 2, and soil 3, reduced it while fly ash and zeolite eliminated it. Soil 1, soil 4 and sand 2, in contrast, released more nickel ions, which may have been related to contamination of those soils.

Chromium had a low concentration of 0.8 µg L^{-1}. The sands, soils 1, 2, and 4 and fly ash reduced it, soil 3 and zeolite eliminated it.

The two sands released lead into the effluent with a concentration of 9 µg L^{-1}. Nickel had a low concentration, 11 µg L^{-1}, but sand 2, soil 4 and the CW released more with concentrations 60, 20, and 40 µg L^{-1}, respectively, possibly because of contamination by those ions.

Table 8 shows that pig slurry treatment by the different filter materials further reduced heavy metals. The variable removal rate was due to the ionic form of each metal, the ability of each bacterium to consume the metal, and the differing physicochemical conditions of each organism.

Indeed, with the richness of silica in the sand, the surface hydroxyl groups were formed by hydration, which allowed the adsorption of metallic cations *(Bourg, 1988)*. Iron oxides and aluminum oxides in fly ash (% ∑ Al_2O_3 + Fe_2O_3 = 45.41%) and soils (% ∑ Al_2O_3 + Fe_2O_3 = soils 1, 17.7%; soil 2,26.1%; soil 3, 26.4%; soil 4, 21.6%) made them good adsorbents with a high metallic ion retention *(Thomas et al., 2006).*

Zeolite has been investigated for its ion exchange capacity, and its high ability to remove heavy metals dissolved in an aqueous solution through ion exchange (Pitcher, Slade, & Ward, 2005), this explains the high removal of all metals presented in the raw pig slurry with an elimination rate of 99.99% .

Table 8. Heavy metals of raw and filtered pig slurry

	Pb (µg L^{-1})		Co (µg L^{-1})		Ni (µg L^{-1})		Cr (µg L^{-1})		Al (µg L^{-1})	
PS	1	±0.00	1	±0.00	11	±0.00	0.8	±0.00	38	±0.00
Sand 1	9	±0.00	10	±0.00	BDL*	±0.00	0.9	±0.00	BDL*	±0.00
% reduction	-727%		-550%		99.99%		-13%		99.99%	
Sand 2	9	±0.00	9	±0.00	60	±0.00	0.9	±0.00	BDL*	±0.00
% reduction	-718%		-542%		-440%		-12.50%		99.99%	
Soil 1	BDL*	±0.00	BDL*	±0.00	14	±0.00	1.8	±0.00	BDL*	±0.00
% reduction	99.99%		99.99%		-26.13%		-125%		99.99%	
Soil 2	BDL*	±0.00	BDL*	±0.00	4	±0.00	1.1	±0.00	BDL*	±0.00
% reduction	99.99%		99.99%		65.77%		-37.50%		99.99%	
Soil 3	BDL*	±0.00	BDL*	±0.00	7	±0.00	0.9	±0.00	BDL*	±0.00
% reduction	99.99%		99.99%		32.16%		-12.50%		99.99%	
Soil 4	BDL*	±0.00	BDL*	±0.00	20	±0.00	1.8	±0.00	BDL*	±0.00
% reduction	99.99%		99.99%		-87.39%		-125%		99.99%	
Fly Ash	BDL*	±0.00	BDL*	0.00	BDL*	±0.00	4.8	±0.00	BDL*	±0.00
% reduction	99.99%		99.99%		99.99%		-500%		99.99%	
Zeolite	BDL*	±0.00	BDL*	±0.00	BDL*	±0.00	BDL*	±0.00	BDL*	±0.00
% reduction	99.99%		99.99%		99.99%		99.99%		99.99%	
CW	BDL*	±0.00	BDL*	±0.00	40	±0.00	3	±0.00	10	±0.00
% reduction	99.99%		99.99%		-266%		-325%		73.75%	

**Below detection limit (BDL)*; Pb, 0.00004 mg L^{-1}; Ni, 0.00051 mg L^{-1}; Cr:, 0.00006 mg L^{-1}; Co, 0.00008 mg L^{-1}; Al, 0.0004 mg L^{-1}*

5.3 Macronutrient removal

As presented in *Table 9,* the two different sands reduced nitrogen at the same rate of 9%. Soil 1, soil 2, soil 3, soil 4, fly ash and the CW reduced it by 51, 64, 58, 61, 39, and 30% respectively. The largest reduction was obtained from zeolite, 75%.

The 8 materials were rich in aluminum oxides, iron oxides and lime (Al_2O_3, Fe_2O_3, and CaO, respectively), which were considered coagulants and reagents for the physicochemical removal of phosphorus because they precipitated out ferrous phosphate and lime phosphate. (Bureau d'Etudes Industrielles, 2015; Li, Liu, Xu, & Qian, 2016; Ramasahayam, Guzman, Gunawan, & Viswanathan, 2014; Rittmann, Mayer, Westerhoff, & Edwards, 2011) Those scenarios explain the high elimination rate of phosphorus.

The water hardness was caused by calcium and magnesium salts *(Oram, 2020)*. Only the two sands and the CW reduced it, just when it achieved 1000 mg L^{-1} using soil 3, soil 4 and fly ash. Those salts were dissolved from filter materials initially formed by lime, dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$).

The materials were divided into three groups according to potassium levels: The first group (sand 1 and sand 2), had no effect as potassium held the same values in filtered and raw effluent. The second group (fly ash) doubled the potassium in the effluent, which was related to the richness of potassium in fly ash. The third group (all the soils and zeolite) potentially reduced the potassium, the organic matter particles held the potassium ions in an exchangeable or available form. According to Charles *(WHITE & SANTANGELO, 2018)*, potassium does not leach from silty or clayey soils and is held between soil particles more tightly and can be stored, which explained the potassium reduction with the four silty soils. According to ion selectivity (Sabadash, Gumnitsky, & Hyvlyud, 2016), zeolite had high potassium absorbency due to ion exchange and exchangeable cations.

The maximum removal rate of sodium was recorded by zeolite then by soil 1. Sand 1 and sand 2 did not have any significant effect. Soils 2– 4 released more sodium in the effluent.

Zeolite had a high cation exchange capacity and selectivity due to its high porosity and sieving properties (Zhao, Vance, Ganjegunte, & Urynowicz, 2008), and it is reported to have replaced sodium ions from the solution with calcium (Santiago, Walsh, Kele, Gardner, & Chapman, 2016), which explains the sodium reduction and calcium increment.

The constructed wetland achieved a high reduction of some micronutrients (calcium, magnesium, and phosphorus) while it released sodium and had s no significant effect on potassium. Zeolite reacted oppositely to the CW by reducing sodium and potassium to a high degree and magnesium slightly as it released calcium. The CW and zeolite were complementary.

Results data obtained in this research shows that adding a new material layer to the CW can increase its quality. It should be noted that the experimental results do not have a control experiment showing the new layer performance compared to the normal CW. Therefore, a new research to compare the CWs with and without the new layer is recommended.

Table 9. Macronutrients of raw and filtered pig slurry

	N (mg L^{-1})		**Na^{+} (mg L^{-1})**		**K^{+} (mg L^{-1})**		**Ca^{2+} (mg L^{-1})**		**Mg^{2+} (mg L^{-1})**		**P (mg L^{-1})**	
PS	150	±0.6	120	±0.3	125	±1.1	105	±1.7	104	±1.2	20.11	±0.0
Sand 1	136	±0.3	120	±0.3	119	±0.6	40.5	±1.6	105	±0.1	1.25	±0.0
% reduction	9%		-1%		5%		61%		-1%		94%	
Sand 2	136	±0.6	120	±0.6	120	±1.7	33.67	±1.2	105	±0.1	1.73	±0.0
% reduction	9%		0%		4%		67.94%		-1%		91%	
Soil 1	74	±0.6	106	±0.6	98	±2.7	129	±2.0	120	±0.1	0.31	±0.0
% reduction	51%		11%		21.33%		-22.86%		-15%		98%	
Soil 2	74	±0.3	195	±0.6	85	±1.1	120	±0.0	102	±0.7	0	±0.0
% reduction	64%		-63%		32.05%		-14.29%		2%		99.99%	
Soil 3	64	±0.3	260	±0.5	108	±1.5	180	±0.3	173	±0.2	0	±0.0
% reduction	58%		-117%		13.60%		-71.43%		-66%		99.99%	
Soil 4	58	±0.2	290	±0.6	107	±1.1	183	±0.1	225	±0.0	0.27	±0.0
% reduction	61%		-142%		14.40%		-74.29%		-116%		99%	
Fly Ash	92	±0.0	150	±0.0	170	±1.1	175	±0.5	11	±0.0	0	±0.0
% reduction	39%		-25%		-36%		-66.98%		89%		99.99%	
Zeolite	38	±0.3	70	±1.1	40	±0.9	132	±0.3	101	±0.3	0.17	±0.0
% reduction	75%		42%		67.73%		-26.35%		3%		99%	
CW	105	±0.6	134	±0.3	132	±0.9	24	±0.1	30.03	±0.1	1.08	±0.0
% reduction	30%		-12%			-6.13%		77.02%	71%		95%	

5. Conclusion of the filtration treatment

Richness in silica and metallic oxides and small particle size were the reasons for the good results from the different filter materials.

In summary, filtration by marine sands, loamy soils, fly ash and zeolite generally reduced physical chemical loads, micro- and macronutrients, and heavy metals with different removal rates, All the materials achieved a high elimination of chemical pollution loads: up to 74% for COD, 75% for BOD_5, 91% for TSS and 89% for nitrogen, except for the two sands and fly ash, which achieve 24 and 32% respectively. Concerning micro- and macronutrients and heavy metals, some materials proved their ability to adsorb ions and release others at the same time.

Comparing the adsorption and release percentages, zeolite proved to be the best material to be integrated into the construction of the wetland. Its adsorbed pig slurry pollution loads with high percentages while it released ions such as calcium (Ca^{2+} 199 mg L^{-1}). The CW proved its ability to reduce calcium; therefore, adding a 20 cm layer of zeolite to the CW will raise its efficiency as a pig slurry filtration system.

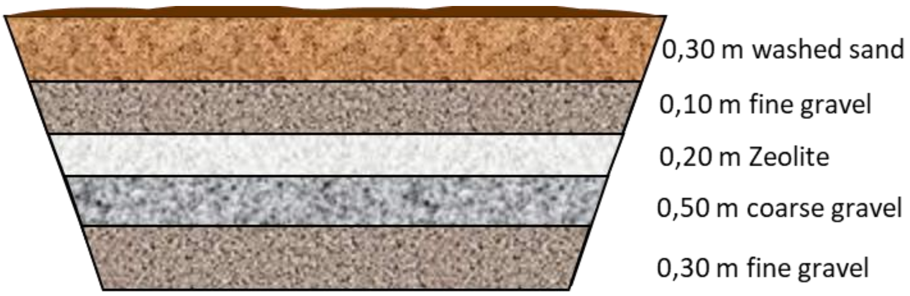
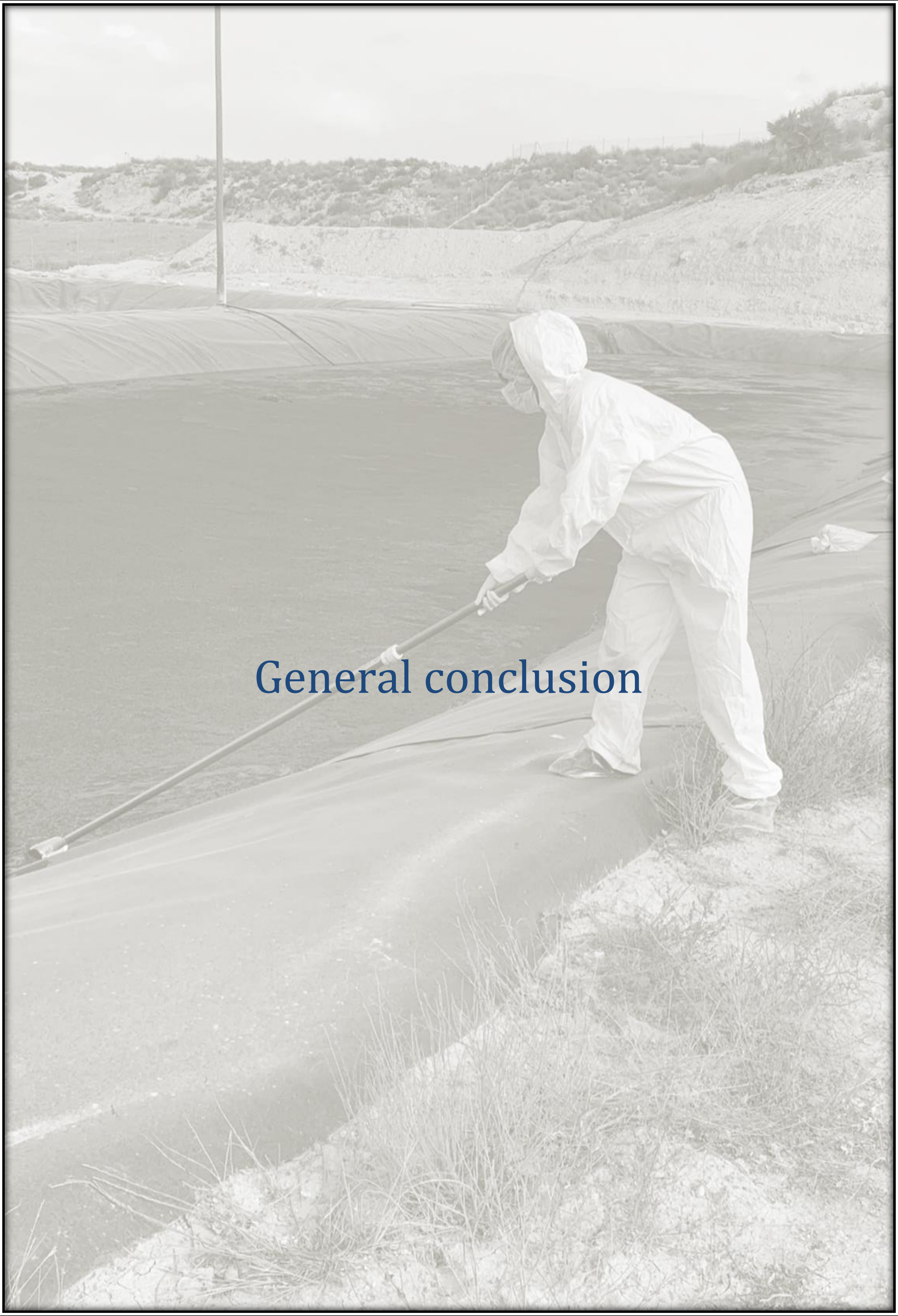


Figure 22. Updated Constructed Wetland

General conclusion



VI. General conclusion

The results obtained in this thesis allowed to reach the following conclusions:

Coagulation flocculation treatment

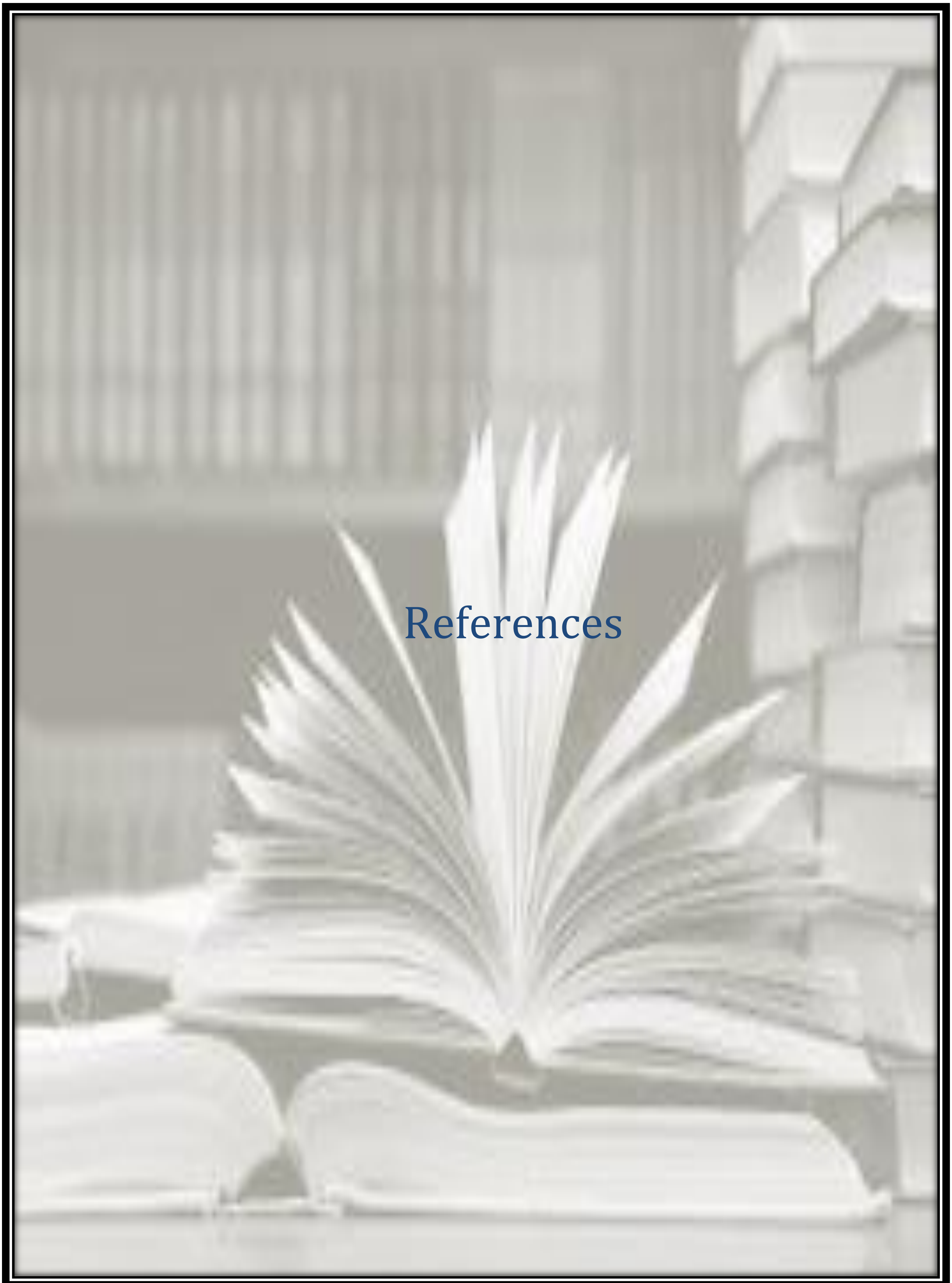
- The pretreatment, composed of the phase separator, filtration and decantation tanks, played a very important role in TSS reduction around 60 % reduction, nevertheless, it doesn´t present a satisfying result and it´s enable to protected the wetland from future obstructions, allowing it to extend its lifespan.
- Chloride ferric as coagulant and DKFLOCC-1598 as a cationic flocculant was used for the treatment of pig slurry proved to be a highly effective coagulant, flocculent for this type of the pig slurry
- The central composite design method (CCD) using the R statistical software was very useful to optimize the levels of coagulant dosage, flocculant dosage and pH, which has been proved at laboratory scale.
- Results affirm that the optimal conditions for the minimum turbidity and COD were coagulant dosage of 0.024 mol L^{-1}, flocculant dosage of 0.1649 ml L^{-1} at pH 7.5.
- The CCD results, those concentrations can achieve 88.25% of COD removal and 99% of turbidity removal.
- The verification experiments proved and demonstrated that the CCD approach was appropriate for optimizing the coagulation–flocculation process by getting the same removal rate of COD and Turbidity.
- It is also worth mentioning that the high turbidity removal of 88% has a positive impact and highly recommended in terms of minimizing clogging risk of the CWs.

Filtration treatment

- Richness in silica and metallic oxides and small particle size were the reasons for the good results from the different filter materials.
- Filtration by marine sands, loamy soils, fly ash and zeolite generally reduced physical chemical loads, micro- and macronutrients, and heavy metals with different removal rates, All the materials achieved a high elimination of chemical pollution loads: up to 74% for COD, 75% for BOD_5, 91% for TSS and 89% for nitrogen, except for the two sands and fly ash, which achieve 24 and 32% respectively.
- Concerning micro and macronutrients and heavy metals, some materials proved their ability to adsorb ions and release others at the same time.
- Comparing the adsorption and release percentages, zeolite proved to be the best material to be integrated into the construction of the wetland. Its adsorbed pig slurry pollution loads with high percentages while it released ions such as calcium (Ca^{2+} 199 mg L^{-1}). The CW

proved its ability to reduce calcium; therefore, adding a 21 cm layer of zeolite to the CW will raise its efficiency as a pig slurry filtration system.

Both proposed treatment both in the pilot-scale, proved to be affective in the optimization and increase the efficiency of the constructed wetland. the comprehensive system made up of constructed wetlands turned out to be efficient in the treatment of swine manure. Despite the great variability of slurry, the treatment strategy based on constructed wetlands complemented with a previous solid-liquid separation treatment and a plantation system, can produce an effluent with an appropriate quality / composition to be valued agronomically. In addition, this type of treatment constitutes a solution to the management of slurry, being technologies with which it is possible to generate a reusable by-product, encouraging the circular economy.



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¨Fe de erratas¨

- En la página 8, imagen 1, añadir la referencia de la imagen (Source: No-till Farmer 2021).
- En la página 9, imagen 2 y 3, añadir la referencia de la imagen (Source: No-till Farmer 2021).
- En la página 11, imagen 5,6,7 y 8, añadir la referencia de la imagen (Source: No-till Farmer 2021).
- En la página 11, imagen 5,6,7 y 8, añadir la referencia de la imagen (Source: No-till Farmer 2021).
- En la página 12, imagen 9, añadir la referencia de la imagen (Source: No-till Farmer 2021).
- En la página 14, imagen 10, añadir la referencia de la imagen (Source: No-till Farmer 2021).
- En la página 20, imagen 11, añadir la referencia de la imagen (Source: Google satellite maps).
- En la página 21, imagen 12, añadir la referencia de la imagen (Source: El PAIS)
- En la página 26, Figura 9, añadir la referencia de la imagen (Source: Google maps).
- En la página 59, en el último parágrafo antes de la figura 21, corregir el error de escritura de la última referencia, ASMT por ASTM.
- En la pagina 15 del documento, ordenar las abreviaciones en orden alfabético.