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PhD Thesis

ASSESSMENT OF DIFFERENT SOLID-LIQUID SEPARATION TECHNIQUES FOR LIVESTOCK SLURRY

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PAPERS

The listed papers have been written during the PhD activities and their results are reported and discussed in the present thesis.

- **I.** Cocolo, G., Curnis, S., Hjorth M., Provolo, G. 2012. Effect of different technologies and animal manures on solid-liquid separation efficiencies. J. Agric. Eng. 43(2), 55-64.
- **II.** Cocolo, G., Riva, E., Provolo, G. 2012. Tecniche per abbattere l'azoto nei reflui zootecnici. L'Informatore Agrario 68(10), 69-72
- **III.** Cocolo, G., Hjorth, M., Zarebska, A., Provolo, G. 2013. The process of separating solid and liquid manure components affected by acidification. Submitted to Chemosphere.
- **IV.** Hjorth, M., Cocolo, G., Jonassen, K., Lone, A., Sommer, S.G. 2013. Changes in chemical and biological processes in manure upon acidification. Sumbitted to Water Research.

1. INTRODUCTION

During the last decades, EU countries became increasingly sensitive about environmental problems related the human activities. Concerning the agricultural sector, livestock production is the activity that presents the highest environmental impact. Among livestock production activities, manure management is the activity mostly involved in negative environmental impact. In fact, livestock productions increased during the 20th century, leading to an increase in herds size and, thus, to a larger production of livestock wastes (Burton and Turner, 2003). The volume of wastes produced often exceeds the capacity of neighboring lands to absorb the nutrient contained within manure; therefore, this leads to environmental problems related to the higher nutrient content of manure compared to crops requirements. These environmental problems are related to emissions to air and water bodies, which are caused by biological, chemical and physical processes associated with the degradation of the organic materials contained in animal manure. The emissions to atmosphere related to agricultural practices are related to nitrous protoxide (N_2O), methane (CH_4) and ammonia (NH_3). Emissions to water bodies are mainly related to the leaching of nitrates (NO_3^-) contained in animal manure, which contribute to eutrophication processes and may lead to the deterioration of drinking waters quality. The same problems are caused by the run off of phosphorus (P).

Animal manure is a valuable resource for fertilizing and amendment, which could replace large amounts of chemical fertilizers when it is properly used (Bouwman and Booij, 1998). Animal manure contains nitrogen (N), phosphorus and potassium (K), which represents the main plant nutrients. Furthermore, livestock wastes provides large amount of organic material, which improves soil physical properties. However, the heterogeneous nature of manure, their unbalanced composition and their long-term over-application make it difficult to control changes in soil properties related to land distribution. Moreover, an improper manure management could lead to nutrient losses, particularly N and P, through run-off and leaching. These nutrients are therefore transported and accumulated to surface- and ground-waters, leading to eutrophication. This process causes the deterioration of water ecosystems, which includes (Dìaz et al., 2012):

- Excessive phytoplankton and microalgae growth, which causes an organic carbon accumulation, a reduced light penetration and, thus, a loss of the aquatic vegetation;
- An unbalanced nutrient ratios that promote the growth of phytoplankton species and create the optimal conditions for toxic microalgae;
- Reduced dissolved oxygen concentration and, thus, the formation of hypoxic or dead zones.

The management of livestock manure could also cause emissions of ammonia (NH_3) and greenhouse gasses (GHG) to air. In particular, ammonia emissions contribute to soil acidification, cause problems to N-limited ecosystems and represent a risk for human and animal health due to the NH_4-based particles in the air (Ndegwa et al., 2008; Petersen et al., 2008). Ammonia losses represent a loss of fertilizer value.

GHG are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O); among these, CH_4 and N2O are of particular importance in the Agriculture, since their emissions are mainly related to the degradation of organic compounds during manure management practices. CH_4 and N_2O emissions are influenced by several factors, such as storage temperature, organic matter and nitrogen contents in manure and the storage time (Peters et al., 2008).

Different treatment processes have been developed in order to minimize the negative environmental impact related to manure management. Among these treatments, solid-liquid separation is one of the widely applied techniques. In fact, separation techniques often represent a relatively cheap technology; furthermore, they lead to the production of two separated fraction, which present different dry matter and nutrient content. Therefore, these fractions can be managed differently, leading to a more appropriate nutrient application to fields and, thus, minimize nutrient losses and their related environmental problems.

1.1. Characteristics of animal manure

The different types of farming systems that are used in the European countries lead to the production of different types of manure. According to their moisture content, manure types are divided in: (i) slurry or liquid manure, (ii) solid manure or farmyard manure, (iii) dirty waters (Pain and Menzi, 2011). Among these three categories, slurries are often the most difficult to manage, since they have a low dry matter content. These are a mixture of feces and urine, bedding material (e.g. straw, wood shavings, sawdust), split feed and drinking water, and water used for washing floors. Slurries are therefore liquid, with dry matter content from 4% to 10% (Pain and Menzi, 2011).

The knowledge of slurry characteristics within a livestock farm is necessary in order to define a proper manure management, which could allow to reduce nutrient losses to water, air and soil. In particular, slurry characteristics that could affect the manure collection, storage and spreading are the total solid content (as dry matter content). The nutrient content, in particular N, P and K concentrations, affects the amount of effluent that should be spread to land (Zhang and Lorimor et al., 2000). These parameters are highly variable, since they are affected by different factors:

- Animal characteristics: species, age, physiological stage and productivity;
- Feed: type of feeding, digestibility, fiber and protein content;
- Environment: climate, season.

Slurry characteristics also vary according to the storage time and to manure treatments (Barth et al., 1999). E.g. High storage temperatures combined to long storage time cause the mineralization of organic compounds and a reduction of the particle size, leading to a reduction of the separation efficiency (Kunz et al., 2009).

1.1.1. Physical characteristics

The main physical characteristics of slurry are: (i) the dry matter and moisture contents, (ii) the particle size, (iii) the density and (iv) the viscosity.

1.1.1.1. Solids

The sum of all the solids contained in the manure is the dry matter (DM). This represents the residual after drying the sample at 105°C. Usually, the DM content is represented as percentage of the weight of the sample.

The DM consists of Suspended Solids (SS) and Dissolved Solids (DS). SS are determined by filtration of the sample through a 0.45 µm filter, while DS correspond to the fraction that passes through the filter. SS are divided in settable solids, floating solids and colloids (IRSA CNR, 2009). Settable solids are solids that settle in an Imhoff cone after 60 minutes, while floating solids are the residual solids contained in the liquid above the settled fraction. Colloids are non separable SS, which consists of particles between 1 nm and 1 µm.

Total solids are also defined as the sum of fixed solids (FS) and volatile solids (VS). Both FS and VS are determined by combustion of the sample at 600°C in a muffle furnace. FS are the residual of this combustion (ash); they represent the content of minerals in the slurry. VS are generally used to represent the content of organic matter in the manure.

1.1.1.2. Density and viscosity

The total solids content affects the density and the viscosity of the slurry. According to the relationship expressed by Thygesen and Jhonsen (2012), the density of animal slurry is affected by the DM content and the animal species, with lower density values for cattle slurry at the same DM content:

Cattle:

$$\rho_{slurry} = \frac{DM + 236}{0.24}$$

Pig:

$$\rho_{slurry} = \frac{DM + 279}{0.28}$$

where ρ_{slurry} is the density ($kg \cdot m^{-3}$) of the slurry and DM is the dry matter content ($kg \cdot t^{-1}$).

When the DM content is higher than 5%, the flow property of the slurry has been found to be non-Newtonian, while at lower DM values the slurry behaves as a Newtonian liquid (Landry et al., 2004; Hjorth et al., 2010).

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress (Sommer et al., 2013). This parameter affects the transport and the movement of the slurry in a porous media such as soil, stored solid manure, stirred liquid manure or slurry transported to pipes. According to Landy et al. (2004), slurry viscosity could be estimated by the equations below:

Dairy Cattle:

$$\mu_{slurry} = 4 \cdot 10^{-5} \cdot DM^{4.4671}$$

Pig:

$$\mu_{slurry} = 4 \cdot 10^{-6} \cdot DM^{4.6432}$$

1.1.1.3. Particle size

Particle size and their distribution within the slurry is one of the main parameter that affects the solid-liquid separation treatment. The size of manure particles is closely related to the animal species and the type of housing and feeding systems. Generally, the particle size is larger for cattle slurry; in fact, according to Møller et al. (2002) the amount of DM in the particle size fraction below to 0.025 mm is larger in pig slurry than in cattle one. Other factors that affect particle size distribution are the feed composition, the diet, the category of animal (Meyer et al., 2007; Sommer et al., 2008) and the storage time and temperature (Møller et al., 2002; Christensen et al., 2009).

Manure treatments could modify particle size distribution in manure. E.g. anaerobic digestion leads to a reduction of small particles, shifting particle size distribution to larger sizes (Martacto et al., 2009). This is related to the easier degradability of small particles, which are mineralized during the anaerobic digestion process (Marcato et al., 2009; Möller and Müller, 2012). Another treatment that modifies manure particle size is slurry acidification. According to Hjorth et al. (2013) lowering the pH of pig slurry causes a reduction of the negative charge of particles, leading the smaller particles to attach to each other and to form larger flocs.

Small particles are often associated to nutrients, especially N and P. In particular, about the 70% of undissolved N and P is related to particle size 0.45-250 µm (Masse et al., 2005).

1.1.2. Chemical characteristics

The chemical characterization of animal manure is important for the definition of the nutrient content, particularly referred to N, P and K and, thus, to its fertilizing value. Chemical characterization also allows analyzing in which form the different nutrients are in the slurry; therefore, it is possible to calculate the plants uptake of nutrients.

1.1.2.1. Nitrogen

N concentration of manure is affected by the protein content of diet: about 5-45% of plant proteins is transformed in animal ones, while the remaining 55-95% is excreted through feces and urines (Hjorth et al., 2010). N production in slurry is also affected by animal species, animal category and type of housing system (Table 1.1).

Table 1.1. Amounts of Nitrogen produced by different animal species: values expressed to fields subtracting ammonia losses. Values are divided by solid and liquid manure. (Regione Lombardia, 2011).

Animal category and housing system	**TN**			
	Total	**In slurry**	**In solid manure**	
	kg/animal/year	**kg/t lw/year**	**kg/t lw/year**	**kg/t lw/year**
Pigs: lactating sow	26,4	101		
• Without bedding			101	
• With bedding				101
Pigs: growing/finishing	9,8	110		
• Without bedding			110	
• With bedding				110
Dairy cow (live weight: 600 kg/animal)	83	138		
• Tied or free-stall without bedding			138	
• Loose housing			62	76
• Tied-stall with bedding			39	99
• Free-stall			85	53
Dairy followers (live weight: 300 kg/animal)	36	120		
• Free-stall with slatted floor			120	
• Free-stall without bedding			120	
• Tied-stall with bedding			26	94
• Free-stall with bedding			61	59
• Free-stall with bedding also in the feedlot			17	103
• Calves on slatted floor			120	
• Calves with bedding			20	100
Beef cattle (live weight: 400 kg/animal)	33,6	84		
• Free-stall with slatted floor			84	
• Free-stall without bedding			84	
• Tied-stall with bedding			18	66
• Free-stall with bedding			43	41
• Free-stall with bedding also in the feedlot			12	72

Both inorganic N and organic N are content in animal slurry. The inorganic form is the fraction readily available for plants, while the organic form can be absorbed by plants only after mineralization.
Among all the nutrients contained in animal slurry, N is the more variable, because of ammonia (NH_3) volatilization. The N species usually determined in laboratory are:

- Total Nitrogen (TN), which represents all N forms;

- Total Kjeldhal Nitrogen (TKN), which is the sum of organic and reduced forms of nitrogen contained in slurry, excluding nitrates;
- Total Ammoniacal Nitrogen (TAN), which is the sum of ammonia (NH_3) and ammonium ion (NH_4^+);
- Nitrates ($N\text{-}NO_3^-$), an ionic form which is not adsorbed by soil complexes because of its negative charge; it could be lost by denitrification processes, or through leaching and run-off processes;
- Nitrites ($N\text{-}NO_2^-$), as nitrites, an anionic form that is not adsorbed by soil complexes; it is an intermediate product of the nitrification process.

1.1.2.2. Phosphorus

The 80% of phosphorus (P) in slurry is in the orthophosphate form (PO_4^{3-}) (Hjorth et al., 2010), with a concentration from 0.1 to 5 $kg \cdot t^{-1}$ and higher values referred to pig slurry. The major part of P is excreted in feces (Meyer et al., 2007). Animals are able to use the ingested P with different efficiencies according to their species: cattle can use the P in feed with a high efficiency, while the 55-60% of P in feed for pigs is excreted in feces and urines (CRPA, 2001).

Even if P is in anionic form, its availability for crop nutrition is low because of the presence of insoluble complexes with calcium (Ca), when the pH is alkaline, or with iron (Fe) and aluminum (Al), when the pH is acid. However, P could be lost through run-off, increasing the risk of eutrophication processes.

1.1.2.3. Potassium

The potassium (K) contained in animal feed is usually absorbed at high rates (> 80%). In animal slurry K is contained in its ionic form (K^+) in concentrations from 0.4 to 7.5 kg·t. Since K is mainly dissolved in slurry (Masse et al., 2005), it is rapidly used by plants or adsorbed by exchange complexes and, thus, it does not represents an environmental problem.

1.1.2.4. Organic matter

Organic matter (OM) could be measured as the content of volatile solids (75-85% of DM). During slurry storage, OM is rapidly mineralized, increasing the amount of nutrients available for plant fertilization.

The organic components in slurry include compounds with the functional groups carboxylates, hydroxyls, sulfur hydryls and phenols (Masse et al., 2005) which, at normal slurry pH, will contribute to a negative charge of both dissolved and particulate organic matter (Hjorth et al., 2010).

1.1.2.5. Micronutrients

Animal slurry contain also microelements, such as copper (Cu) and zinc (Zn), which are added to animal pig feed as high concentrations as additives. The adsorption efficiency of these elements is very low, therefore the 72-80 % of Cu and the 80-97% of Zn are excreted.

Table 1.2 shows the amount of excreted P. K, Cu and Zn from different animal categories.

Table 1.2. Amounts of phosphorus, potassium, copper and zinc excreted in a year by different livestock categories (CRPA, 2001).

Species	P (kg/t lw)	K (kg/t lw)	Cu (kg/t lw)	Zn (kg/t lw)
Dairy cattle	33-42	93-138	0.1-0.3	0.6-3.0
Steer	36-49	81-96	0.1-0.2	0.4-1.9
Calves	60-85	54-124	0.1-0.2	1.4-2.7
Pigs	46-60	89-114	0.5-1.6	1.2-2.0

1.1.2.6. Electrochemical Properties

Electrochemical properties of slurry are ionic strength and the electric surface potential of particles.

Ionic strength (I) expresses the concentration of ions in a solution. I is a function of the concentration and valence of ions in a solution (Sommer et al., 2013). Ionic strength has been shown to be high in most animal slurry; this is revealed by high electric conductivity (EC), which is related to the concentration and the species of ions in the solution. EC has been observed to be higher than 10 $mS \cdot cm^{-1}$ in several animal slurry studies (Sommer and Husted, 1995; Christensen et al., 2009, Hjorth et al., 2010; Masse et al., 2010). It is linearly related to EC, as described by the following equation (Sommer et al., 2013):

$$I = 15.8 \cdot EC_{20}$$

Where EC_{20} ($S \cdot cm^{-1}$) is the EC at 20°C.

The electric surface potential (mV) of particles decreases from the surface of particles to the bulk solution. Usually, it is calculated as the double-layer model (Hjorth et al., 2010; Sommer et al., 2013), as shown in Figure 1.1. Near the surface the potential changes linearly due to the adsorbed ions (Stern layer); after the Stern layer, the potential decreases exponentially depending on the ionic strength (Guoy diffuse layer). It is difficult to measure the electric surface potential, therefore the electronic potential (zeta potential) is used to measure the surface potential (Hjorth et al., 2010; Sommer et al., 2013). Zeta potential is the potential that exists at the shear plane of the particles. The shear plane of the particles lies in the liquid phase surrounding the particle and is usually located close to the Stern layer (Sommer et al., 2013).

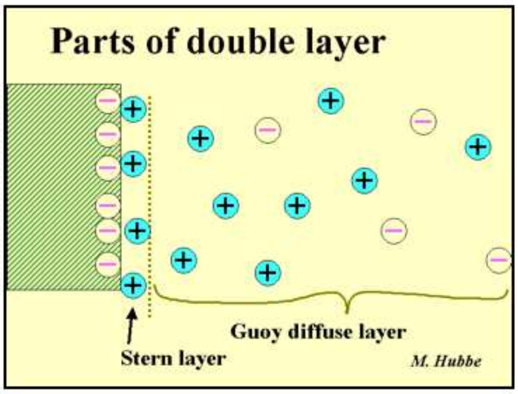

Figure 1.1. Double-layer model.

Organic particles in the manure often have a negative surface charge; therefore particles repel each other (Hjorth et al., 2010). Christensen et al. (2009) showed that the particle charge density of pig slurry is -0.18 $meq \cdot g^{-1}$ organic solid. Moreover, the negative charge contributes to the alkalinity of the slurry (Hjorth et al., 2010). Alkalinity and charge density are two interrelated ways to express the negative charge of organic particles. The negative surface charge of particles affects the distribution of ions in solution by adsorbing cations in the Stern layer, with the remaining counter-ions being distributed in the diffusive layer (Hjorth et al., 2010)

Electrochemical characteristics of slurry are very important when a chemical separation process occurs. In fact, they could affect the use, type and dosage of flocculants. An increased ionic strength of the slurry will reduce the electrostatic repulsion of the particles and, thus, will affect flocculation processes. Furthermore, at high ionic strength a linear polymer will change to a more sphere-shaped form, which will lower the efficiency of the polymer (Hjorth et al., 2010). Furthermore, at high ionic strength the extent of the diffuse layer decreases, affecting the particle charge density (Hjorth et al., 2010); this affects the type and the dosage of the polymer.

1.2. Solid-liquid separation of livestock slurry

The increasing nitrogen load on agricultural lands and the related European legislations, led the farmers to adapt in order to abide the new legislation. In some case, this resulted in the introduction of treatment techniques that can improve manure management, use manure as a valuable resource and reduce environmental problems related to livestock practices, such as nutrient losses to air, water and soil (Burton, 2007). However, most of the available treatment technologies are expensive for the major part of farms. Solid-liquid separation is one of the most utilized treatment techniques, since it allows to improve manure management within the farm and it could be a cheaper treatment compared to other technologies.

1.2.1. Why separate the slurry?

Solid-liquid separation of animal slurry is the partial removal of suspended particles (both coarse and small) from the liquid manure. This treatment produces a liquid fraction, characterized by a lower content of DM and nutrients, and a solid fraction with a high concentration of DM and nutrients. Since the two resulting fractions present different characteristics, they can be used for different aims.

Slurry separation produces a large amount of liquid fraction, which presents a lower concentration of DM, N and P than the raw slurry. The N/P ratio is increased in the liquid fraction, fitting the requirements of crops and leading to a reduction of P losses. Also the TAN/TN ratio increases, hence a higher amount of N is readily available to plants. Furthermore, the energy requirement for its homogenization and pumping are lower and the risk of clogging of pipelines is reduced. The liquid fraction can be used for fertigation or, alternatively to land spreading, it can be used for further membrane filtration (Masse et al., 2007), evaporation (Veeken et al., 2004), struvite crystallization and striping (Hjorth et al., 2010).

The produced solid fraction is in a lower amount compared to the liquid one, but it contains the major part of DM, P and organic matter (Møller et al., 2002). Due to the low moisture content, the solid fraction can be transported to field far from the farmstead with low energy and transport costs. It may also be used for green energy production through anaerobic digestion. Solid-fraction is also used for composting treatment or as input material for the production of mineral fertilizer. Furthermore, thanks to the high concentration of organic materials, the solid fraction improves the structure of soils.

Solid-liquid separation can be carried out through different processes: filtration, pressurized filtration, drainage, centrifugation, sedimentation and flotation. In order to increase separation efficiency, physical and mechanical separation can be combined to chemical separation.

1.2.2. Separation efficiency and the factors that affect it

In order to compare different separators and choose the separation technologies that better match the farmer needs, it is an advantage to use the separation efficiency as indicator of the separator performances.

The separation index (*Et*), expresses the distribution of a specific compound (*x*) between the solid and the liquid fraction (Svarovsky et al., 1985):

$$Et(x) = \frac{m(x)_{solid}}{m(x)_{slurry}}$$

where $m(x)_{slurry}$ and $m(x)_{solid}$ are the masse (g) of a specific compound in the treated input slurry and in the solid fraction, respectively. The greater Et(x), the higher is the amount of the compound x being retained in the solid fraction.

The simple separation index gives no indication of an increase in concentration of x in the solid fraction; therefore, the reduced separation index, *Et'*, could represent an improve of the Et (Svarovsky, 1985):

$$Et'(x) = \frac{Et(x) - \frac{m(solid)}{m(slurry)}}{1 - \frac{m(solid)}{m(slurry)}}$$

where *m(slurry)* and *m(solid)* are the total mass (g) of the treated raw slurry and of the produced solid fraction, respectively.

Solid-liquid separation efficiency is affected by different factors, as described by Burton and Turner (2003).

1. Separation technique. Every separation system present different operating characteristics and functioning; therefore, the characteristics of the produced liquid and solid fractions will be affected by the separating system that will be used. According to Jørgensen and Hjorth (2009), chemical and biochemical characteristics of the separated solid fraction are different according to the separation device and make it suitable for different purposes. The main characteristics of the separation techniques that affect separation efficiency are:
    - The input flow rate: the lower is the input flow rate, the higher is the separation efficiency (Møller et al., 2007; Hjorth et al., 2010);
    - Mesh size (where used), which affects the size of the retained particles;
    - Centrifugal force, for separation through centrifugation;
    - The applied pressure, for separation through pressurized filtration;
    - The size of air bubbles, for flotation systems.
2. Manure type. The characteristics of the input slurry that mainly affect the separation efficiency are the animal species, the DM concentration and the size of the particles. These parameters affect not only the efficiency of the separation process, but also the choice of the separation technique. Slurries with a low DM content should be treated by high efficiency separation systems, while slurries having a high DM concentration could lead to clogging problems and, thus, should be previously treated through separation processes that allow to remove larger particles. The characteristics of the input slurry and, thus, the separation efficiency may be

modified by pre-treatments, such as anaerobic digestion, slurry acidification or solid-liquid separation (Masse et al., 2005, Hjorth et al., 2013).

3. Additives. Additives such as coagulating and flocculating agents are added to slurry in order to improve separation efficiency. The main characteristics that affect separation efficiency are:
    - The type of additive used:
    - The added dosage.

1.2.3. Mechanical and physical separation

Mechanical and physical separation could be distinguished according to the particle size that they are able to retain. In particular, some separator types can retain only large particles (> 0.1 mm), while the most efficient separation types can retain both large and smaller particles (<0.1 mm) and, thus, separate nutrients related to the finest solids.

1.2.3.1. Filtration

The separation devices that separate slurry through filtration are: stationary inclined screen, rotating screen and vibrating screens. The separation efficiency of these filtrating systems is affected by the particle size distribution of the treated slurry. In fact, the filtering system is characterized by different mesh size: the smaller the size of the mesh, the smaller the size of the retained particles.

The separation efficiency of this separator type is strongly affected by the content of total solids in the input manure and by the input manure type. In particular, the optimal separation performances are obtained using slurries with a DM content lower than 5% (Ford and Flemming, 2002; Bicudo, 2001).

1.2.3.1.1. Stationary inclined screens

Stationary inclined screens are characterized by an inclined plastic or metal sieve with a mesh size of 1-2 mm. The slurry is pumped to the top edge of the inclined screen and flows on the screen area by gravity. The liquid pass through the screen, while particles larger than the mesh size are retained on the screen (Figure 1.2). The solid fraction move downward due to gravity forces and fluid pressure (Ford and Flemming, 2002).

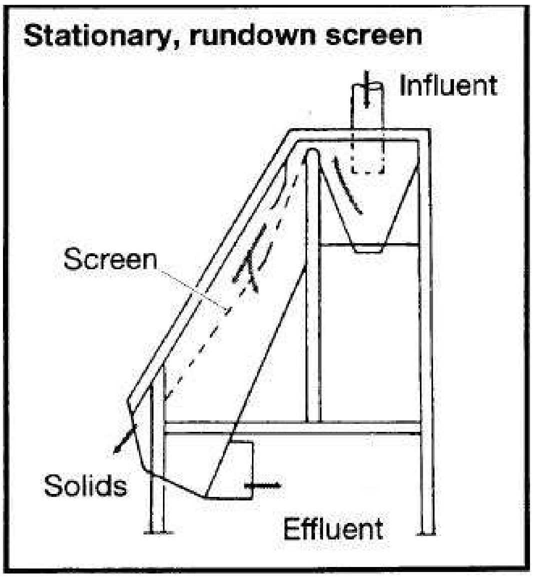

Figure 1.2. Stationary inclined screens (Sheffield et al., 2000).

Stationary inclined screens have a lower separation efficiency compared to other separator types (Table 1.3). However, the total costs and the energy requirements are lower; therefore, they are one of the cheapest separation technologies.

Table 1.3. Separation efficiency of DM, N and P for stationary screens (Provolo et al., 2008).

Separation efficiency (%)		
DM	**N**	**P**
20-25	4-7	8-12

1.2.3.1.2. Vibrating screens

Inclined stationary screens present problems related to the clogging of the pores. In vibrating screens the vibrating system avoids that clogging problems could occur.

Vibrating screens can consist of 1 to 4 screens with different mesh sizes. The input slurry is pumped to the flat vibrating screen at a controlled rate (Figure 1.3). The liquid fraction passes through the filter pores, while the short, rapid motion moves the retained solid fraction to the screen edge, where it is collected.

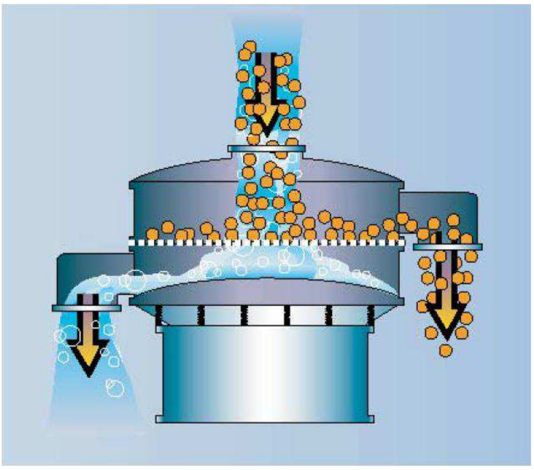

Figure 1.3. Vibrating screen (Provolo et al., 2008).

Vibrating screens are more efficient than stationary inclined screens (Table 1.4). However, separation efficiency is affected by the mesh size.

Table 1.4. Separation efficiency of DM, N and P for vibrating screens (Zhang and Westerman, 1997).

Separation efficiency (%)		
DM	**TN**	**TP**
3-25	2-7	1-34

The energy requirements are higher than stationary screens. Moreover, vibrating screens require frequent maintenance operations and, therefore, are seldom applied in animal manure treatment systems.

1.2.3.1.3. Rotating Screens

Rotating screens are composed by a cylindrical screen with a mesh size of 0.8-2.0 mm. The input slurry is pumped to the rotating screen at a controlled rate (Figure 1.4). The liquid pass through the screen and it is collected at the bottom, while the solid fraction is scraped to the filtrating area into a collection pit.

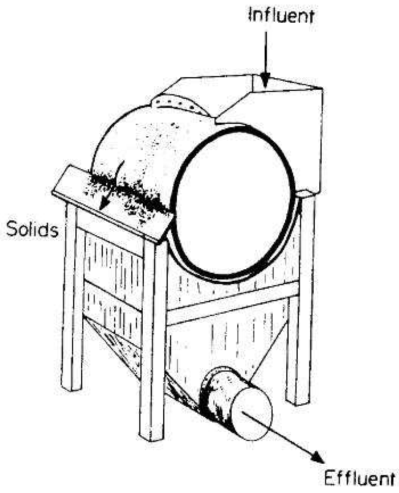

Figure 1.4. Rotating screen (Zhang and Westerman, 1997).

This separation technology has low energy costs. However, the produced solid fraction have a high moisture content, which makes it difficult to manage. The separation efficiency for rotating screen are shown in Table 1.5.

Table 1.5. Separation efficiency of DM, N and P for rotating screens (Zhang and Westerman, 1997)

Separation efficiency (%)		
DM	**TN**	**TP**
4-24	5-11	3-9

1.2.3.2. Pressurized filtration

This type of separators applies a pressure in addition to the filtering system in order to increase the separation efficiency. Generally, pressurized filtration processes leads to a high level of dewatering; therefore, the produced solid fraction have a high DM concentration and can be managed as solid manure (Hjorth et al, 2010).

The separation devices that operate through pressurized filtration processes are: screw, roller and belt presses.

1.2.3.2.1. Screw press

Screw presses are one of the separation type mainly used for the separation of livestock slurries. In a screw press separator, the input slurry is conveyed screw in the centre that forces the slurry through a tube and past a screen (Figure 1.5). The liquid fraction passes through the screen and is collected in a container surrounding the screen. The screw conveys the retained solids to the end of the axle, where the solid fraction is pressed against the plate and more liquid fraction is drained. The solid fraction is then discharged from the opening between the plate and the cylindrical mesh.

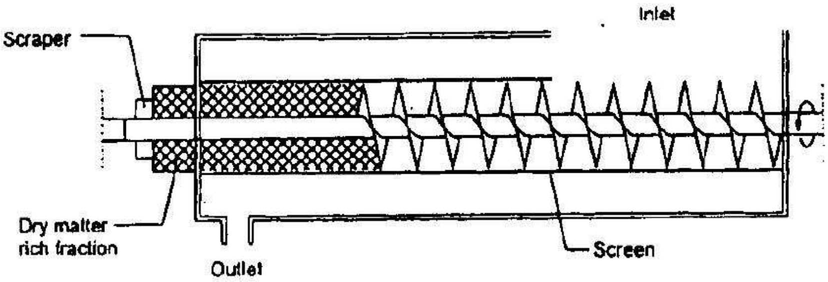

Figure 1.5. Screw press separator (Møller et al., 2000).

Average separation efficiencies of screw press separators are shown in Table 1.6. The separation efficiency of screw press separators is highly influenced by the applied pressure and by the particle size distribution of the input slurry (Christensen and Keiding, 2007).

Table 1.6. Separation efficiencies of screw press separators (Hjorth et al., 2010).

Slurry Origin	**Separation efficiency (%)**			
	Volume	**DM**	**TN**	**TP**
Pig slurry	4-7	21-64	4-31	7-46
Cattle slurry	2-13	13-64	4-36	3-28

Screw press separators produce a solid fraction with a high DM concentration (25-30%) compared to other separation technologies (e.g. belt presses). However, a large amount of small particles has been found in the liquid fraction (Møller et al., 2002), leading to a low separation efficiency for N, P and K. The energy requirements of a screw press separator are higher than filtrating systems. In particular, energy consumption is influenced by the treated manure type: separation of pig slurries leads to energy consumptions of 0.3-1.1 kWh m^{-3} of manure, while the separation of cattle slurry leads to energy consumptions of 0.4-0.8 kWh m^{-3} of manure (Balsari et al., 2006).

1.2.3.2.2. Roller press

Roller press separators consist of a cylindrical screen (0.8-1.5 mm) and a series of rollers (Figure 1.6). The manure is deposited onto the screen and squeezed by rollers. The liquid pass through the filter pores, while the solid fraction scraped to the cylindrical filter and drop in to a collection pit.

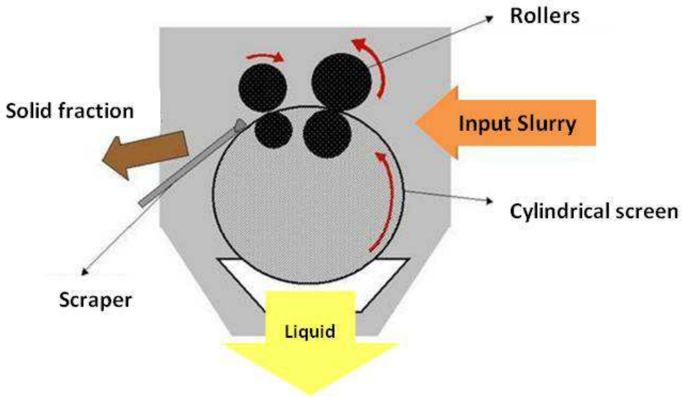

Figure 1.6. Roller press (http://sustag.imamoter.cnr.it).

Roller press separators are usually utilized for the separation of slurry with a high DM concentration, such as cattle slurry, for which separation efficiencies are higher (Table 1.7). In order to increase separation efficiency for pig slurries, the mesh size of the sieve should be reduced from 1.5 mm (typically used for cattle slurry) to 0.8-1.00 mm (Ford and Flemming, 2001).

Table 1.7. Separation efficiency of roller press separators (Provolo et al., 2008).

Slurry Origin	Separation efficiency (%)			
	Volume	**DM**	**TN**	**TP**
Pig slurry	4-6	10-35	2-10	10-45
Cattle slurry	8-16	35-60	10-28	45-55

Operating costs related to this separation type are low; however, this technology is rarely applied as slurry treatment technology due to the frequent maintenance operations and the energy costs.

1.2.3.2.3. Belt press

The belt press separators consist of two flat, wove, fabric belts that run horizontally between rollers (Figure 1.7). The liquid fraction is forced through the belt by the rollers and the solid fraction is carried along the belt and dropped in a collection chamber.

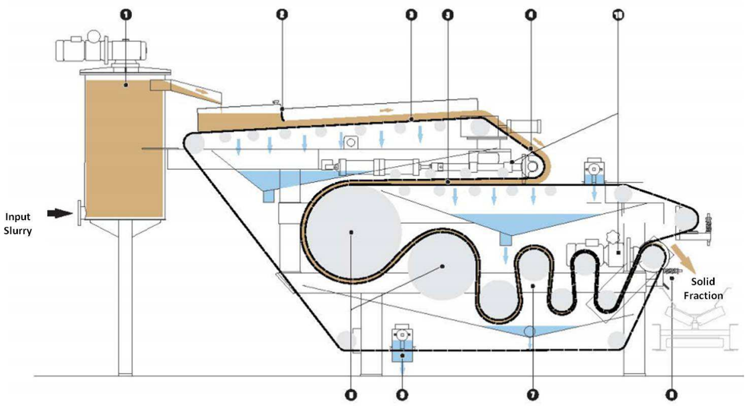

Figure 1.7. Belt press (Provolo et al., 2008).

Belt presses are often used in combination with coagulating and/or flocculating agents, in order to improve the drainage of the liquid fraction and, thus, the separation efficiency.
Belt presses have not been widely tested for slurry treatments.

1.2.3.3. Centrifugation

The typical separator device that separates slurry through centrifugation is a decanting centrifuge (Figure 1.8). In this type of devices, solid-liquid separation is caused by applying a centrifugal force that reduces the settling time of solid particles and produces a liquid and a solid fractions (Hjorth et al., 2010). The decanter centrifuge consists of a closed cylinder with a continuous turning motion. The centrifugal force separates solids and liquids at the wall into an inner layer with a high DM content (solid fraction) and an outer layer containing colloids, organic components and salts (liquid fraction). The solid fraction is conveyed to the conical end of the centrifuge by a screw conveyor that rotates at a speed that differs from the speed of the centrifugal bowl. The resulting liquid and solid fractions are discharged at opposite ends of the centrifuge (Balsari et al., 2006; Hjorth et al., 2010).

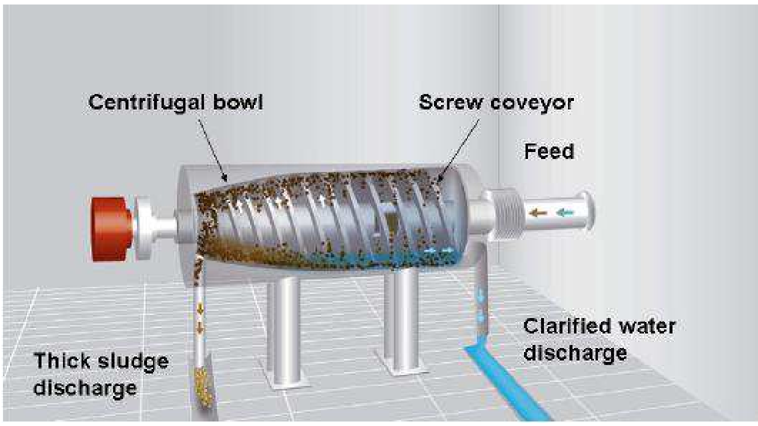

Figure 1.8. Decanter centrifuge (Hjorth et al., 2010).

The separation efficiency of centrifuges is affected by the flow rate of the input slurry. At the same time, the input flow rate of a decanting centrifuge is affected by the DM content of the treated slurry; in particular, the lower the DM concentration of the raw slurry, the higher the separation efficiency. Generally, the separation efficiency of decanter centrifuges is higher than other separation systems (Table 1.8), since it allows the separation of both large and small particles. The efficiency could also be improved by adding coagulating and/or flocculating agents to the slurry.

Table 1.8. Separation efficiencies of decanter centrifuges (Regione Lombardia, 2009).

Slurry Origin	**Separation efficiency (%)**			
	Volume	**DM**	**TN**	**TP**
Pig slurry	3-10	31-70	9-26	60-84
Cattle slurry	12-20	54-69	20-29	76-94

Decanter centrifuges have higher functioning and energy costs (Balsari et al., 2006). Furthermore, operating costs can be increased by the use of additives for slurry flocculation.

1.2.3.4. Sedimentation

Slurry separation through sedimentation is an attractive solid-liquid separation technique due to the simplicity of the technologies and the low operating costs. During this treatment process, the slurry is collected in specific devices where particles are left to settle for a determined period of time. In order to improve separation efficiency, coagulating and/or flocculating agents can be added to the slurry.

Generally, sedimentation systems produce a solid fraction with low DM content (8-12%) that could not be manages as solid waste; therefore, further treatments should be applied in order to reduce the moisture content of the solid fraction.

Separation through sedimentation can be carried out by: sedimentation thickener, Dorr separators and settling basins.

1.2.3.4.1. Sedimentation thickener

A sedimentation thickener consists of a container cylindrical at the top and conical at the bottom (Figure 1.9). Slurry is added at the top of the container and solid particles settle at the bottom of the conical part, where the solid fraction is removed. In order to encourage the settling of particles, a vibrating rake can be added in the middle of the container.

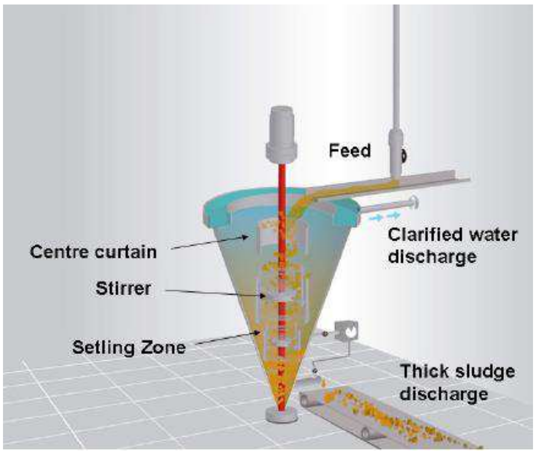

Figure 1.9. Sedimentation thickener (Hjorth et al., 2010).

1.2.3.4.2. Dorr separator

A Dorr separator consists of a circular tank with a central cylindrical container (Figure 1.10). The raw slurry is added in the central container and moves to the bottom of the tank at high speed. This quick flow causes the larger particles to settle, while smaller particles settle in a secondary time. The liquid fraction moves to the top of the tank, where it is removed. The solid fraction is scraped from the bottom edge of the tank to the center and collected in a hopper placed at the bottom of the tank.

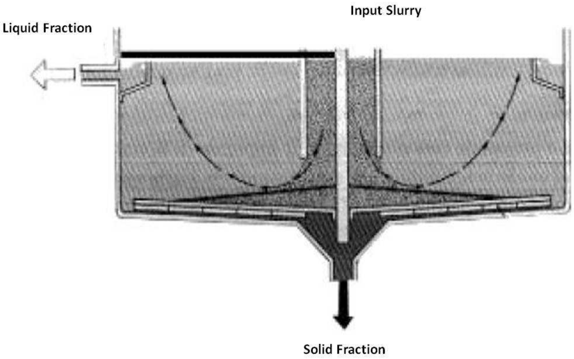

Figure 1.10. Dorr separator (Provolo et al., 2008).

1.2.3.4.3. Settling basin

Settling basins consists of tanks that are used for both storage and separation of slurry (Figure 1.11). The solid fraction settles to the bottom at it is periodically removed from the liquid fraction. Sedimentation basins should have a minimum size in order to allow the storage of the volume of slurry produced in a month.

Settling basins are one of the cheapest separation technologies, but the resulting solid fraction has high moisture content.

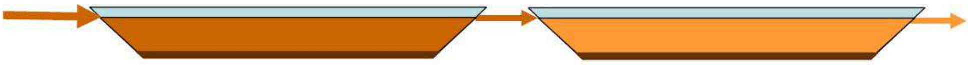

Figure 1.11. Settling basin (Provolo et al., 2008).

1.2.3.5. Flotation

Flotation is a gravity separation process based on the attachment of air or gasses bubbles to solid particles, which are then carried to the liquid surface (Masotti, 2002). The flotation process consists of two stages: (i) the production of suitably small bubbles (40-60 µm) and (ii) their attachment to particles. The solid fraction is then scraped off and collected in a specific container (Figure 1.12).

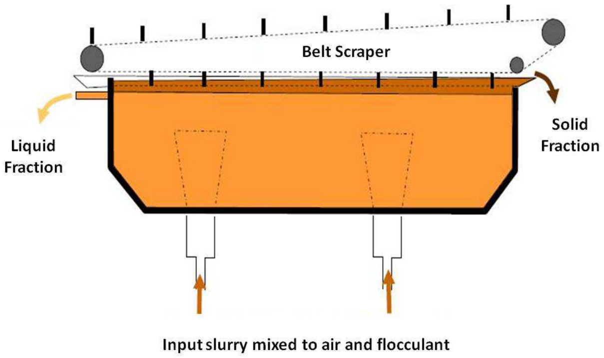

Figure 1.12. Flotation system (Provolo et al., 2008).

Depending on the way the gas bubbles are generated, flotation is divided into dispersed air, dissolved air and electrolytic air. The Dissolved Air Flotation (DAF) is the most diffused flotation system. It consists of a system that adds air at a specific pressure; the air pressure is then reduced till atmospheric values, leading to the production of small bubbles.

Compared to settling basins, the floating systems have higher separation efficiencies and smaller sizes. The resulting solid fraction have a DM content from 3 to 8%, a N concentration from 30 to 40 % and a P content from 70 to 90%. In order to improve the separation efficiency, coagulating and/or flocculating agents can be added to the slurry. However, the separated solid fraction have a high moisture content, therefore further treatment processes should be installed in order to manage the solid fraction as solid manure.

1.2.4. Chemical separation

Mechanical and physical separation processes can be combined to chemical separation processes in order to (i) reduce the P content in the liquid fraction, (ii) reduce the moisture content in the solid fraction and/or (iii) increase the separation efficiency of the different separation devices (Hjorth et al., 2008).

Chemical additives are divided in coagulating and flocculating agents, according to their reactions in the slurry. In general, they enhance the aggregation of small particles, leading the formation of larger flocs which results easier to separate (Bolto and Gregory, 2007). The aggregation of particles can be facilitate by (i) adding multivalent cations that cause particle coagulation and/or (ii) adding polymers that cause flocculation.

At coagulation, multivalent cations neutralize the negative charge of particles in the slurry by adsorbing the oppositely charged ions to the particles surface, creating a double layer (Figure 1.13a).

The flocculation process is often associated to coagulation and is carried out by the addition of polymers. The polymer can promote particles aggregation through two different mechanisms: (i) patch flocculation (Figure 1.13b) and (ii) polymer bridging (Figure 1.13c). Patch flocculation is the adsorption to particles of oppositely charged polyelectrolytes with a charge density much higher than the charge density of the particles. Local positively and negatively areas are formed on the surface of particles; therefore, a strong electrical attraction between particles occurs, leading to the formation of larger flocs.

Polymer bridging is the main reaction mechanisms that occur when a polyelectrolyte polymer is added. This process occurs when long-chain polymers adsorb the surface of more than one particle, causing the formation of strong aggregates of larger dimensions.

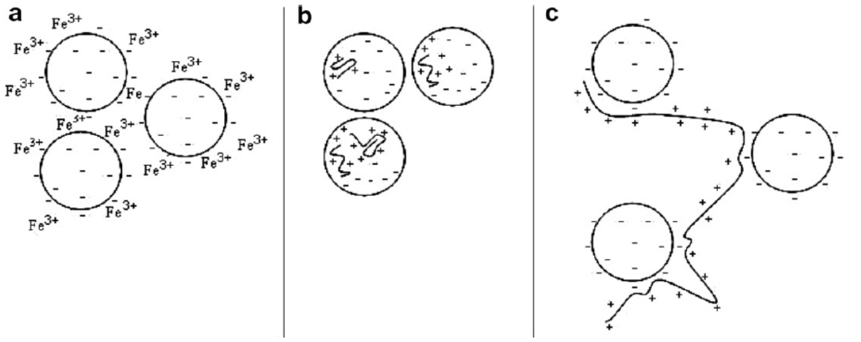

Figure 1.13. Coagulation (a), patch flocculation (b) and polymer bridging (c) (Hjorth et al., 2008).

1.2.4.1. Coagulants

The coagulants that are mostly used for slurry treatments are trivalent cations salts, such as iron (Fe^{3+} and Fe^{2+}) and aluminum (Al^{3+}), and calcium (Ca) salts. These compounds enable not only to aggregate smaller particles into larger flocs, but also to precipitate P and increase its concentration in the solid fraction.

The mostly used coagulants for slurry treatments are:

- Iron chloride, $FeCl_3$;
- Iron sulfate, $Fe_2(SO_4)_3$;
- Iron sulfate, $FeSO_4$
- Aluminum chloride, $AlCl_3$;
- Aluminum sulfate, $Al_2(SO_4)_3$;
- Lime, CaO;
- Calcium hydroxide, $Ca(OH)_2$.

According to Hjorth et al. (2010), if the multivalent cation is calcium, the efficiency is ranked as CaO > $Ca(OH)_2$; if the multivalent ion is iron, the efficiency is ranked as $FeCl_3 > Fe_2(SO_4)_3 > FeSO_4$; while if the ion is aluminum, the efficiency is ranked as $Al_2(SO_4)_3 > AlCl_3$.

The addition of these products to the slurry could lead to environmental problems related to the plant toxicity of the residual of iron and aluminum. Furthermore, the application of sulfates could lead odor emissions during the slurry storage.

1.2.1.2. Flocculants

Flocculants used for slurry treatments are usually long-chained polymers with a cationic charge. They are characterized by the structure of the molecule (linear or branched), the charge, the charge density and the molecular weight. Flocculants used in slurry treatments are water soluble polymers, usually polyelectrolytes. They are broadly divided according to their ionic nature: cationic, anionic and non-ionic (Bolto and Gregory, 2007). When diluted in water, flocculants adopt a random coil configuration, which represents the most probable configuration.

The main characteristics of polyelectrolytes are the molecular weight (MW) and the charge density (CD). The MW is usually distinguished in low, medium and high, corresponding to MW values in the ranges $<10^5$, 10^5-10^6 and $>10^6$, respectively (Bolto and Gregory, 2007). In case of polyelectrolytes, CD is a very important parameters, which represents the amount of charged groups related to the amount of polymer. It can be expressed as mole per cent of charged groups (mol%) or as milliequivalents per gram ($meq \cdot g^{-1}$). CD is highly dependent on the pH of the slurry, which should be monitored during the choice of the flocculant type and dosage. Usually, CD of polyelectrolytes is divided as low, medium or high if the mol% of the ionic groups is approximately: 10%, 25% and 50-100%, respectively (Bolto and Gregory, 2007).

Synthetic polyelectrolytes, i.e. polyacrylamide (PAM), are broadly used in chemical treatment of livestock slurry. Several studies indicate that a cationic polymer is superior to anionic and non-ionic polyelectrolytes; this is related to the negative charge

1.3. Aim of the study

Solid-liquid separation of livestock manure is a widely used treatment process that allows to improve the manure management on farms. Slurry separation is often combined to other treatments in order to enhance an overall reduction of nutrient losses to air, water and soil. Therefore, the evaluation of the different separating system and the optimization of this process is crucial in order to improve the performances of the treatment systems and the minimization of the environmental impact related to manure management.

The present study aims to: (i) evaluate the solid-liquid separation treatment in a treatment plant under different operating conditions; (ii) investigate the optimization of the separation process through natural and synthetic chemicals.

The solid-liquid separation will be explored under different aspects:

- The performances of different separation systems under different operating conditions (type of manure, type of separator, flow rates, pre-treatments, use of chemicals);
- The optimization of mechanical and physical separation through coagulation and flocculation pretreatments;
- The evaluation of predictive models as decision support tools for the prediction of the efficiency of different separation systems.

2. EVALUATION OF THE SOLID-LIQUID SEPARATION IN A TREATMENT PLANT

2.1. Introduction

Solid-liquid separation of animal slurry is often used as pre-treatment in order to improve the performances of the further treatment processes. In fact, the two separated fractions present different characteristics and, hence, they could be used for different purposes within a manure treatment plant.

Solid-liquid separation is frequently used in combination to anaerobic digestion processes for the production of energy. This process consists in the degradation of organic compounds under anaerobic conditions and the production of biogas, which is composed by methane (CH_4) and carbon dioxide (CO_2) (Burton and Turner, 2003). The anaerobic digestion allows to reduce the greenhouse gas (GHG) emissions since it avoids CH_4 emissions from manure storage and produces energy without the utilization of fossil fuels (Itten et al., 2013). Furthermore, it allows to stabilize the characteristics of animal manure, to reduce odor emissions and to decrease the pathogen content in animal slurries. Solid-liquid separation could precede anaerobic digestion. In this case, the solid fraction is used to maximize the production of biogas, since this fraction presents the higher concentration of organic compounds. Slurry separation could also be used to treat the anaerobic digested slurry, in order to produce a liquid and a solid fraction that can be used for further treatments.

Manure separation is also used in combination to other biological treatment, such as Sequencing Batch Reactor (SBR) processes for nitrogen (N) removal (Beline et al., 2007). The SBR process consists in particular reactors where the nitrification and the denitrification processes occur in the same reactor, which are designed in order to have a temporal distribution of the different phases (Magrì and Flotats, 2008). A conventional SBR system operates in a fill and draw sequence (cycle) that is repeated over time. Each cycle is composed of various consecutive phases (fill, anoxic mixing phase, oxic reaction, settling, draw and idle) that can last a different period of time according to the scope of the treatment plant. The principal reactions occurring in a SBR system are nitrification and denitrification processes.

Nitrification is an aerobic autotrophic process that consists of the sequential oxidation of the ammonium (NH_4^+) to nitrites (NO_2^-) and the further oxidation of nitrites in nitrates (NO_3^-):

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + 2H^+ + 2H_2O$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$

In order to allow the correct oxidation of ammonium and nitrites, the optimum concentration of dissolved oxygen in the manure is 2 mg/l (Ndegwa et al., 2005).

Denitrification is a heterotrophic anaerobic process during which the nitrites and the nitrates produced during the nitrification process are reduced to molecular nitrogen N_2.

In order to optimize these two reactions, the SBR system is often combined to a mechanical solid-liquid separation step. In fact, the major part of the dry matter (DM) contained in the input slurry is transferred to the solid fraction, while the larger amount of nitrogen remains in the liquid fraction and could be removed through the biological treatment. Furthermore, the lower DM concentration of the liquid fraction allow a better aeration of the manure and, thus, to improve the biological reactions. According to Béline (2007), the maximum DM content of the slurry to be treated through an SBR process should be equal to 2%. The performances of the solid-liquid separation treatment are therefore crucial for the correct functioning of the SBR process. For this reason, the separation technique should be selected according to the characteristics of the obtained liquid fraction, which have to be optimal for the SBR treatment.

In this chapter, two different separation systems are investigated in order to evaluate their suitability in a manure treatment plant.

2.2. Materials and Methods

2.2.1. The Agroenergie Bergamasche treatment plant

The Agroenergie Bergamasche plant is a collective treatment plant with an anaerobic digestion phase for energy production and a nitrogen removal phase (Figure 2.1). It covers an area of 16000 m^2 and it is located in northern Italy, Bergamo province, in an intensive livestock area where there is a high surplus of nitrogen and has been designated as vulnerable zone (NVZ).

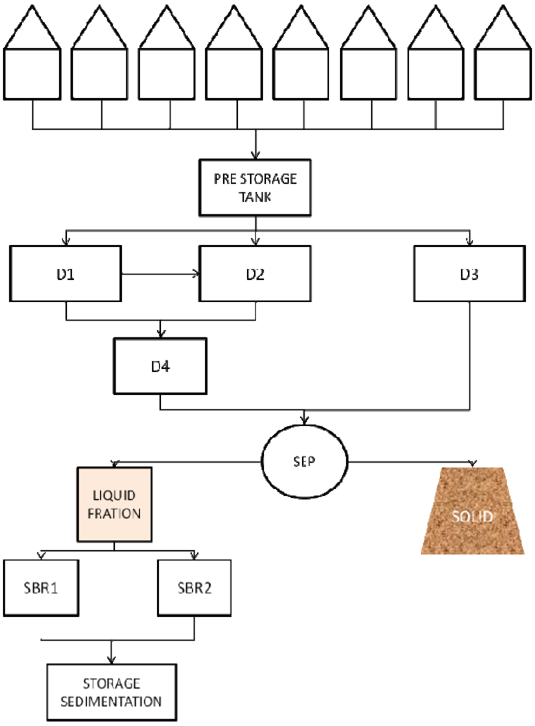

Figure 2.1. Scheme of the treatment processes.

The treatment plant involves 10 farms and 13 farmsteads: 8 cattle farms, 1 fattening pigs farm and 1 laying hens farm. The farmsteads are located 0.5 to 6 km far away from the plant, for a total daily production of around 300 m^3 of manure.

The manure produced by the different farms is collected in a continuously mixed pre-storage tank (885 m^3). The slurry produced is transported to the treatment plant by slurry tankers, excepting for the nearby farmstead, which is connected directly to the plant by mean of a pipeline. Concerning the slurry transported by slurry tankers, the tare is registered every morning in order to measure the amount of slurry collected from every farm.

The collected manure is firstly processed in an anaerobic digestion phase for the production of energy. This step is carried out under mesophilic conditions (38-40°C) in three digesters (D1, D2, and D3) and a post-digester (D4). The total volume of the reactors D1 and D2 is 2280 m^3, while D3 and D4 have a capacity of 3185 m^3. The slurry is pumped to D1, D2 and D3. The reactor D1 is fed not only with slurry, but also with other biomasses that are collected in a hopper (30 m^3) (Figure 2.2). The biomasses added to the D1 are: silages, solid manure, poultry manure, corn flower and molasses. The second digester D2 is fed with raw manure and receives the digestate out coming from D1. The anaerobically digested slurry produced in D1 and D2 is then conveyed to the post-digester D4. The biogas produced in each reactor is collected, treated for sulphur (S) removal and then conveyed to a 1MW cogenerator for energy production.

Figure 2.2. Biomasses added to the hopper.

The digested slurry out coming from D3 and D4 is then separated for the production of a liquid and a solid fraction (SEP).

The solid fraction is sold to horticultural farms placed nearby the treatment plant, while the liquid fraction is treated through a nitrification-denitrification step for N removal. This treatment is carried out in to two Sequencing Batch Reactors (SBR), each of 660 m^3 and working in parallel. In each SBR, four phases occur:
Fill and draw phase (15 minutes). 15 m^3 of liquid fraction are pumped in to the reactor and $15m^3$ of treated slurry are conveyed to storages.
Mixing phase (90 minutes).
Aerobic phase (120 minutes). Air is pumped to the bottom of each reactor through two compressor, till the oxygen concentration (O_2) in the manure is 2 mg/l. During this phase, an anti-foaming reagent is added.
Sedimentation (20 minutes).
The treated effluent is then pumped to the final storage, consisting of two covered storage tanks of 2280 m^3 each. Here, the slurry tankers collect the effluent and return it to farms, where it is utilized for plant fertilization. The amount of effluent transported to each farms by slurry tankers is weighed.

2.2.2. Manure Separation

Since March 2013 the solid-liquid separation treatment was performed through two screw presses (FAN PSS 3.2) working in parallel (Figure 2.3). These two devices treated the digested slurry produced by the anaerobic digestion treatment, before the biological nitrogen removal. The performances of the screw press separators were monitored periodically in order to evaluate the correct functioning of the system according to the SBR requirement. In particular, samples of the treated digested slurry and of the resulting liquid and the solid fractions were collected every two months. The samples were stored at – 18°C and analyzed for DM concentration, in order to evaluate the DM separation efficiency and the DM concentration of the liquid fraction.

Figure 2.3. Screw press separator (FAN PSS 3.2)

During July 2012 a decanter centrifuge (Jumbo 3, Pieralisi, Italy) was evaluated as separation technology alternative to the screw press. Two manure types were used (Table 2.1): (i) anaerobically digested slurry (AD) and (ii) digested liquid fraction (ADLF) from a screw press separator. AD was produced by the co-digestion of pig, cattle and poultry manure with biomasses (corn and triticale silages) from a collective treatment plant. AD was then separated through a screw press separator (FAN PSS 3.2, Italy) in order to obtain ADLF.

AD and ADLF were then separated through a decanter centrifuge (Jumbo 3, Pieralisi, Italy) operating under different conditions (Table 2.1). At first, AD and ADLF were treated under different input flow rates, in order to understand how the flow rate could affect the separation performances. Then, the input flow rate was maintained constant and a flocculating agent was added at different flow rates. The flocculating agent was a linear cationic polymer (0.7% concentration), with a charge density of 40% and a medium-high molecular weight (Hidrofloc CL1704, Hidrodepur, Italy).

Table 2.1. Operative conditions tested for the decanter centrifuge.

Test ID	Manure type	Input flow rate (m^3/h)	Polymer flow rate (m^3/h)
Tests with different input flow rates			
1	ADLF	6	0
2	ADLF	8	0
3	ADLF	10	0
4	AD	4	0
5	AD	6	0
6	AD	8	0
Tests with different polymer flow rates			
7	ADLF	6	1.2
8	ADLF	6	0.8
9	ADLF	6	0.6
10	ADLF	6	0.4
11	ADLF	6	0.2
12	AD	6	1.15
13	AD	6	0.8
14	AD	6	0.6
16	AD	6	0.4
17	AD	6	0.2

During each test, the input flow rate was measured through a flow meter, while production rate of the liquid fraction was measured by measuring the level of liquid fraction in the collection pit and converting it as volume. The volume of the solid fraction was calculated as the difference between the volumes of the input slurry and the volume of the liquid fraction.

Samples of raw slurries and of liquid and solid fraction were collected in duplicate after each separation test and stored at -18°C.

2.2.3. Data analysis

The separation efficiencies for the analyzed parameters were calculated using the simple separation index (Section 1).

2.3. Results and discussion

2.3.1. Screw press performances

The DM content of the raw manure and of the liquid and the solid fractions were evaluated. Average values are represented in Table 2.2.

Table 2.2. Characteristics of raw manure and separated fractions with screw press. Mean (n=10), standard deviations in brackets.

Fraction	DM (%)
Digested slurry	5.6 (0.4)
Liquid fraction	3.9 (0.6)
Solid fraction	25.4 (5.0)

Although the input slurry is previously treated through anaerobic digestion, the input digested slurry presents a high DM content. This is due to the addition of biomasses during the biogas production. For this reason, although the average DM separation efficiency is equal to 30% (Figure 2.4a), the resulting liquid fraction presents a DM content higher than 2% required for the nitrification-denitrification process (Figure 2.4b). This is due to the operation principles of screw press separators, which allows the separation of coarse particles, while small particles are contained in the liquid fraction. In fact, anaerobic digestion lead to the degradation of most of the organic compounds, decreasing the particle size of digested slurry (Masse et al., 2005). Therefore, the major part of particles in the digested slurry are smaller than the screw press' mesh size and, thus, are not retained in the solid fraction.

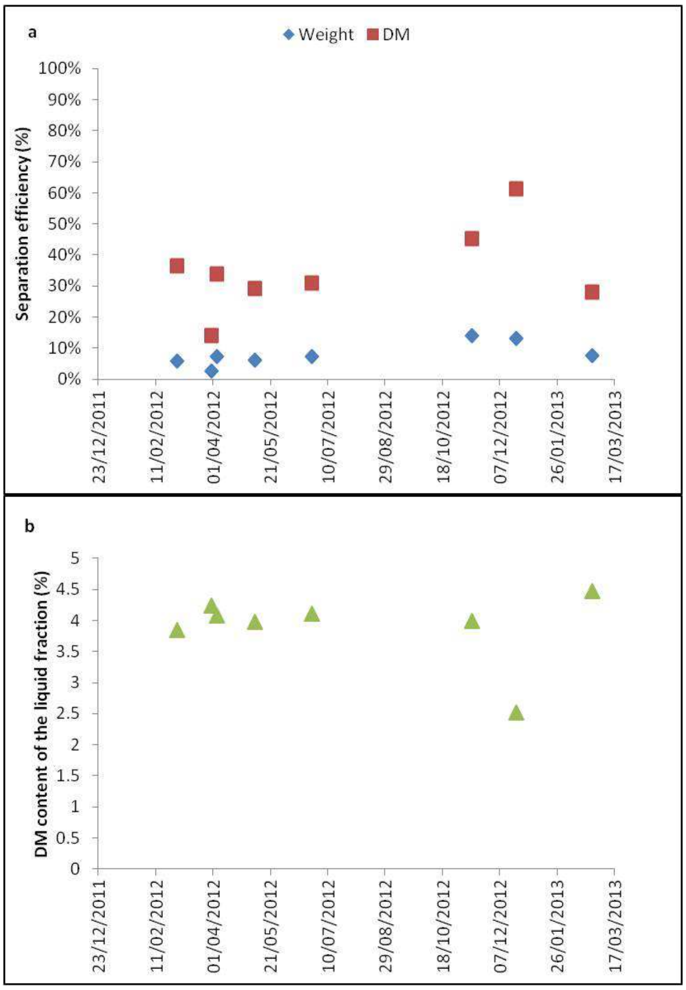

Figure 2.4. Separation efficiency (a) and DM content of the liquid fraction (b) for the screw press.

The screw presses produce a liquid fraction characterized by a high D content, which lead to problems during the SBR process. Therefore, another separation system should be evaluated in order to improve the biological nitrogen removal.

2.3.2. Decanter centrifuge performances

2.3.2.1. Characteristics of the fractions

Since total solids, measured as DM content, are one of the main manure parameters involved in the solid-liquid separation treatment (see Section 1), raw slurries and separated solid and liquid fractions were characterized only for the DM content (Table 2.3).

Table 2.3. Characteristics of raw slurries and liquid and solid fractions for each separation test with decanting centrifuge.

Raw manure			Liquid fraction		Solid fraction	
Test ID	**Manure type**	**DM (%)**	**Volume (%)**	**DM (%)**	**Volume (%)**	**DM (%)**
Tests with different input flow rates						
1	ADLF	3.7	93	2.5	7	20.6
2	ADLF	3.7	94	2.5	6	21.0
3	ADLF	3.7	94	2.7	6	21.3
4	AD	5.0	86	2.3	14	21.4
5	AD	5.0	86	2.3	14	21.6
6	AD	5.0	87	2.4	13	21.9
Tests with different polymer flow rates						
7	ADLF	3.0	94	1.4	6	27.0
8	ADLF	3.1	94	1.7	6	25.5
9	ADLF	3.2	94	1.8	6	26.1
10	ADLF	3.3	94	2.0	6	26.1
11	ADLF	3.5	95	2.2	5	25.8
12	AD	3.8	89	1.5	11	22.7
13	AD	4.0	89	1.6	11	22.8
14	AD	4.2	88	1.7	12	22.6
15	AD	4.3	88	1.9	12	22.3
17	AD	4.5	88	2.1	12	22.0

The different tests led to the production of different amounts of liquid and solid fractions, which presented different DM concentrations. For the tests with different input flow rates, the produced amounts of liquid and solid fractions were different for the different flow rates. In particular, the higher was the input flow rate the lower was the volume of the produced solid fraction. This trend was observed also when the polymer flow rate was changed, even if the difference between a polymer flow rate and the following one was less significant.

2.3.2.2. Separation efficiency affected by input and polymer flow rate

In order to evaluate the effect of the different input and polymer flow rate, the simple DM separation index was calculated for both AD and ADLF (Figure 2.5).

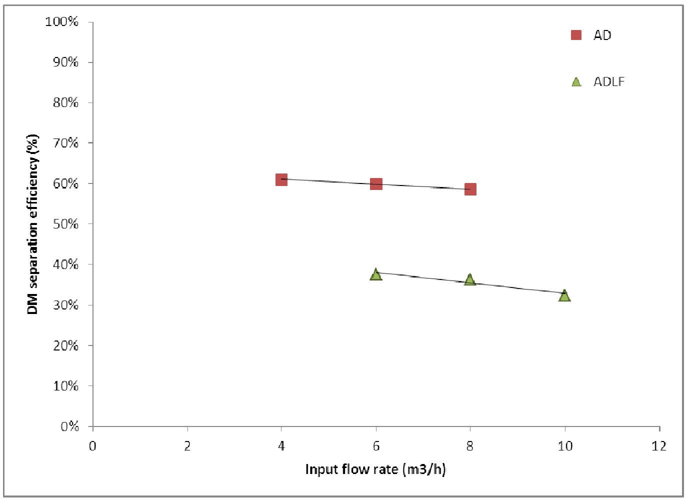

Figure 2.5. DM separation efficiencies at different input flow rates for AD and ADLF. DM separation efficiency was calculated as reduced separation index.

For all the tests that was performed, the increase of flow rate caused an average reduction of the DM separation index of 3% and 10% for AD and ADLF, respectively. In fact, an increase of the input flow rate causes a decrease of the retention time of the slurry in the decanter centrifuge (Møller et al., 2007) and, thus, to a reduction of the separation efficiency (Hjorth et al., 2010).

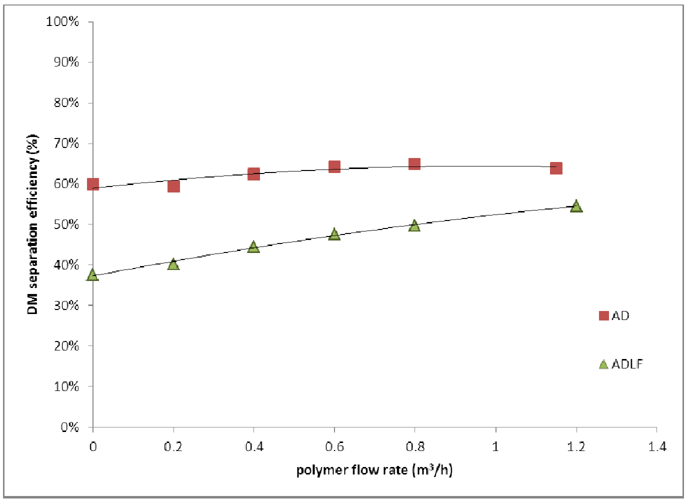

Figure 2.6. DM separation efficiencies at different input flow rates for AD and ADLF. DM separation efficiency was calculated as reduced separation index. The 0 m3/h values correspond to the tests 1 and 5 for ADLF and AD, respectively.

The DM separation efficiency increased when the polymer was added for both AD and ADLF (Figure 2.6). This is related to the flocculating properties of the polymer that enhance the aggregation of smaller particles, which are more difficult to aggregate, and thus improve the separation efficiency. In particular, the separation index increased at increasing amounts of added polymer till a maximum value, as previously observed (Vanotti et al., 2002). This increase resulted higher for ADLF, while it was less significant for AD. This is due to the higher amount of coarse particles contained in the digested slurry, which result more heavy and, hence, easier to separate by centrifugation. Therefore, the polymer dosage required for the separation of AD by centrifugation is lower.

2.4. Considerations

The solid-liquid separation does not allow to retain smallest particles in the solid fraction and, thus, the resulting liquid fraction presents a high DM content. Therefore, the liquid fraction produced by the two screw presses separators is not suitable for manure treatments that require a low DM concentration of the input slurry, such as nitrification-denitrification processes. Separation systems with higher DM separation efficiency, such as decanting centrifuges, could allow to improve the retention of small particles in the solid fraction and to reduce the DM content of the liquid fraction below 2%. Flocculant can be added in order to increase the separation efficiency, but increasing the costs of the separation treatment.

3. EVALUATION OF SEPARATION PERFORMANCE UPON MANURE ACIDIFICATION PRE-TREATMENT

3.1. Introduction

The increasing intensification of farming systems, combined with an improper manure management led to an increase of greenhouse gas (GHG) emission, eutrophication of waters and acidification from ammonia (NH_3) volatilization (Lopez-Ridaura et al., 2008).

The 94% of NH_3 emissions comes from the agricultural sector, for which swine livestock represent one of the main sources (EEA, 2012). NH_3 volatilization represents not only a loss of fertiliser value, but also an environmental problem and a health risk for animal and human beings (Ndegwa et al., 2008). Several solutions have been proposed to reduce NH_3 emissions from livestock, as described by Ndegwa et al. (2008). Among these, slurry acidification is a treatment process widely applied by different farms in Denmark (Eriksen et al., 2008; Petersen et al., 2012) to reduce NH_3 emissions from slurry storage. This technique consists in acidifying a portion of slurry by adding concentrated acid to lower pH; the acidified slurry returns to buildings, except the 5%, which is transferred to storage tanks (Peters et al., 2010). Slurry acidification allows to reduce NH3 emissions by 70% (Kai et al., 2007), but it allows to decrease also methane (CH_4) and sulphate emissions from slurry storage and field application (Petersen et al., 2012; Ottosen et al., 2009). According to Hjorth et al. (2013), it increases the occurrence of de-mineralization processes, which lead to the dissolution of P precipitates (e.g. struvite and Ca-P compounds) and to the increase of P dissolved species in slurry. Furthermore, acidification inhibits microbial activity, reducing the content of sulphides (Ottosen et al., 2009), volatile fatty acids (VFA) and ammoniacal nitrogen (Hjorth et al., 2013). In addition to these chemical effects, slurry acidification decreases the buffer capacity of the slurry. Finally, the acidification treatment also affects the characteristics of particles suspended in slurry; in fact, it reduces their surface negative charge and increases particle size by increasing particles attraction (Hjorth et al., 2013).

Solid-liquid separation of manure is often combined to other manure acidification. Since, the acidification treatment modifies physical and chemical characteristics of the slurry; it could affect the efficiency of solid-liquid separation technologies. According to Fangueiro et al. (2009), the separation of acidified slurry leads to a general decrease of elements retained in the solid fraction and of Total Carbon in both solid and liquid fraction. Furthermore, it causes an increase of DM and ammoniacal nitrogen (TAN) in liquid and solid fractions, and an increase of P, calcium (Ca) and magnesium (Mg) concentration in liquid fraction. However, more information is necessary in order to better understand the possible effect of slurry acidification on solid-liquid separation.

In this section, the separation performances of different separation systems are evaluated under different operating conditions. In order to separately evaluate the effects of input flow rate and the polymer flow rate and the effect of pre-treatments on separation efficiency, two experiments were carried out. In the first one, the effect of different flow rates and different polymer flow rates were evaluated by using the same separation system. In the second experiment, the effect of a pre-treatment on different separation technologies was investigated.

3.2. Materials and methods

3.2.1. Manure treatments

The experiment took place in Grønhøj Research Station in Denmark, using slurry produced by pigs at the slaughtering stage of growth, i.e. finishing pigs (ca. 31 to 108 kg). The manure was collected from two comparably operated houses with two different slurry treatments: manure maintained at its natural condition having a pH value of approximately 7 (PS) and acidified manure having a pH value of approximately 5.5 (APS), as explained by Hjorth et al. (2013). During the entire period of production of the finishing pigs, the pig manure accumulating under slated floors was pumped to an acidification device, consisting of a 14 m^3 acidification tank, where slurry pH was lowered to 5.5 by adding concentrated sulphuric acid (96% H_2SO_4). Acidified manure was then returned to slurry channels, except for 5% of slurry daily production, which was diverted to storage tanks from which samples were taken to pass through various separation techniques.

The APS and the PS were each separated using three different separation techniques (Table 3.1): pressurized filtration (screw press), centrifugation (decanter centrifuge) and flocculation and drainage (flocculation and belt thickener drainage). For each separation device, manure was pumped from continuously stirred storage tanks. All three separators were operated under optimal full-scale conditions (Table 3.1). The screw press and decanter centrifuge operated with automatic adjustment of the flow rate according to the velocity of the solid fraction pump. The flocculation and drainage treatment operated using polymer characteristics and polymer volume that had been optimized for the manure type (Table 3.1) as described by Hjorth and Jørgensen (2012). A 0.11% emulsion of the two polymers was prepared immediately before the separation test. Separation experiments were run one time for each separation technology for one to four hours.

Table 3.1. Operating conditions of the tested separators.

Separator	**Parameters**	**PS**	**APS**
SCREW PRESS Bioselector 550, Bröger, Germany			
	Mesh size (µm)	400	400
	Flow rate manure ($m^3 \cdot h^{-1}$)	10	22
DECANTING CENTRIFUGE GEA Westfalia, Germany			
	Centrifugal force (rpm)	45000	45000
	Flow rate manure ($m^3 \cdot h^{-1}$)	1.9	2.7
FLOCCULATION and BELT THICKENER DRAINAGE AL-2 Teknik A/S, Denmark			
	Polymer use	K133L (Praestol-Ashland, DK)	K144L (Praestol-Ashland, DK)
	Polymer charge density (mol %)	60% cationic	75% cationic
	Mesh size (µm)	390	390
	Length of the belt (cm)	2800	2800
	Width of the belt (cm)	300	300
	Flow rate manure ($m^3 \cdot h^{-1}$)	0.6	0.7
	Flow rate polymer ($m^3 \cdot h^{-1}$)	0.1	0.1

The total amount of manure used in each experiment was calculated by measuring differences in the level of manure in the slurry storage tanks before and after the treatment.

During the experiments, for each separation trial, the production rate of liquid and solid fractions was measured in order to estimate the mass separation efficiency. For each separation technology, the liquid and solid fractions from the equipment were collected simultaneously in buckets for identical durations of time (3 seconds for screw press: 10 seconds for centrifugation; 1 minute for flocculation and drainage), weighed, and converted to masses. The input flow rate was calculated as a sum of the mass of liquid and solid fractions by assuming no material was retained in the separation device. This was repeated five times.

Subsequently, for each separation technology, samples of liquid and solid fractions were collected for both PS and APS. Samples were collected in triplicates; some were stored at 5 °C for immediate analysis, and some were stored at -18°C for the analyses were performed later.

3.2.2. Analysis

Electrochemical (zeta potential) and physical (viscosity and filtration velocity) properties of PS and APS were analyzed. The zeta potential was determined by preparing a 1:10 dilution with 0.2 M KCl and measuring with a zeta sizer (Master Sizer 2000; Malvern Instruments Ltd., Worcestershire, UK). Viscosity was measured using a Viscometer and a LV-1 spindle (Brookfield, MA, USA). Filtration velocity was determined by adding 100 ml of manure into a cylinder (8 cm dia., 30 cm height), bottom-covered by a 250 µm metal filter sieve, and measured by recording the weight of the filtrate after 2 minutes.

Analyses were performed on raw manures (PS and APS) and their respective liquid and solid fractions after separation. Measured properties were pH, electrical conductivity (EC), density, dry matter (DM), volatile solids (VS), total nitrogen (TN), total ammoniacal nitrogen (TAN), total phosphorus (TP), water soluble phosphorus (Soluble P), total potassium (TK), total sulphur (S tot), total sulphide (H_2S tot), copper (Cu), zinc (Zn), volatile fatty acids (VFA) and particle size distribution.

pH and electrical conductivity (EC) were determined immediately after the collection of samples, using standard instruments.

The DM concentration was determined after drying at 103°C for 20 hours. VS was determined by drying the sample in a muffle furnace from 105°C to 550°C for 2h and measuring the weight loss (European Commission, 2009).

Total N (TN) was measured by the Kjeldahl method. Total Ammoniacal Nitrogen (TAN) was determined by the methodology proposed by the European Regulation 2009/152/EC (European Commission, 2009).

TP, TK, S tot, Cu and Zn were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), as described by the European Regulation 2009/152/EC (European Commission, 2009).

$H_2S/HS\text{-}/S^{2-}$ (H_2S tot) was determined through precipitation with zinc, capture of H2S gas, color reaction and spectrometric quantification using the method described by Eriksen et al. (2010).

Water soluble P was determined by extraction with the reagent used for ascorbic acid technique and centrifugation three times (10000 rpm for 10 minutes), during which the supernatant was withdrawn after every centrifugation cycle. After extraction, the concentration of water soluble P was determined through color reaction and spectrometric quantification as described by Murphy and Riley (1962).

Volatile fatty acids (C2-C5) were measured by means of gas chromatograph (Hewlett Packard 6850A) with flame ionization detector (FID). The column used was a HP-INNOWax, 30 m x 0.25 mm x 0.25 µm. The carrier gas was helium (He). The temperature of the column was gradually increased from 110°C to 220°C at the rate of 10°C min-1 as described by Møller et al. (2002).

Particle size distribution was measured for raw slurries and for liquid fractions through laser diffraction (Master Sizer 2000; Malvern Instruments Ltd., Worcestershire, UK). The cut-off particle size was considered as the median of the particle size cumulative distribution.

3.2.3. Data analysis

The separation efficiencies for the analyzed parameters were calculated using the simple separation index (Section 1). The simple separation index gives no indication of an increase in concentration of x in the solid fraction; therefore, the reduced separation index, Et'(x), also was calculated (Section 1).

The water addition associated with polymers in the flocculation techniques was high for both the experiments. Therefore, the amount of water was subtracted from the concentration of the different compounds in both solid and liquid fractions, in order to express the true distribution of the input manure's components. The distribution of water between the liquid and the solid fraction was assessed as:

$$\frac{m(water)_{liquid}}{m(water)_{solid}} = \frac{m_{liquid} - m(DM)_{liquid}}{m_{solid} - m(DM)_{solid}}$$

where m(water)liquid and m(water)solid are the water content (g) in the liquid and in the solid fraction, respectively; m_{liquid} and m_{solid} are the masses (g) of the collected liquid and solid fractions respectively; m(DM)liquid and m(DM)solid are the DM contents (g) in the liquid and solid fractions, respectively.

For the experiment 2, results related to particle size distribution and to particulate species were elaborated. Particle size distribution was plotted as cumulative distribution. The cut-off particle size for each distribution was calculated as the median of each distribution and was evaluated in order to compare the effect of the acidification treatment on the different separation techniques. Particulate species were calculated by subtracting dissolved compounds from the total concentration, e.g., Particulate P was calculated by subtracting Soluble P from TP.

3.3. Results and discussion

3.3.1. Separation performances

The working principles of solid-liquid separators are different, therefore the performance of each is affected by manure characteristics in different ways (Hjorth et al., 2010). APS differs from PS in terms of median particle size, filtration velocity, viscosity and zeta potential (Table 3.2).

Table 3.2. Characteristics of the input slurries and of the liquid outputs. Means (n = 3), standard deviations in brackets.

Fraction	Separator	Parameter	PS	APS
Input Manure				
	-	Median particle size[a] (µm)	58 (15)	142 (10)
	-	Filtration velocity [b] (g/2min)	7 (2)	16 (2)
	-	Viscosity (mPas)	66(1)	25 (1)
	-	Zeta potential (mV)	-14 (2)	-10 (1)
Liquid Fraction				
	Screw press	Cut-off particle size[a] (µm)	112 (7)	308 (21)
	Decanting Centrifuge	Cut-off particle size[a] (µm)	14 (1)	334 (24)
	Flocculation and Drainage	Cut-off particle size[a] (µm)	160 (18)	54 (4)

[a] Median and cut-off calculated equally as the median of the cumulative distribution of the particle size of each fraction

[b] Mass of input slurry filtrated after 2 minutes using a 250 µm metal filter sieve

The median particle size in the range 0.1 to 1000 µm is higher in APS, which proves a larger amount of small particles in PS than in the APS; previous experiments has indicated this to be due to particle aggregation in the acidified slurry (Hjorth et al., 2013). The viscosity of the APS is also lower than the PS, thus, the settling resistance of the slurry may be lowered by manure acidification. APS presents also a less negative zeta potential, which indicates a reduction of the negative charge on particles upon acidification. For the screw press and the decanter centrifuge, the resulting acidified liquid fractions presented a higher cut-off particle size compared to the PS ones; in contrast, the cut-off particle size of acidified liquid fraction obtained by flocculation and drainage was lower than the liquid fraction obtained from PS.

Due to these different characteristics, the performance of the three tested solid-liquid separators was found to differ for APS and PS.

The lower amount of small particles below 100 µm in APS would lead to a relatively porous filter cake on a screw press filter and, thus, a low resistance to flow (Masse et al., 2005). Consequently APS can be more easily dewatered than untreated slurry, and indeed this was the observation in these experiments. The observed higher cut-off particle size in the acidified liquid fraction from the screw press (Table 3.2), can be explained by the more rapid dewatering causing increased flushing of compounds through the filter.

Centrifugation increases a particle's settling rate by applying a centrifugal force. Therefore, as compared to PS, the lower viscosity of APS, together with the larger sized particles, decreases the settling time. The larger median particle size found in the acidified liquid fraction supports the indication of a more rapid separation, as the quicker separation allows less time for settling of slowly settling components.

Flocculation and drainage is mainly controlled by the particle charge. Because APS is characterized by a lower amount of small particles, and because the less negative particles charge causes the slurry solution to be less stable, it is easier to aggregate (Sievers et al., 1994). The polymer for slurry flocculation of APS proved necessary to have a higher charge density (Table 3.1). Therefore, the flocs obtained after slurry acidification are denser and contain less liquid than those found in PS. The dense and therefore more stable flocs formed resulted in fewer particles being lost in the liquid fraction, which supports the observed presence of only small particles in the liquid fraction. Because of the more easily aggregatable particles being aggregated into more stable flocs, the flocculated APS proved to dewater faster than untreated slurry.

Generally, slurry acidification appears to result in more rapid separation upon treatment for all the studied manure separation techniques.

3.3.2. Characteristics of the fractions

The different separation technologies produced different amounts of liquid and solid fractions (Table 3.3). Generally, the volumes of solid fractions are higher for PS, with the highest amount produced by flocculation and drainage

Table 3.3. Characteristics of solid and liquid fractions from PS and APS. Means (n=3), standard deviations in brackets

Manure Type	Fraction	Separator	Relative Proportion (%)	pH	DM (%)	VS (%)	TN (kg/t)	TAN (kg/t)	TP (kg/t)	Soluble P (kg/t)	SolubleP/TP (%)	K (kg/t)	S tot (kg/t)	H_2S (g/t)	H_2S/Stot (%)	VFA (kg/t)	Cu (g/t)	Zn (g/t)
PS	Liquid	SCREW PRESS	82 (0.0)	7.0 (0.1)	6.6 (0.1)	4.6 (0.0)	7.5 (0.0)	5.5 (0.1)	2.0 (0.1)	0.2 (0.0)	10.0	3.5 (0.1)	0.5 (0.0)	7.3 (0.4)	1.4	19.2	14.0 (0.0)	83.5 (0.7)
		DECANTER CENTRIFUGE	79 (0.0)	7.8 (0.0)	4.3 (0.0)	3.0 (0.0)	6.8 (0.0)	5.1 (0.1)	0.5 (0.0)	0.1 (0.0)	8.7	3.6 (0.1)	0.5 (0.0)	4.8 (0.8)	1.0	16.0	13.0 (0.0)	68.5 (0.7)
		FLOCCULATION And DRAINAGE	45[a] (0.0)	7.1 (0.1)	1.2[a] (0.1)	0.8[a] (0.1)	2.8[a] (0.0)	2.5[a] (0.0)	0.2[a] (0.0)	0.1[a] (0.0)	36.0	1.8[a] (0.0)	0.1[a] (0.0)	0.7[a] (0.1)	0.7	23.9[a]	1.3[a] (0.0)	2.5[a] (0.2)
	Solid	SCREW PRESS	18 (0.0)	7.9 (0.1)	27.1 (0.6)	24.6 (0.5)	7.4 (0.1)	4.5 (0.4)	2.4 (0.1)	0.1 (0.0)	5.9	3.2 (0.0)	1.1 (0.0)	2.4 (1.4)	0.2	13.9	12.5 (0.7)	71.5 (2.1)
		DECANTER CENTRIFUGE	21 (0.0)	7.6 (0.1)	33.2 (0.6)	28.0 (0.3)	9.5 (0.3)	6.0 (0.3)	7.3 (0.6)	0.2 (0.0)	2.9	3.1 (0.1)	1.6 (0.0)	0.5 (0.1)	0.0	7.1	17.0 (1.4)	135.0 (7.1)
		FLOCCULATION And DRAINAGE	55[a] (0.2)	7.0 (0.0)	12.9[a] (0.8)	10.5[a] (0.7)	7.7[a] (0.3)	4.9[a] (0.3)	2.5[a] (0.0)	0.1[a] (0.0)	6.0	2.8[a] (0.1)	0.7[a] (0.0)	3.9[a] (0.4)	0.6	18.4[a]	18.8[a] (0.7)	111.5[a] (0.0)
APS	Liquid	SCREW PRESS	91 (0.0)	5.4 (0.0)	6.7 (0.0)	4.6 (0.1)	6.3 (0.0)	4.2 (0.0)	1.4 (0.0)	0.4 (0.1)	25.7	3.0 (0.1)	4.3 (0.6)	0.5 (0.2)	0.0	12.2	10.0 (0.0)	56.5 (0.7)
		DECANTER CENTRIFUGE	88 (0.0)	5.4 (0.1)	5.4 (0.2)	3.0 (0.0)	6.0 (0.0)	4.1 (0.0)	1.2 (0.0)	0.4 (0.0)	30.1	3.0 (0.1)	4.5 (0.1)	0.4 (0.1)	0.0	9.8	9.3 (1.0)	45.0 (2.8)
		FLOCCULATION And DRAINAGE	58[a] (0.1)	5.1 (0.3)	2.4[a] (0.0)	0.8[a] (0.1)	3.1[a] (0.0)	2.5[a] (0.0)	0.7[a] (0.0)	0.2[a] (0.0)	30.2	1.9[a] (0.1)	2.7[a] (0.1)	0.0[a] (0.0)	0.0	14.2	1.2[a] (0.0)	1.22[a] (0.1)
	Solid	SCREW PRESS	9 (0.0)	5.4 (0.1)	24.7 (0.6)	24.6 (0.5)	6.4 (0.3)	3.5 (0.1)	1.5 (0.1)	0.36 (0.0)	24.7	2.6 (0.0)	4.0 (0.1)	0.0 (0.1)	0.0	9.9	10.4 (0.9)	54.5 (6.4)
		DECANTER CENTRIFUGE	12 (0.0)	5.5 (0.1)	32.7 (0.4)	28.0 (0.3)	8.0 (0.0)	3.4 (0.0)	2.5 (0.1)	0.32 (0.0)	12.9	2.3 (0.0)	3.9 (0.1)	0.3 (0.0)	0.0	6.2	19.5 (0.7)	145.0 (7.1)
		FLOCCULATION And DRAINAGE	42[a] (0.1)	5.4 (0.1)	14.2[a] (0.8)	11.4[a] (0.7)	7.6[a] (0.3)	3.7[a] (0.2)	1.6[a] (0.0)	0.37[a] (0.0)	26.2	2.8[a] (0.0)	4.2[a] (0.1)	0.6[a] (0.1)	0.0	11.9	21.4[a] (0.8)	121.2[a] (8.2)

The concentrations of the different parameters are lower in solid fractions obtained by flocculation and drainage, for both PS and APS (Table 3.3); this is due to the higher amount of water retained by the polymers that thus remains in the solid fractions, while additional water related to polymers emulsions were removed using the equations from 3 to 7. These results agree with results of Popovic et al. (2012).

DM and VS concentrations are lower in liquid fractions obtained by flocculation and drainage. As demonstrated by previous experiments, polymers aggregate the smaller particles together to form larger flocs, which can be separated from the solution (Hjorth et al., 2010). This mechanism allows separating the finest particles and, thus, decreasing the DM and the VS content in liquid fraction. Comparing the fractions obtained by PS and APS, the concentrations of both DM and VS were higher in acidified liquid fractions; this indicates a lower retention of these compounds of separators when treating APS.

Since smaller particles (0.45-10 µm) are related to nutrients, in particular N and P (Masse et al., 2005; Meyer et al., 2007), liquid fractions deriving from flocculation and drainage present lower concentration also for TN and TP, and an increasing content in the solid fractions. On the contrary, the concentrations of these compounds in liquid fractions obtained with screw press are similar to the concentrations in raw manure (Hjorth et al., 2013). Hence, screw presses are unable to retain smaller particles and, therefore, nutrients related to these. This is confirmed by the results obtained by Møller et al. (2000).

Since TAN is prevalently related to the dissolved fraction and smaller particles, the screw press and the centrifuge did not reduced the concentration of ammoniacal nitrogen in liquid fraction (Table).

Generally, TP presents an increasing concentration in solid fraction of flocculation and drainage, excepting for the fraction obtained with centrifuge for PS. In fact, approximately 50% of TP is related to smaller particles, between 0.45 and 10 µm (Masse et al., 2005), which could aggregate during centrifugation (Møller et al, 2002). This does not occur for APS, since the pH reduction leads to the dissolution of P precipitates (e.g. struvite, Ca-P precipitates) (Christensen et al., 2009) and the modification in the species that compose the buffering system (Sommer and Husted, 1995). The dissolution of P precipitates is highlighted also by the increase in concentration in soluble P. This leads to higher Soluble P/TP ratios for acidified fractions, even if there is little difference in TP concentration in fractions deriving from the same technology but from different manure types.

Liquid and solid fractions produced by the screw press and the decanting centrifuge present similar K content for both PS and APS. Liquid fractions from flocculation and drainage present a lower K concentration, indicating a higher retention of this compound. In fact, 99.8% of K is related to dissolved particles (Massè et al., 2005; Meyer et al., 2007) and it is thus better separated when flocculants are added to manure.

Fractions derived from APS have higher content of S tot, due to the addition of H_2SO_4 during the acidification treatment (approximately 5 kg S/t of manure). The concentrations of this compound in LF derived from screw press and centrifugation are not significantly different from raw slurries; while they decrease in flocculated fractions because of the attraction between cationic polymers and the S compounds, generally negative.

Even if S tot increases in acidified fractions, H_2S decreases; this is due to the microbial inhibition caused by the low pH that consequently causes the decrease of sulfide (Ottosen et al., 2008; Hjorth et al., 2013). Therefore, the H_2S/Stot ratio reduces for acidified fractions. Microbial inhibition is proved also by VFA content, which decreases in acidified fractions (Table 3.3).

Cu and Zn concentrations highly increased in SF produced by decanting centrifuge and flocculation and drainage. In fact, 90% of Cu and 80% of Zn are associated to particles between 0.45 and 10 µm

(Masse et al., 2005); therefore they are retained in solid fraction only by separation techniques that remove particles smaller than 10 µm, such as flocculation and centrifugation.

3.3.3. Separation efficiency

APS presented a quicker drainage in all three separation units and, hence, led to a lower retention of particles and, thus, to a smaller mass of solid fraction (Figure 3.1).

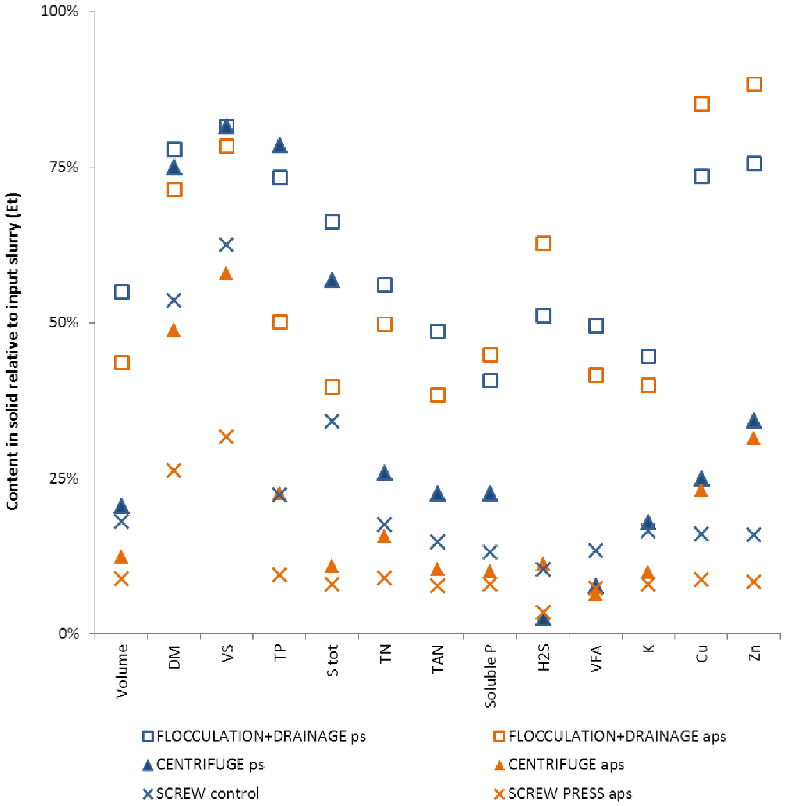

Figure 3.1. Separation efficiency (Et), divided by manure type and separation technology.

In 90% of samples, the three separation technologies resulted in a lower retention of different compounds in the solid fraction of APS than in PS (Figure 3.1). Overall, the DM separation efficiency of the screw press, the decanting centrifuge and the flocculation and drainage treatment decreased by 50%, 35% and 10%, respectively, upon acidification. For example, for the screw press filtration of APS, a higher ratio of small particles was lost in the liquid fraction during fast drainage, as these small particles washed with the liquid through the filter. Hence, the APS's shorter time for the separation process caused a higher proportion of compounds to remain in the liquid fraction than in the solid fraction.

The relative content in the solid fraction was also influenced by the variation of flow rates of the screw press and the decanter centrifuge (Table 3.1). In the present study, the flow rate of the screw press was twice as high when APS was treated as a consequence of the more rapid dewatering. According to the results obtained by Balsari et al. (2006), an increased flow rate of the screw press by 45 to 60% reduced the average separation efficiency by 10%. Concerning the decanter centrifuge, in the present study the flow rate was increased by 40% when treating APS. The results obtained in section 2 show an average reduction of separation index by 10% when the flow rate of a decanter centrifuge is increased by 25%. Hence, if the varying flow rates in this study affect the separation efficiencies equivalently to those in previous studies, the reduction of the DM separation index related to the acidification pre-treatment is equal to 40% and 25% for the screw press and the centrifuge, respectively, instead of 50% and 35%. Hence, the average solids content in the solid fraction was lowered upon acidification; acidification thus indeed reduced the overall separation efficiency.

The average separation efficiency for VS, TP, S tot and TN followed the same trend as for DM (Figure 3.1). For flocculation and drainage Et reduction was 4%, and 32%, 40 % and 12% for VS, TP, S tot and TN, respectively. Soluble species such as TAN, K and VFA were also present in higher concentration in the solid fraction coming from the PS than for the APS. Some exceptions to this general rule were observed when APS was treated with flocculation and drainage. In particular, separation indexes for soluble P and H_2S increased by 10% and 23%, respectively, when APS was treated. Furthermore, separation indexes for Cu and Zn were 16% larger when the slurry was acidified before the flocculation and drainage.

Acidification treatment prior to the solid-liquid separation also changed the concentration of some the compounds in the solid fraction. This proved dependent on the chemical speciation, i.e., particle related species, monovalent ions and divalent ions (Figure 3.2).

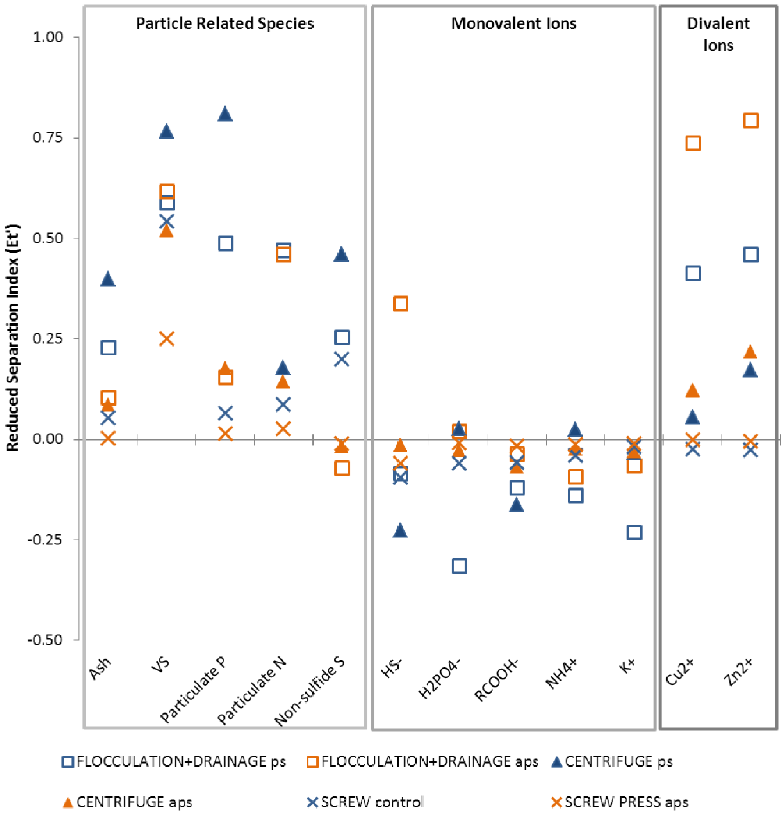

Figure 3.2. Reduced separation index (Et') of the different separation technologies divided by PS and APS. Chemical species are divided into 3 groups. Ash indicates inorganic compounds, while VS the organic ones. Particulate P and N and Non-sulfide S were calculated subtracting Soluble P, TAN and H_2S, respectively. Ionic species are presented in their ionic forms.

The concentration of the particle related species (ash, volatile solids (VS), particulate P, particulate N and particulate S) increased in the solid fraction (Et'>0), while the concentration of the dissolved monovalent compounds were unaffected by the separation (Et'=0) (Figure), i.e. particle related species were better retained by the different separators than the dissolved species. The concentration of the particulate species in the solid fraction decreased upon acidification of the slurry due to the more rapid dewatering of APS (Table), which causes the particles to be more easily flushed into the liquid fraction. Previous studies demonstrated that centrifugation efficiently separates small particles, in which P is primarily retained (Møller et al., 2002; Hjorth et al., 2010), leading to aggregation of P-containing particles. In these experiments that behavior was not observed for APS, because of the enhanced de-mineralization processes during the slurry acidification and later the dissolution of precipitates (Christensen et al., 2009; Hjorth et al., 2013). After acidification, the non-sulphide S showed an exception of the tendencies. In fact, its concentration decreases in acidified liquid fraction (Et' < 0), probably because of the addition of H_2SO_4 that increases the concentration of dissolved S, which could not be retained in the solid fraction.

The monovalent ions considered in this study are sulphide (HS^-), phosphate (PO_4^{3-}) or water soluble P ($H_2PO_4^-$), volatile fatty acids ($RCOO^-$), ammoniacal (NH_4^+) and potassium (K^+). The concentrations of these compounds does not significantly change (Et' = 0) in either the solid or liquid fraction. Due to their dissolved nature (Masse et al., 2005; Marcato et al., 2008), the concentration of these ions in solid and liquid fractions is controlled by the distribution of manure's liquid part between these two fractions. Thus, in these experiments the acidification treatment did not change the concentration of the dissolved monovalent ions in the two separated fractions.

In contrast to the monovalent ions, the divalent cations such as Cu^{2+} and Zn^{2+} were found in higher concentration in solid fraction (Et' > 0). This may be due to the fact that cationic polyvalent ions attach more strongly to the negative particles than the monovalent ones. In particular for the flocculation and drainage treatment, the increase in Cu and Zn concentrations in the solid fraction, compared to those in the raw manure, was higher for APS than for the PS, in contrast to the observations for the particle related compounds. This could be explained by the fact that the flocculation of APS required a polymer with higher charge density, thus more charge attachments occurred upon aggregation, thus the higher charge of Cu and Zn caused increased attachment, and thus larger solid fraction detainment after acidification.

3.4. Considerations

Manure pre-treatments, such as acidification, modify slurry characteristics and, thus, they could affect the performances of different separation systems. In particular, slurry acidification increases the rate of dewatering of liquid from bulk slurry; thus, considerable quantities of solid particles from acidified slurry are flushed with the liquid and end up in the liquid fraction. Slurry acidification generally decreased the content of species in the solid fraction. The acidification caused the concentration in the solid fraction of particle related species to decrease, of dissolved monovalent species not to be affected, and of divalent cations to be increased.

In general, the different operating conditions (e.g. manure type, separation technology, flow rate and polymer addition) may lead to different characteristics of the produced solid and liquid fractions and, thus, modify their management within the farms, especially concerning their fertilizing characteristics.

4. SOLID-LIQUID SEPARATION ENHANCED BY CHEMICAL AND NATURAL POLYMERS

4.1. Introduction

Chemical separation allows to improve mechanical separation efficiency, since coagulants and polymers enhance the aggregation of small particles related to nutrients (N and P) (Section 1). Synthetic polymers have been most commonly used because of their flocculating effectiveness and low cost (Vanotti and Hunt, 1999). However, natural organic flocculants can be produced economically in large scale and with lower input energy (Garcia et al., 2009). Among the natural polymers, chitosan is one of the most prominent ones. It is a modified, natural carbohydrate polymer derived from the chitin component of the exoskeleton of crustacean such as shrimp, crab and crawfish (No and Meyers, 1989). In particular, chitosan is a partially deacetylated chitin which is as a 1:4 random copolymer of N-acetyl-α-D-glucosamine and α-D-glucosamine (Figure 4.1) (Rinaudo, 2006). Chitosan has a medium molecular weight and a charge density that is pH dependent; at neutral pH levels it is slightly positively charged (17%), therefore it can be used as polycationic polymer. The optimal pH value for the utilization of chitosan emulsion for waste waters treatments is 6.0 (No and Meyers, 1989).

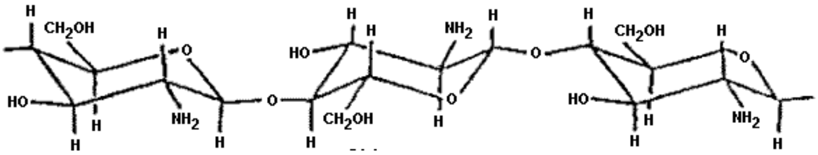

Figure 4.1. Structure of the chitosan polymer.

According to previous experiments, chitosan can be used in waste water purification to reduce the organic matter content, the water turbidity and the concentration of total suspended solids (TSS) and nutrients, such as nitrogen and phosphorus (Bolto et al., 1998; Garcia et al., 2009).

Although the efficiency of chitosan for wastewater treatment has been frequently reviewed, few information are available about its effectiveness on livestock manure treatments. According to Garcia et al. (2009), a 0.45% chitosan emulsion can reduce the 95% of TSS, the 73% of nitrogen and the 54% of phosphorus from the separated liquid fraction deriving from dairy manure with a total solids content of 3.2%. However, more information is necessary in order to understand the possible use of chitosan for livestock manure treatments having different physico-chemical characteristics.

Among the separation devices used in combination to chemical pre-treatments, flotation technologies are widely used for wastewater treatments, but they are seldom applied in livestock slurry treatments. Therefore, little information is available for the utilization of this technology in a manure treatment plant.

The aim of this section is to evaluate the possible use of chitosan instead of synthetic treatments and to investigate the effect of chitosan on different manure types. The results obtained by laboratory test were then used for the evaluation of physico-chemical separation of manure through a pilot scale flotating system used in combination to flocculants.

4.2. Materials and Methods

4.2.1. Laboratory scale experiment

4.2.1.1. Manure type

Manure produced by pig livestock and anaerobic digestion plants were treated. In particular, 20 different manure samples were used: (i) 5 samples were collected from farrow-to-finish pigs livestock; (ii) 5 samples were collected from finishing pigs livestock; (iii) 10 samples were collected from co-digestion plants for energy production.

Manure samples were collected and stored at 15°C for two days before the treatments.

4.2.1.2. Manure treatment

The collected samples were flocculated through two different treatments: (i) a synthetic treatment (PAC+POLY), consisting in the addition of aluminum polychloride (PAC) and a branched cationic polymer of medium molecular weight and with a charge density of 40% (Hidrofloc CL5336/RC, Hidrochem, Italy); (ii) a natural treatment (CHITOSAN), consisting in the addition of chitosan (Sigma Aldrich). The PAC was used in a 18% emulsion, while the cationic polymer was diluted using tap water in order to obtain a 0.4% polymer solution. Chitosan was dissolved in 2% acetic acid (No and Meyers, 1989) for a final concentration of 0.4%.

Samples of 0.5 L were placed in 1-L beakers using one of the different volumes of a 0.4% polymer solution of one of the two treatments. For the synthetic treatment, 8 ml of PAC were added before the addition of the cationic polymer. The polymer solution was added stepwise in amounts of 15 mL. Each sample was stirred rapidly (200 rpm) for 20 s and then stirred slowly (80 rpm) for two minutes before each addition, using a jar test equipment (JLT6, Velp, Italy) (Figure 4.2). To obtain equal dilution of the manures, water was added to the samples so that the total volume of polymer solution and water was equal to the maximum addition of polymer solution (Hjorth and Jørgensen, 2012).

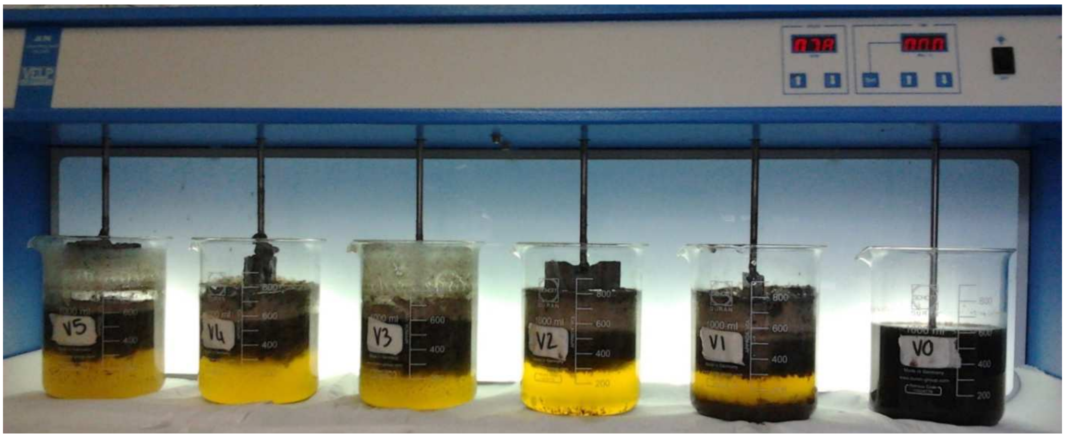

Figure 4.2. Example of flocculation test through the jar test equipment.

The flocculated samples were left in static conditions for 15 minutes. After this period, each sample was pre-sieved using a 1 mm stainless steel filter (Figure 4.3) and then drained through a filter with 0.2 mm pore size for 40 minutes (Figure 4.4).

Figure 4.3. Pre-sieving through the 1 mm filter.

Figure 4.4. Filtration of the sample through the 0.2mm belt filter.

For each treatment, the optimal dosage was assessed through: the floc size, the separation efficiencies of weight, total solids (TS) and total suspended solids (TSS) (Hjorth and Christensen, 2008; Garcia et al., 2009). The floc size was assessed visually and rated from 1 to 5, where 1 = raw manure, 2 = visual flocs smaller than ~ 0.5 mm, 3 = floc size ~ 0.5 to 2 mm, 4 = floc size ~ 2 to 5 mm, 5 = floc size larger than ~ 5 mm. Separation efficiency for weight, TS and TSS where calculated through the simple separation index (Section 1).

4.2.2. Pilot-scale experiment

4.2.2.1. Manure treatment

The treated slurry is composed by the pig and cattle manure produced by 10 livestock farms. The raw slurry was collected in the Agroenergie Bergamasche treatment plant from the equalization tank and then treated by a pilot-scale flotating system combined to a chemical pre-treatment (Figure 4.5). The input slurry is collected in a 0.3 m^3 tank (1) and then pumped in a coagulation tank (2) where the coagulant is added. The coagulated slurry is mixed in order to distribute the coagulant an all the slurry volume and reduce the foam-formation due to the coagulant addition. The treated slurry flows in a flocculation tank (3), where a 0.4% polymer emulsion is added and slurry is mixed in order to achieve a satisfactory particle aggregation. Finally, slurry flows into the pilot scale flotating system (4), which consists of two chambers. The flocculated slurry fills the first chamber from the bottom; in the meantime, air is injected through an air sparger. The small air bubbles attach the particles aggregates and carry them to the liquid surface, while the liquid fills the second chamber by overflowing; when the flotating system is completely filled, the solid fraction is removed from the top of the liquid by skimming, while the liquid fraction is collected from the bottom.

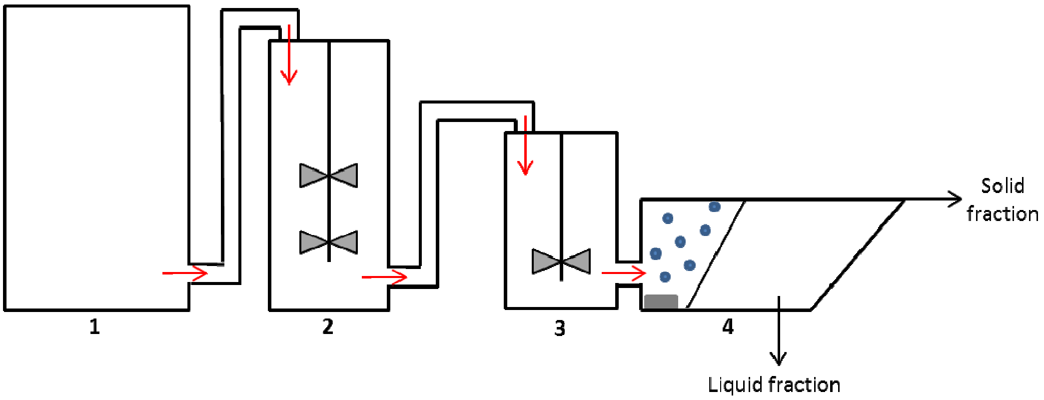

Figure 4.5. Treatment system scheme.

Figure 4.6 shows the set-up of the experiment in the treatment plant.

Figure 4.6. Pilot-scale treatment plant.

The coagulant used in this experiment was aluminum polychloride (PAC 180, Hidrochem, Italy), while the flocculant added in the container 3 was a cationic branched polymer, with 40% of charge density and a medium-high molecular weight (Hidrofloc CL5336/RC, Hidrochem, Italy). The optimal coagulant and flocculant dosages were determined through a jar test (Section 4). The flow rates of the input slurries and the two additives were set according to the optimal dosages.

Samples of the input slurry and of the produced liquid and solid fractions (Figure 4.7) were collected in duplicates and stored at -18°C before the analyses.

Figure 4.7. Collection of the liquid fraction.

4.2.2.2. Evaluation of the separation performances

The produced amounts of the solid and the liquid fractions were weighted after the separation experiment. These values were used to calculate the weight separation efficiency.

Total solids (TS) concentrations of the raw manure and of the produced liquid and solid fractions were analyzed by drying the sample at 105°C till constant weight.

Separation efficiencies of weight and TS were calculated through the simple separation index (Section 1).

4.2.3. Chemical analyses

The DM and TSS contents of the raw slurries and of the obtained solid and liquid fractions were analyzed by standard procedures (APHA, 1992).

Raw slurries and the liquid and solid fractions obtained by the separation without chemical additives and by the optimal dosages were characterized chemically for volatile solids (VS), total Kjeldahl N (TKN), ammoniacal nitrogen (TAN), total phosphorus (TP) and potassium (TK).

VS content was determined by drying the sample in a muffle furnace from 105°C to 550°C for 2h and measuring the weight loss (APHA, 1992).

TKN and TAN were determined using the analytical methods for wastewater sludges (IRSA CNR, 1994).

TP and TK contents were analyzed by inductively coupled plasma mass spectrometry (Variant, Fort Collins, USA), which was preceded by acid digestion (EPA, 1998) of the sample.

4.2.4. Data analyses

The separation efficiencies were calculated using the simple separation index, Et (x), and the reduced separation index, Et'(x) (Section 1).

A large amount of water was added through the polymer addition; therefore the dilution of the two samples was calculated before the calculation of the separation efficiency. In particular, the dilution of the analyzed parameters was calculated as:

$$C(x)_{slurry+water} = \frac{C(x)_{slurry} \cdot m(slurry)}{m(slurry + water)}$$

Where: $C(x)_{slurry+water}$ and $C(x)_{slurry}$ are the concentrations ($g \cdot kg^{-1}$) of the compound x (e.g. TS, TKN, TP) in the diluted slurry and in the raw slurry, respectively; *m(slurry+water)* and *m(slurry)* are the masses (kg) of the diluted slurry and of the raw slurry, respectively.

4.3. Results and discussion

4.3.1. Laboratory scale experiment

4.3.1.1. Characteristics of the input slurries

The 20 collected samples were characterized for TS, TSS, VS, TKN, TAN, TP and TK (Table 4.1).

Table 4.1. Average characteristics of the input slurries (standard deviation in brackets).

Manure type	N	DM (%)	TSS (% ts)	VS (%ts)	TKN ($g \cdot kg^{-1}$)	TAN ($g \cdot kg^{-1}$)	TP ($g \cdot kg^{-1}$)	TK ($g \cdot kg^{-1}$)
Digested	10	3.8 (1.4)	66.2 (21.6)	70.9 (5.4)	3.03 (0.8)	2.3 (0.4)	0.7 (0.3)	2.5 (1.4)
Farrow-to-finish pigs	5	2.6 (1.1)	64.8 (22.0)	68.7 (3.1)	3.4 (1.0)	2.4 (0.6)	0.7 (0.4)	1.4 (0.7)
Finishing pigs	5	4.5 (2.6)	75.3 (12.6)	66.1 (11.2)	3.7 (1.2)	2.6 (0.7)	1.0 (0.6)	3.3 (2.7)
Pigs (Farrow-to-finish and finishing)	10	3.6 (2.1)	70.1 (17.8)	67.4 (7.9)	3.5 (1.0)	2.5 (0.6)	0.9 (0.5)	2.4 (2.1)
Total	20	3.7 (1.8)	68.1 (19.4)	69.2 (6.8)	3.3 (0.9)	2.4 (0.5)	0.8 (0.4)	2.4 (1.7)

The characteristics of the collected samples of same manure type presented a high variability for all the analyzed parameters. This is due to different factors, as described in Section 1: type of housing, the diet, the animal category, the type and amount of biomasses for digested manure.

Since the optimal dosage of the polymer is affected by the physico-chemical characteristics of the input slurry (Hjorth and Jørgensen, 2012), the different characteristics led to different optimal dosages of both PAC+POLY and CHITOSAN treatments.

4.3.1.2. Evaluation of the optimal dosage

Due to the highly variable manure characteristics, the different samples required different flocculant rate for both the cationic polymer and the chitosan emulsion.

In general, the different polymer rates led to increasing separation efficiency, due to the increase of the amount of cationic charges that could attract the negative manure particles, as observed by Vanotti et al. (2002). For some of the treated samples, over dosages and the relative decrease of the separation efficiencies were observed for higher flocculant rates. Figure 4.8, Figure 4.9 and Figure 4.10 show the separation efficiencies for weights and TS according to the flocculant rate for three samples of each manure type.

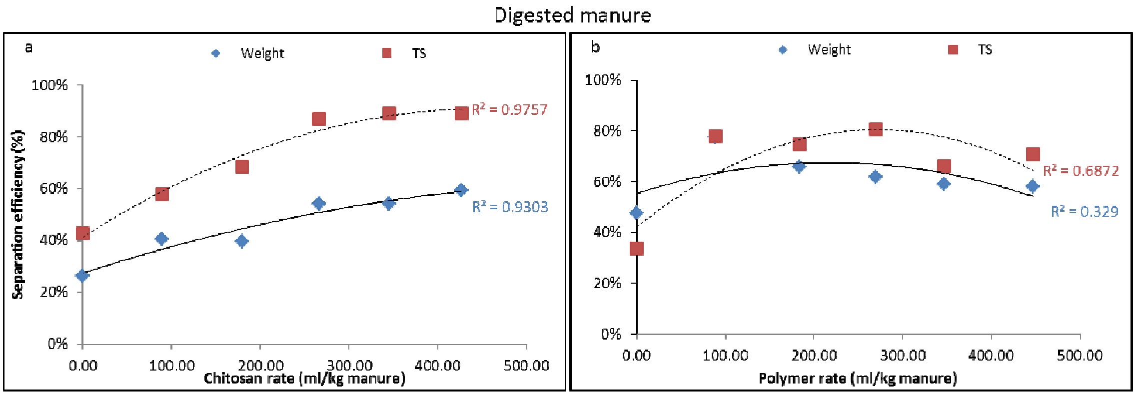

Figure 4.8. Separation efficiencies according to chitosan (a) and polymer (b) rates for a digested manure sample.

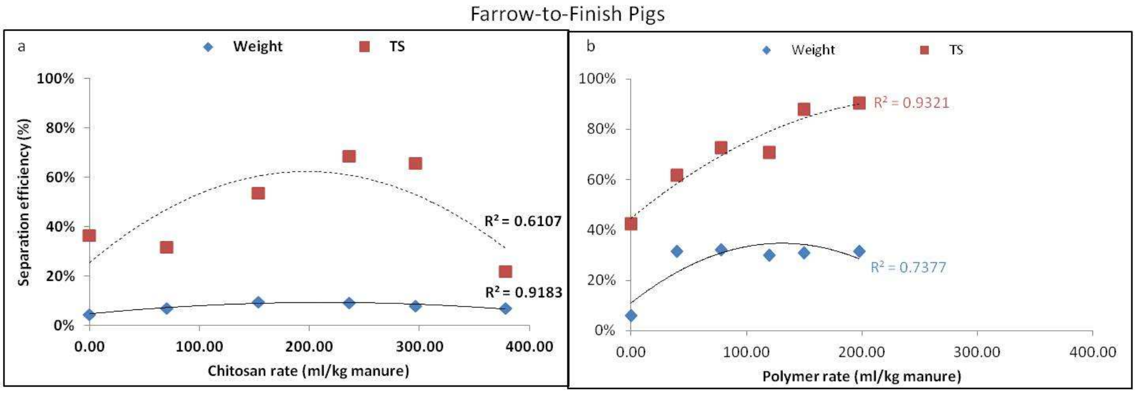

Figure 4.9. Separation efficiencies according to chitosan (a) and polymer (b) rates for a farrow-to-finish pig manure sample.

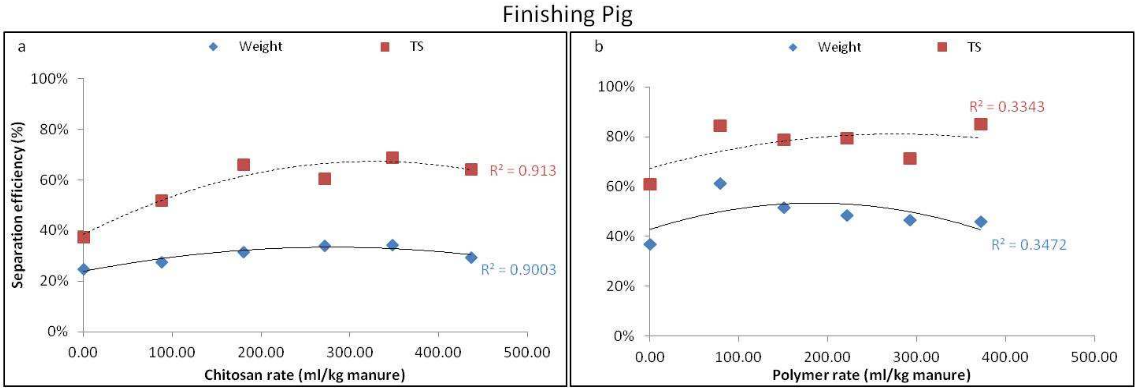

Figure 4.10. Separation efficiencies according to chitosan (a) and polymer (b) rates for a finishing pigs manure sample.

The optimal dosages obtained were highly dependent on the manure treated sample, as shown in Table 4.2.

Table 4.2. Descriptive statistics for flocculants optimal dosages divided by manure type. Minimum (Min), Maximum (Max) and Mean (standard deviation in brackets).

Manure type	Treatment	N	Min (ml)	Max (ml)	Mean (ml)
Digested	PAC+POLY	10	20	300	142.50 (83.30)
	CHITOSAN	10	95	220	131.50 (34.56)
Farrow-to-finish pigs	PAC+POLY	5	100	190	128 (36.84)
	CHITOSAN	5	75	125	97 (22.80)
Finishing pigs	PAC+POLY	5	35	150	86 (41.89)
	CHITOSAN	5	100	175	141 (31.5)

The defined optimal dosages resulted to be not affected by the manure type (digestate, farrow-to-finishing pigs, fattening pigs) or by the manure characteristics that are more rapidly analyzable, such as the DM concentration of the input slurry. In fact, the DM consists of all the solid particles that are contained in the manure. However, a portion of these solid particles is not charged and, thus, does not affect the optimal dosage of a flocculant (Hjorth and Jørgensen, 2012). The obtained results refer to a large number of manure, but no significant correlations were observed (Figure 4.11)results were observed for the VS concentration of the input slurry (Figure 4.12).

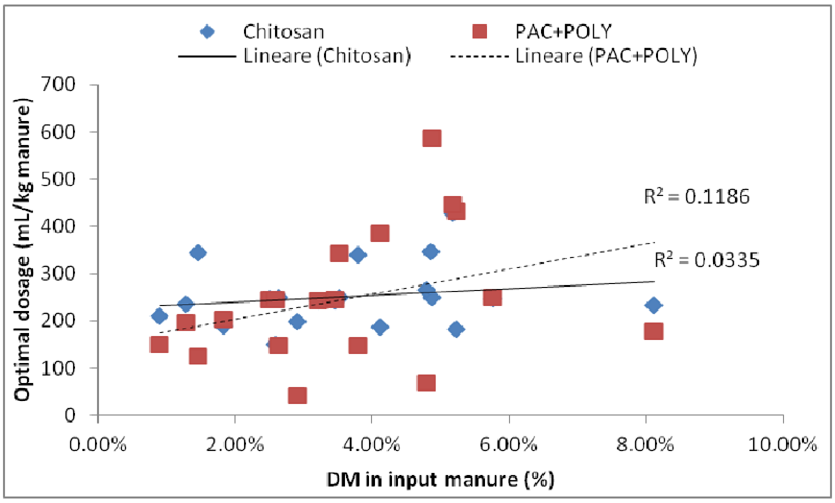

Figure 4.11. Correlation between the DM content of the input slurry and the flocculant optimal dosage.

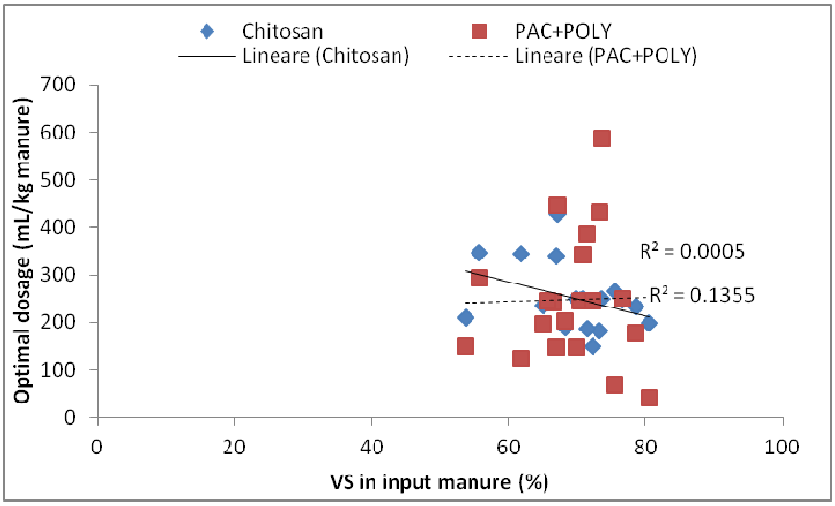

Figure 4.12. Correlation between the VS content of the input slurry and the flocculant optimal dosage.

4.3.1.3. Separation efficiencies

The different dosages led to different separation efficiencies for the analyzed parameters. The separation efficiencies obtained through the optimal dosage were compared to the separation efficiencies calculated without the addition of flocculants (V0) (Table 4.3 and Table 4.4).

Table 4.3. Separation efficiencies (%) for optimal polymer dosages and control (V0). Means, standard deviations in brackets.

Manure type	Polymer dosage	Weight	DM	VS	TKN	TAN	TP	TK
Digested								
	V0	22.6 (10.0)	47.4 (10.4)	42.4 (15.1)	20.9 (34.3)	29.6 (27.6)	39.2 (13.3)	12.2 (6.3)
	Optimal	56.9 (6.9)	88.5 (7.5)	91.6 (24.5)	73.1 (10.5)	67.4 (10.7)	79.4 (43.9)	34.7 (21.7)
Farrow-to-finish pigs								
	V0	13.2 (6.9)	43.4 (10.6)	49.9 (15.9)	12.0 (8.3)	6.0 (17.5)	42.9 (24.0)	9.9 (5.4)
	Optimal	41.2 (7.3)	85.1 (5.7)	104.2 (14.1)	65.2 (7.2)	41.0 (5.4)	102.9 (35.7)	31.1 (9.1)
Finishing pigs								
	V0	29.0 (16.7)	50.5 (16.0)	52.2 (10.6)	30.7 (22.2)	25.7 (16.2)	42.4 (27.0)	16.6 (10.6)
	Optimal	52.9 (12.1)	84.9 (10.6)	108.5 (31.8)	62.9 (19.5)	56.8 (17.5)	108.1 (27.4)	30.4 (14.0)
Pigs								
	V0	21.1 (14.6)	47.0 (13.4)	51.1 (12.8)	21.4 (18.6)	15.9 (19.0)	45.5 (23.0)	13.2 (8.7)
	Optimal	47.1 (11.2)	85.0 (8.0)	106.3 (23.3)	58.9 (14.4)	30.8 (11.1)	93.6 (30.8)	30.8 (11.1)
Total								
	V0	21.8 (12.2)	47.2 (11.7)	46.7 (14.3)	21.1 (26.9)	22.7 (24.1)	42.4 (18.6)	12.7 (7.4)
	Optimal	52.0 (10.4)	86.7 (7.8)	98.9 (24.5)	66.0 (14.3)	58.2 (15.7)	86.5 (37.6)	32.7 (16.9)

Table 4.4. Separation efficiencies (%) for optimal chitosan dosages and control (V0). Means, standard deviations in brackets.

Manure type	Chitosan dosage	Weight	DM	VS	TKN	TAN	TP	TK
Digested								
	V0	22.4	46.0	57.2	29.9	31.4	39.1	14.4
		(77.9)	(11.1)	(23.8)	(17.7)	(13.0)	(9.1)	(6.0)
	Optimal	38.8	76.5	77.7	51.5	47.6	78.8	39.4
		(13.3)	(15.4)	(20.0)	(15.4)	(14.4)	(27.4)	(43.0)
Farrow-to-finish pigs								
	V0	13.4	40.5	54.3	22.9	24.6	35.4	17.7
		(9.2)	(12.9)	(23.5)	(24.8)	(12.8)	(17.2)	(9.9)
	Optimal	21.1	70.0	83.4	30.3	23.0	96.8	27.0
		(11.3)	(20.4)	(26.6)	(32.9)	(19.5)	(66.4)	(21.6)
Finishing pigs								
	V0	23.9	48.3	59.1	29.3	30.5	34.2	18.2
		(14.9)	(21.9)	(15.2)	(16.9)	(13.2)	(12.3)	(23.6)
	Optimal	33.6	69.2	80.7	50.3	51.1	83.9	19.8
		(17.7)	(20.5)	(14.3)	(25.0)	(14.6)	(32.5)	(20.4)
Pigs								
	V0	18.7	44.4	48.9	13.4	14.5	47.8	15.7
		(12.9)	(17.5)	(18.5)	(28.1)	(24.4)	(21.1)	(16.7)
	Optimal	27.3	69.6	82.1	40.3	37.0	90.4	23.4
		(15.4)	(19.3)	(20.2)	(29.5)	(22.0)	(94.7)	(18.1)
Total								
	V0	20.5	45.1	45.9	21.6	22.9	43.4	19.8
		(10.6)	(14.4)	(17.1)	(24.3)	(20.9)	(17.6)	(15.9)
	Optimal	33.1	72.7	79.9	45.9	42.3	96.8	31.4
		(15.2)	(17.5)	(19.7)	(23.6)	(19.0)	(45.8)	(33.2)

Both PAC+POLY and CHITOSAN treatments led to an increase of separation efficiency, as shown also in Figure 4.13.

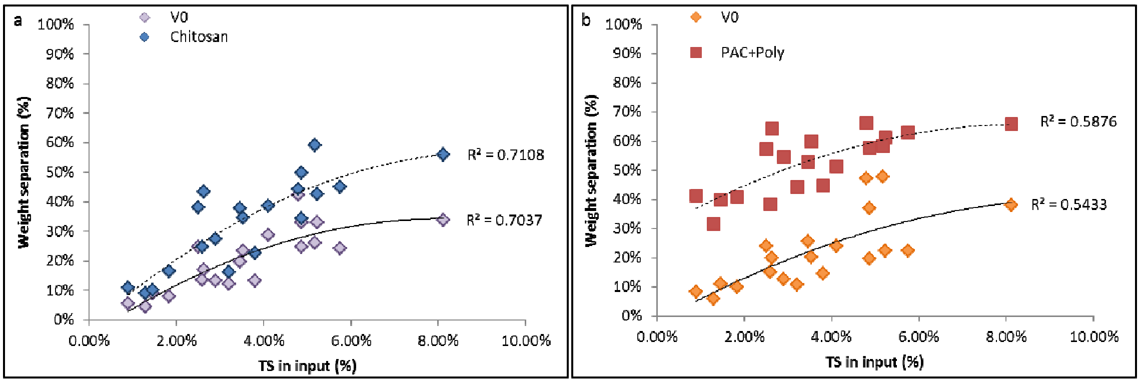

Figure 4.13. Weight separation for V0 and optimal dosages of chitosan (a) and polymer (b) according to the DM concentration of input slurries.

The optimal dosage and the related separation efficiency resulted highly dependent on the sample characteristics; therefore, no correlation was observed between the optimal dosage rate and the related separation efficiencies (Figure 4.14, Figure 4.15 and Figure 4.16).

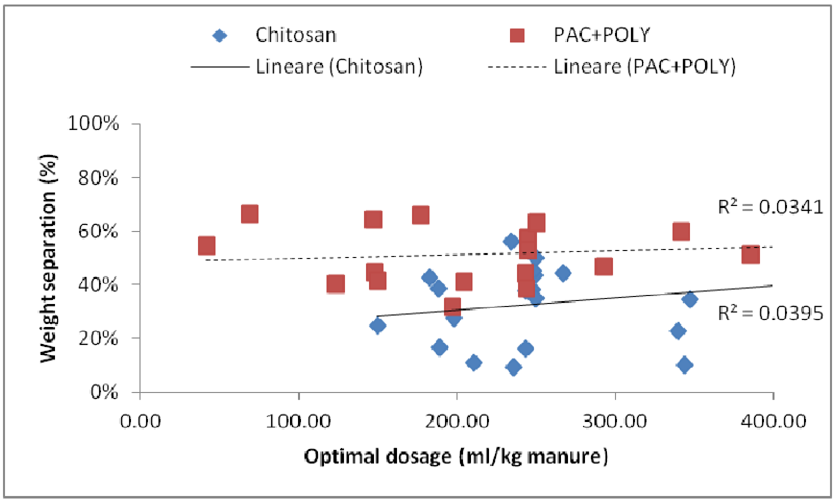

Figure 4.14. Correlation between the flocculant optimal dosage and the separation efficiency for weight.

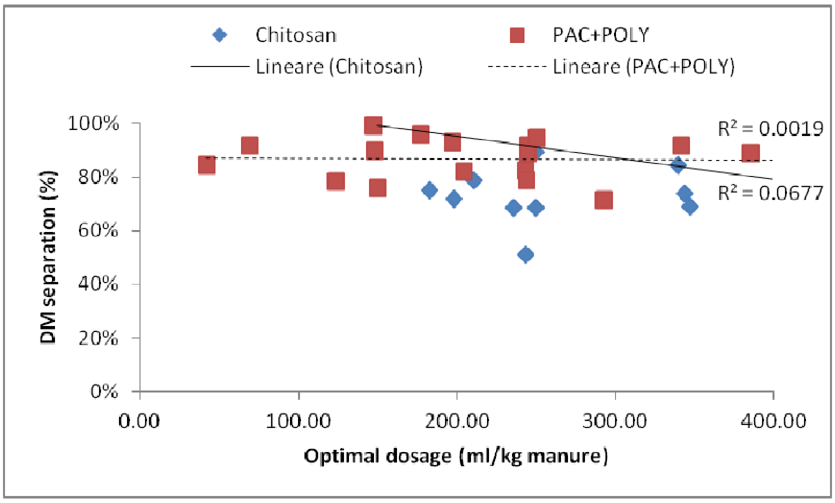

Figure 4.15. Correlation between the flocculant optimal dosage and the separation efficiency for DM.

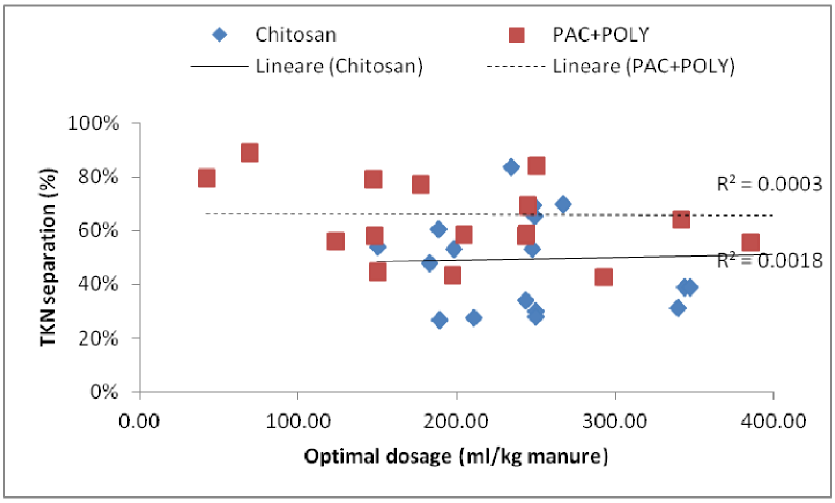

Figure 4.16. Correlation between the flocculant optimal dosage and the separation efficiency for TKN.

Compared to the synthetic treatment, the chitosan addition led to a lower increase of the calculated separation efficiencies. This could be due to the more weak attachment to manure particles and the formation of less structured flocs, which could be easily destroyed during the separation of the solid and the liquid fractions (Figure 4.17).

Figure 4.17. Floc formation after chitosan addition.

4.3.2. Pilot-scale experiment

4.3.2.1. Optimal dosage definition

According to the procedure described in section 4.3.1, optimal dosage was defined through floc size and separation efficiencies for weight and DM. In particular, optimal dosage was defined as the volume of polymer that led to the highest floc size and the largest separation efficiency for weight and DM (Figure 4.18).

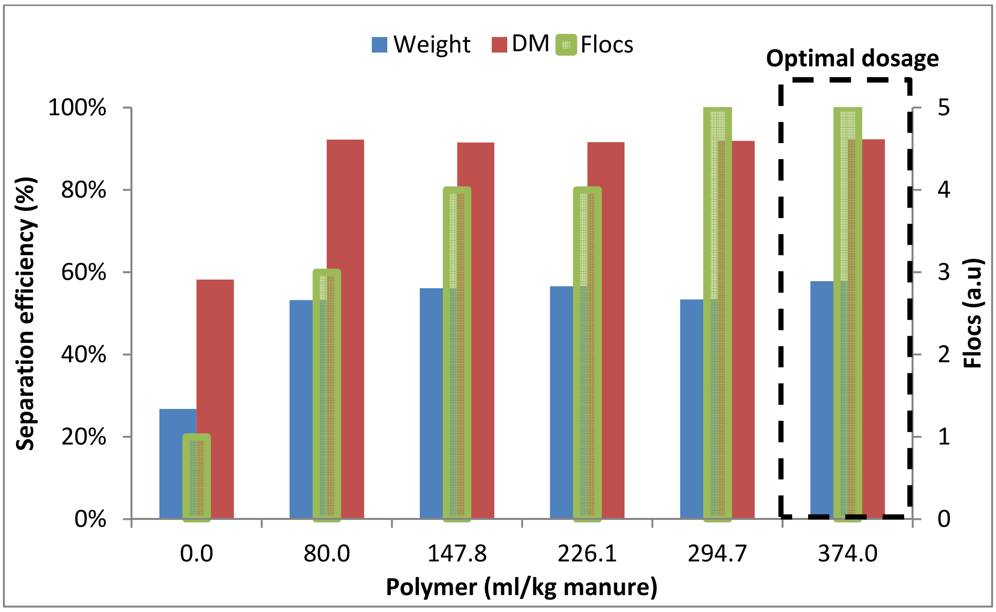

Figure 4.18. Evaluation of the optimal dosage.

After the definition of the optimal PAC and polymer dosages at laboratory scale, the flow rates of the two additives were defined, in order to maintain the same ratios between the additives and the manure during the pilot scale experiment. The flow rates of the input slurry and of the two additives are defined in Table 4.5.

Table 4.5. Optimal dosages and flow rates.

	Optimal dosage (ml·l^{-1} manure)	**Flow rate (l·h^{-1})**
Input slurry	-	52.0
PAC	19.7	1.0
Polymer	374	19.2

4.3.2.2. Separation performances

The pilot-scale separator allowed to separate the 67% of the total weight of the input slurry and the 88% of the total solids (Figure 4.19).

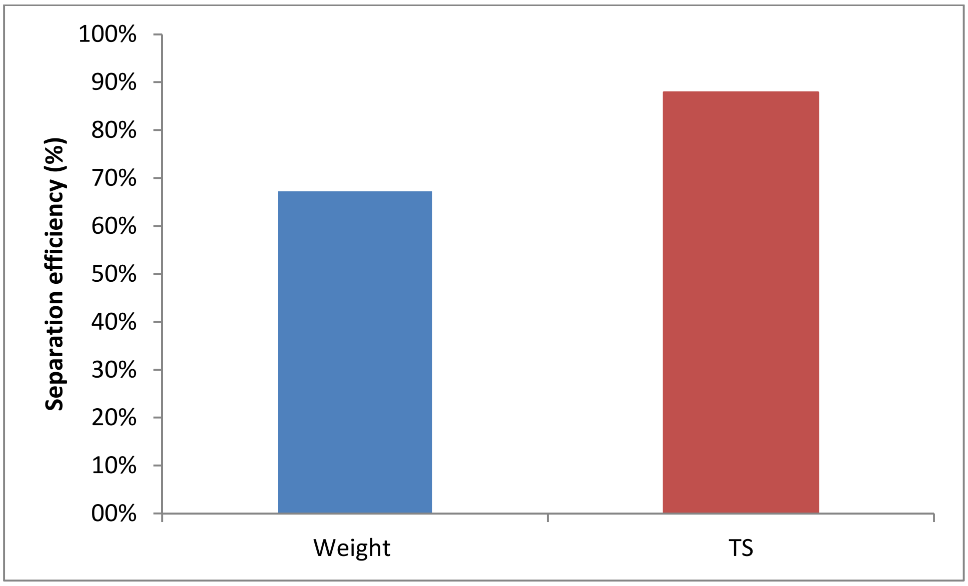

Figure 4.19. Weight and DM separation efficiency.

Due to the low turbidity of the liquid fraction (Figure 4.20), the major part of suspended solids and organic fraction were also retained in the solid fraction (Garcia et al., 2009). Therefore, the produced solid-fraction presents a high theoretical biogas production and could be treated through an anaerobic digestion process. The resulting liquid fraction has a low DM concentration (0.9%) and, therefore, it results suitable for fertigation or biological treatment processes that require a low dry matter content of the input slurry. Therefore, the liquid fraction could be treated through the SBR process of the Agroenergie Bergamasche treatment plant (Section 2). However, the solid fraction will present a high liquid content, which could not be treated for biological nitrogen removal.

Although the pilot-scale separation system combined to the addition of flocculating agents presented a high separation efficiency, the combination of PAC and the branched cationic polymer led to the production of large aggregates, which settled in the separator and were not removed by skimming (Figure 4.20).

Figure 4.20. Dimension of the aggregates after flocculation.

The formation of large flocs is due to the characteristics of the two additives combined to the characteristics of the input slurry. In fact, the raw slurry presented a large amount of bedding residues and other coarse materials, which enhanced the formation of aggregates of large dimensions. Furthermore, the branched polymer attracts a higher amount of charged particles, leading to the formation of flocs of bigger dimensions compared to a linear polymer (Hjorth et al., 2008).

For this reason, the separation process lead to the formation of three layers: (i) a upper layer characterized by the floating solid fraction; (ii) an intermediate layer composed by the liquid fraction; (iii) a lower layer characterized by the larger aggregates.

4.4. Considerations

The optimal dosage of both the chitosan and the cationic polymer emulsions resulted highly dependent on the manure sample characteristics.

Both the synthetic and the natural treatments allowed to improve the separation efficiencies, retaining a larger amount of solids and nutrients in the solid fractions. However, the chitosan addition lead to the formation of flocs more weak and with a non-well-defined structure compared to the synthetic treatment. For this reason, the separation efficiency of TS, VS, TKN, TP and TK was lower for the chitosan optimal dosage compared to the synthetic treatment.

The pilot-scale flotating system allowed separating a large amount of solid fraction, which can be more easily managed and treated through different processes. However, the input slurry presented a large amount of coarse particles, which led to the formation of bigger flocs that tended to settle instead of floating on the liquid surface. For this reason, the input slurry should be pre-treated in order to remove the lager particles from the liquid manure. Furthermore, linear polymers with a lower molecular weight could be more suitable for the flotating systems, since they lead to the formation of smaller aggregates that can float on the liquid surface more easily. Finally, the set-up of the pilot-scale flotator should be modified, in order to enhance the transportation of the solid particles to the liquid surface. In this way the solid-liquid separation of livestock slurries through flotation could be better evaluated.

5. EMPIRICAL MODEL FOR PREDICTING SEPARATION EFFICIENCY

5.1. Introduction

As described in Section 1, the separation efficiency is traditionally defined as the ratio of the total mass recovery of a given component (DM or nutrients) in the solid phase, divided by the total input of that component (DM or nutrient) (Møller et al., 2000; Burton, 2007). The separation efficiency is influenced by several factors (Burton and Turner, 2003): separator type; manure type (including species, pre-treatments and total solids content); and use of additives (coagulants, flocculants). Therefore, as described by Zhang and Westerman (1997), the different separator types have different separation efficiencies, leading to the production of end-products with different characteristics that make them preferable for certain use. Thus, because the performances of the various separator types are different, a decision support tool is necessary to allow the identification of the separation technology most suitable for farmer's needs.

In recent years several decision support systems (DSSs) for manure management have been developed (Karmakar et al., 2007), but only some of them take into consideration manure treatment processes. Additionally, few models have been elaborated for solid liquid separation processes. For instance, Rico et al. (2006) obtained a predictive empirical model to estimate the concentrations of DM, VS (Volatile Solids), COD (Carbon Oxygen Demand) and TOC (Total Organic Carbon) in the solid fraction, as functions of the doses of ferric chloride ($FeCl_3$) and a medium cationic polyacrylamide (MCP1). In other studies, Chastain and Vanotti (2003) defined some correlation equations to predict the separation efficiencies for DM, VS, COD, N and P for gravity settling of swine manure. However, the proposed models for solid liquid separation concern only one separation process (i.e., chemical separation or gravity settling). For this reason, they could not be used as tools to support our decisions because they do not estimate and compare the separation efficiencies of different devices and then identify the better solution according to farmers' needs.

The aim of this section is to: i) identify the main factors, among those taken into consideration, affecting the separation efficiency to distinguish different operational groups, and ii) define and validate empirical predictive models for different separation technologies that enable the estimation of the separation efficiencies using data available from published experiments on manure solid liquid separation.

5.2. Materials and Methods

5.2.1. Database Construction

To define and validate the model, the necessary data were firstly collected through published papers. This bibliographical research allowed us to collect publications about solid liquid separation published from 2000 to 2010.

To obtain data expressed in the same units of measurement, the collected data were revised, if necessary, using the relationship between the relative density and the dry matter (DM) or nutrient concentrations in the raw slurry proposed by Piccinini et al. (1990) (Section 1).

Bibliographical data were collected in a database, organized as follows.

- **Input related to the effluent:** animal species (cattle and swine); effluent type (raw, digested and liquid from separation).
- **Input related to the technology:** separator type; use of chemical additives (Additive yes/no).
- **Slurry characteristics:** dry matter concentration, DM ($g \cdot l^{-1}$).

- **Output:** separation efficiency for DM (Eff.DM), nitrogen (Eff.N), ammoniacal nitrogen (Eff.NH_4), phosphorus (Eff.P).
- **References.**

5.2.2. Data processing

The statistical package SPSS 18.0 was used to analyze the collected data. First, dispersion plots were produced. These were used to compare separation efficiency values, making reference to separation efficiencies for DM, N and P, distinguishing the values by separator type.

Error bar plots were then produced. In this case, error bars represent the double mean standard error (SE) of separation efficiencies for DM, N and P, based on different categorical variables (animal species, effluent type, use of flocculants, separator type). This analysis allowed us to identify the variables which mainly affect separation efficiency.

5.2.3. Definition of relationships and model validation

Model definition and validation was carried out on each of the groups using the two methods described below.

1. ***Random.*** Using the statistical package SPSS 18.0, we first divided the database into the identified groups. Then, each dataset was randomly split into two fractions, containing 70% and 30% of observations respectively (Preece et al., 2009). The first observations were used to define linear regressions that allowed us to model the relationships between the separation efficiencies and the dry matter concentration, distinguishing data through the presence or absence of chemical additives. Data sets containing 30% of the observations were used for model validation.
2. ***Cross-validation.*** The leave-one-out cross-validation was performed using the software *The Unscrambler© X 10.0.1* (Soriano-Disla et al., 2010). This method was applied to each group.

For every regression, we calculated the coefficient of determination (r^2) and the significance values. For cross-validation, the coefficients of determination for calibration (r^2 cal) and validation (r^2 val) were calculated.

Finally, for every validation method, the reliability of predictions and their deviation from observed values were analysed both graphically and by means of error calculations. In particular, we calculated the RMSE (Root Mean Squared Error) and the RRMSE (Relative Root Mean Squared Error):

$$RMSE = \left[n^{-1} \sum_{i=1}^{n} (P_i - O_i)^2 \right]^{1/2}$$

$$RRMSE = \left({RMSE}/{\bar{O}} \right) \cdot 100$$

where n is the number of data used; P_i are the predicted values; O_i are the observed values and $\bar{O}$ is the mean of the observed data.

RMSE evaluates the model's accuracy as the difference between predicted and measured values, and it indicates the fitting's absolute mean error, while RRMSE shows the magnitude of the error. Therefore, they were used to quantify the accuracy of the models and to compare them.

5.3. Results and Discussion

5.3.1. Data collection

The database is composed of data gathered from 98 publications, mainly consisting of scientific papers, but also including proceedings from conferences, book chapters, graduation theses and publications of universities and public institutions. Some of the 98 articles were excluded because they did not provide the necessary information for model definition. In some cases, articles by the same authors referred to the same experiments. After this selection, 60 publications were used. It is worth noting that data concerning experiments were gathered for a different purpose, so they are not completely comparable and homogeneous.

The collected data were revised, if necessary, so as to be expressed in the same units of measurement. The final results of these elaborations were a database consisting of 482 observations.

The DM concentration of input slurry had more data than the considered separation efficiencies. In fact, some papers did not report the separation indexes, but instead, the DM and nutrient concentrations in the solid and liquid fractions. Other papers did not give any information about the separation efficiencies, but provided nutrient concentrations of the input slurry and of the final products. In those cases where the data were not complete, separation efficiencies were not calculated and, therefore, the data were not used in the analysis.

Furthermore, some separator types such as inclined screens, centrifuges, gravity settling and screw presses, present a high number of observations, whereas for other separator types, particularly belt presses and vibrating screens, there is little data.

5.3.2. Data analysis

5.3.2.1. Dispersion plots

Separation efficiencies for DM, N and P were analysed as functions of dry matter content in untreated slurry, dividing values by separator type. Moreover, results were distinguished through the presence or absence of additives.

For instance, in Figure 5.1 dispersion plots of separation efficiency for DM are represented.

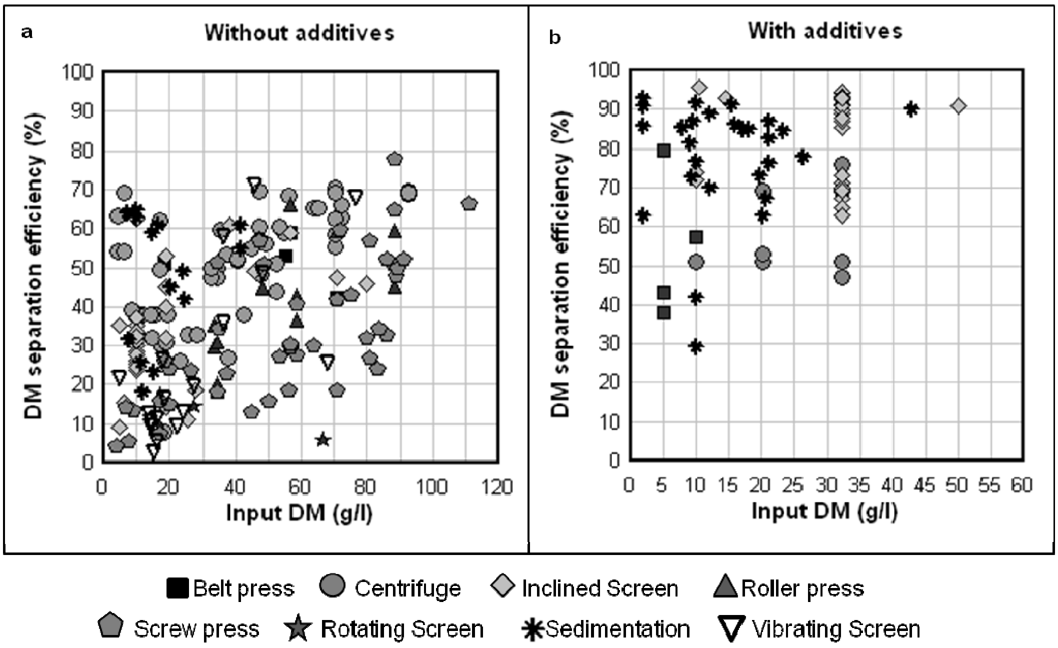

Figure 5.1. Dispersion plots of separation efficiency for DM as a function of dry matter content of untreated slurry, without (a) and with (b) chemical additives.

Groupings of the data according to separator type are indicated, with centrifugation resulting in higher separation efficiency of DM than sedimentation (Figure 5.1a). Since the separation techniques differ in operation as described previously, this was expected.

For each separator type, separation values present a wide range of variation and, generally, higher values (0-80% versus 35-95%) are related to the presence of chemical additives (Figure 5.1). The applied chemical additives (e.g., polyacrylamides) typically cause aggregation of small particles to form larger particles. Hence, improved retention of dry matter in the solid fraction is indeed expected. This observation is in accordance with previous studies (Møller et al., 2007).

5.3.2.2. Error Plots

Error bar plots allowed us to identify the categorical variables mainly affecting the separation efficiencies. In particular, the separation efficiencies for DM, N and P were considered; these were expressed as functions of species, effluent type, use of additives and separator type (Figure 5.2).

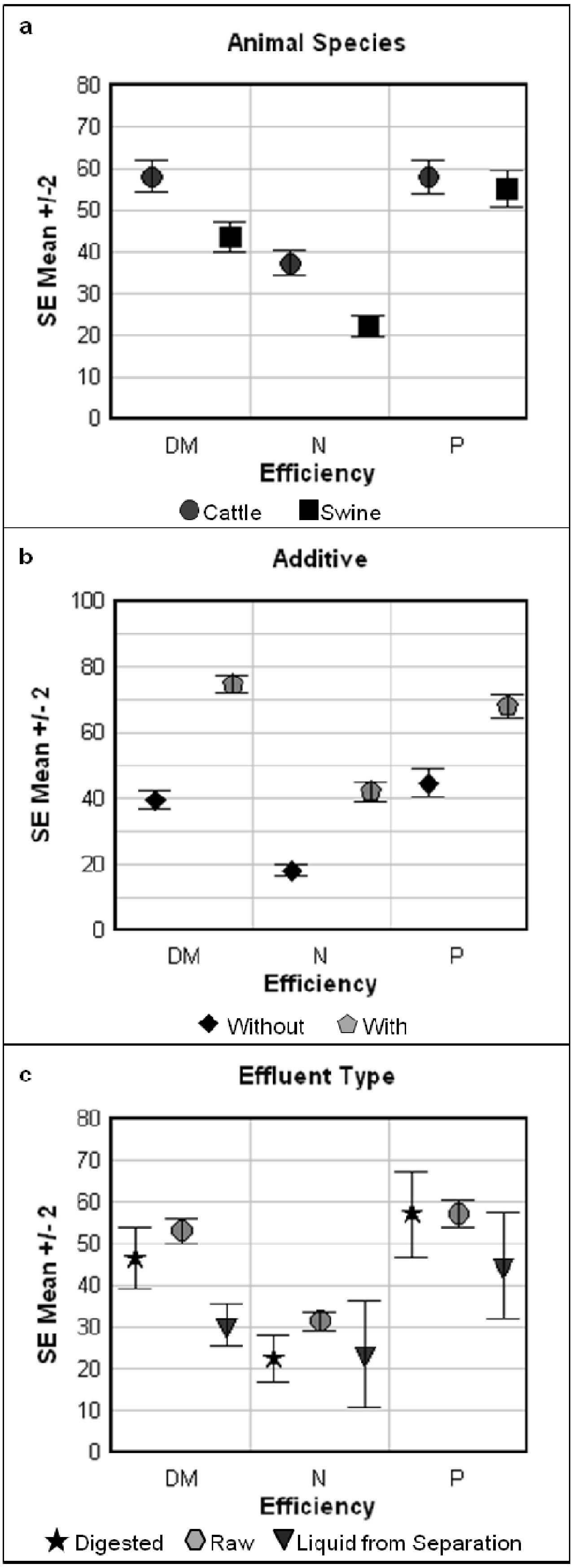

Figure 5.2. Error bar plots of separation efficiencies for DM, N and P grouped by species (a), use of chemical additives (b) and effluent type (c).

When the separation efficiencies are grouped by the species (Figure 5.2a), mean values have significantly different variations for all the considered separation efficiencies. Specifically, the separation efficiencies for cattle slurries are higher, meaning more DM, N and P end up in the solid fraction at separation of cattle slurry than in swine slurry. This result is supported by previous findings (Peters et al., 2010).

The mean values also present different variations when separation efficiencies are classified by the use of chemical additives (Figure 5.2b). As also shown by dispersion plots, flocculants improve the separation efficiencies. However, we could not consider the type of additives and their amounts because of the wide variety of flocculants and coagulants used in the different experiments.

Digestion and removal of solids with separation reduce the DM content of the liquid fraction and increase relative content of the dissolved TAN (Total Ammoniacal Nitrogen) in the nitrogen pool. Thus, effects on the separation index could be expected. However, considering separation efficiency for DM (Figure 5.2c), means have different variations only for separated slurry, whereas the three effluent types (digested, raw and liquid from separation) do not present different variations in the means for the separation efficiency of N and P. Therefore, we could not affirm that the effluent type statistically affects the separation efficiencies. This absence of a significant statistical difference could be ascribed to the fact that manures from different origins are included in the different pool; thus, they are not suitable to rule out a correlation/variation definitively.

Finally, the separator type was used to group separation efficiencies (Figure 5.3). Since the use of additives affects separation efficiency (Figure 5.1 and Figure 5.2a), results were divided by the use of chemical additives. Only some separator types were used with flocculants; these present higher separation efficiencies with chemical additives, reinforcing the previous results (Figure 5.1 and Figure 5.2a).

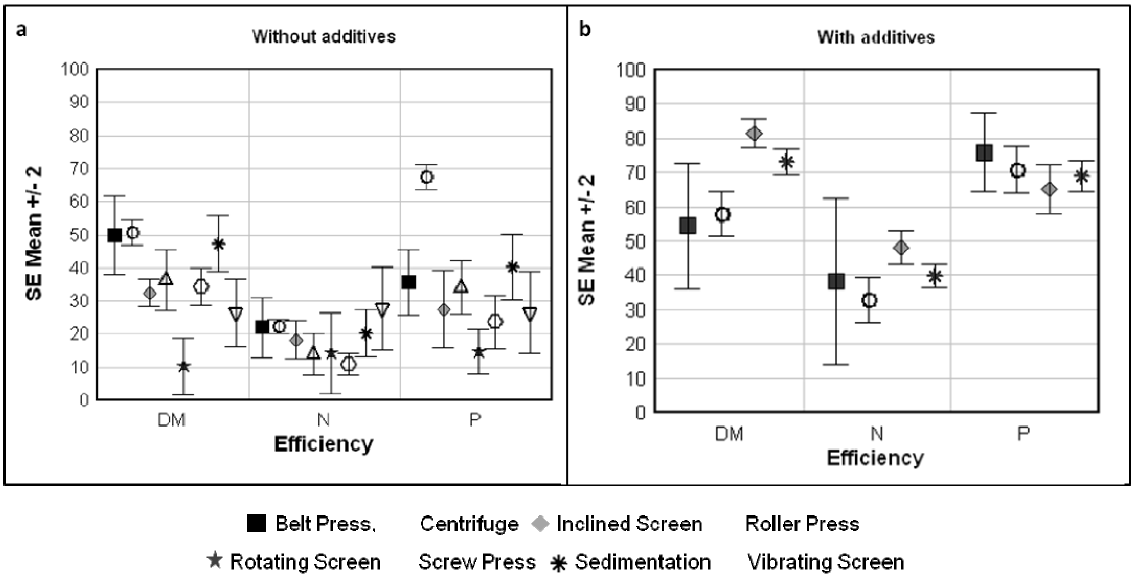

Figure 5.3. Error bar plots of separation efficiencies for DM, N and P grouped by separator type without additives (a) and with additives (b).

For separation indexes of DM, N and P, some separator types have different variation of mean values. That is, separation efficiency depends on the separator type, as also indicated by the dispersion plots (Figure 5.3a). Without the addition of flocculants, the belt press, centrifuge and roller press present similar separation efficiencies for DM and N, while the centrifuge is superior for P separation efficiency. With chemicals, the various separation types present different behaviors in DM separation, while the separation efficiencies for N and P are similar. Moreover, without chemical addition, the separation efficiencies of sedimentation techniques are higher than the efficiencies of filtration techniques.

Therefore, after analyzing error plots, we noticed that the categorical variables which mainly affect separation efficiencies are animal species, use of chemical additives and separator type.

5.3.2.3. Separator Grouping

Some separator types present similar behaviors (Figure 5.3). However, the plots presented in Figure 5.3a and b do not allow us to identify accurate groups. Therefore, separator types were grouped according to their constructional and operating characteristics (gravity filtration, pressurized filtration, settling and centrifugation) (Ford and Flemming, 2002; Hjorth et al., 2010), taking into consideration the results of dispersion and error bars plots. Thus, separation devices were divided in eight groups: four for cattle slurry and four for swine slurry.

- **Cattle slurry:**
  1) Static screen, rotating screen and vibrating screen (gravity filtration)
  2) Screw press, roller press and belt press (pressurized filtration)
  3) Sedimentation (settling)
  4) Centrifuge (centrifugation)
- **Swine slurry:**
  5) Static screen, rotating screen and vibrating screen (gravity filtration)
  6) Screw press, roller press and belt press (pressurized filtration)
  7) Sedimentation (settling)
  8) Centrifuge (centrifugation)

Finally, for every group, data were distinguished by the presence or absence of chemical additives. Since some separator types are not used with chemical additives in the collected experiments (groups 2 and 4), 14 subgroups were obtained.

For each identified group, descriptive statistics were calculated (Table 5.1).

Table 5.1. Descriptive statistics of each group for the entire database divided by the use of chemicals.

Group	Additive	Efficiency (%)	N	Min	Max	Mean	Standard Deviation
1 Cattle Filtration	No	DM	35	6.00	71.70	32.26	16.43
		N	11	8.30	49.20	28.21	14.26
		N-NH$_4$	4	19.60	45.70	32.23	11.06
		P	11	12.10	62.80	35.46	16.56
	Yes	DM	31	63.00	95.70	81.99	11.52
		N	41	14.00	86.00	51.97	16.00
		N-NH$_4$	0				
		P	41	16.30	99.00	66.86	26.22
2 Cattle Pressurised Filtration	No	DM	36	4.34	77.80	40.17	16.69
		N	22	3.97	39.28	17.25	10.48
		N-NH$_4$	5	2.90	24.50	13.00	7.96
		P	22	5.72	73.70	31.44	20.57
3 Cattle Settling	No	DM	11	18.10	64.90	44.58	17.51
		N	11	1.60	40.00	20.25	11.59
		N-NH$_4$	6	0.00	21.30	3.55	8.70
		P	11	13.50	61.40	40.24	16.45
	Yes	DM	44	29.30	92.80	78.38	11.59
		N	60	3.71	74.00	40.25	14.39
		N-NH$_4$	0				
		P	61	16.30	91.70	66.05	20.17
4 Cattle Centrifugation	No	DM	11	53.50	69.10	59.84	5.61
		N	11	20.30	49.12	28.64	7.42
		N-NH$_4$	2	16.00	16.10	16.05	0.07
		P	11	45.50	93.80	71.84	16.64
5 Swine Filtration	No	DM	21	3.00	58.70	26.75	16.86
		N	15	3.50	42.00	16.34	11.67
		N-NH$_4$	6	3.70	11.11	7.75	2.75
		P	12	3.00	46.50	17.55	14.11
	Yes	DM	0				
		N	7	13.00	35.00	25.71	8.24
		N-NH$_4$	0				
		P	15	21.00	80.30	60.37	18.16
6 Swine Pressurised Filtration	No	DM	28	5.50	68.25	31.01	18.94
		N	25	0.83	33.50	9.34	8.47
		N-NH$_4$	0				
		P	27	7.00	73.70	25.33	18.37
	Yes	DM	4	38.10	79.37	54.40	18.50
		N	6	13.11	79.50	38.16	29.61
		N-NH$_4$	0				
		P	6	53.97	90.48	75.94	14.26
7 Swine Settling	No	DM	3	49.00	64.00	57.33	7.64
		N	0				
		N-NH$_4$	0				
		P	0				
	Yes	DM	11	34.00	87.00	65.57	16.15
		N	15	16.10	58.30	37.77	14.76
		N-NH$_4$	12	6.60	47.19	22.83	13.69
		P	14	70.00	91.30	81.44	8.53
8 Swine Centrifugation	No	DM	46	8.00	70.40	48.53	15.29
		N	45	7.00	35.50	20.84	7.22
		N-NH$_4$	17	6.00	37.20	14.59	8.67
		P	45	26.00	90.95	66.57	13.34
	Yes	DM	12	47.00	76.00	57.83	11.19
		N	12	17.00	48.00	32.83	11.65
		N-NH$_4$	0				
		P	12	54.00	88.00	71.00	11.82

In Table 5.1, it is apparent that for some groups the amount of available data is higher (e.g., groups 2 and 8). For every group, each variable has a different number of observations, which are more numerous for separation efficiencies achieved without chemical additives, except for sedimentation (groups 3 and 7). Considering all the groups, some separation indexes present few data, particularly the TAN, which presents little if any information. Furthermore, for each cluster, the data present a high range of variation, particularly without flocculants.

The descriptive statistics support the observation in the error plot that the separation efficiency of DM and N are higher for cattle slurry than for swine slurry.

The order of the separation efficiencies for DM, N and P within swine and cattle slurry are equivalent, i.e., pressurized filtration < gravity filtration < centrifugation (with additive) < settling (with additive). Hence, sedimentation is superior to filtration techniques. Applying filtration without chemical addition is the least effective technique. Application of additives causes the most efficient separation, as also indicated in the dispersion and error plots. Without chemical addition, sedimentation techniques are superior to filtration techniques, as also indicated in the error bar plots. Gravity filtration without chemical addition requires large mesh; hence only large particles are retained in the solid fraction. Settling under optimal conditions, i.e., high force applied and long retention time also cause retention of small particles in the solid fraction. This is supported by previous findings (e.g. Møller et al., 2002).

The order of efficiency of the separator types for N and P separation efficiencies were similar to DM separation efficiency. This is supported by the fact that N and particularly P are associated with the particles (Christensen et al., 2009). N-NH_4 does not strictly follow the other separation indexes because, in addition to being correlated to the total N, it is also dependent on the volume separation (Hjorth et al., 2010).

5.3.3. Model definition

The regressions for model definition were described using the two methods previously described (Random and Cross-validation). In particular, the defined regressions allow the identification of the relationships between the separation efficiencies for DM, N, N-NH_4 and P with the DM concentration of the slurry.

Some separator types, corresponding to groups 2 (cattle slurry/pressurized filtration) and 4 (cattle slurry/centrifugation), are not used with chemical additives. Moreover, for group 6 (swine slurry/pressurized filtration), data for separation indexes achieved with chemicals refer only to belt presses and have a high variability. For this reason, only regressions for separation efficiencies of swine manure treated by pressurized filtration without additives were calculated.

Table 5.2 presents the coefficients of equations (b_0 an b_1 values) and their r^2 and significance (F) values. In some cases, the methods used did not achieve the regressions for all the separation efficiencies because of the lack of data or because of the presence of some anomalous values for the DM concentration of the input slurry.

Table 5.2. Coefficients, r^2 and significance values of regressions achieved by the three methods used. For each group, values are distinguished by the use of chemical additives

Group	Additive	Efficiency (%)	N	Random			Cross Validation		
				b_1[a]	r^2	F[b]	b_1[a]	r^2	F[b]
1 Cattle Filtration	No	DM	35	25.8 + 0.4·x	0.3	*	23.3+0.4·x	0.3	*
		N	11	27.5+0.16·x	0.2	NS	39.9-0.03·x	0.0	NS
		NH_4	4	32.2-0.1·x	0.0	NS	34.6-0.1·x	0.0	NS
		P	11	35.1-0.0·x	0.0	NS	41.3-0.04·x	0.0	NS
	Yes	DM	31	81.6+0.32·x	0.0	NS	81.9	0.0	NS
		N	41	52.5-0.5·x	0.1	NS	59.8-0.4·x	0.09	**
		P	41	107.6-2.1·x	0.9	*	104.9-2·x	0.8	*
2 Cattle Pressurised Filtration	No	DM	36	8.97+0.5·x	0.69	*	10.3+0.5·x	0.47	*
		N	22	-3.49+0.3·x	0.34	**	-2.1+0.3·x	0.29	*
		NH_4	5	-9.8+0.3·x	NA	NS	NA	NA	NA
		P	22	-2.48+0.5·x	0.25	NS	7.5+0.3·x	0.11	NS
3 Cattle Settling	No	DM	9	43	0.2	NS	41.3+0.3·x	0.05	NS
		N	9	19.9	0.2	NS	13.5+0.4·x	0.13	NS
		NH_4	6	5.3	0.8	NS	NA	NA	NA
		P	9	40.5	0.1	NS	44.2-0.3·x	0.04	NS
	Yes	DM	44	85.4-0.6·x	0.3	*	NA	NA	NA
		N	60	39.2	0.0	NS	NA	NA	NA
		P	61	86.8-1.1·x	0.5	*	NA	NA	NA
4 Cattle Centrifugation	No	DM	11	59+0.03·x	0.04	NS	58.3+0.04·x	0.04	NS
		N	11	24.9+0.1·x	0.2	NS	24.1+0.1·x	0.21	NS
		P	11	86.1-0.4·x	0.5	**	85.4-0.4·x	0.60	**
5 Swine Filtration	No	DM	21	25.8-0.2·x	0.06	NS	21.7+0.2·x	0.04	NS
		N	14	6.1+0.4·x	0.4	NS	2.3+0.3·x	0.29	NS
		P	9	1.2+0.6·x	0.15	NS	-8.1+0.9·x	0.54	NS
6 Swine Pressurised Filtration	No	DM	26	11.4+0.6·x	0.32	**	8.04+0.6·x	0.32	*
		N	23	-1.9+0.34·x	0.42	**	-2.8+0.3·x	0.40	*
		NH_4	0	NA	NA	NA	NA	NA	NA
		P	25	16.5+0.2·x	0.04	NS	13.6+0.3·x	0.08	NS
7 Swine Settling	No	DM	5	70.8-0.9·x	0.99	NS	NA	NA	NA
	Yes	DM	11	48.5+0.9·x	0.4	**	51+0.9·x	0.42	**
		N	8	34.7	0.0	NS	29.9+0.3·x	0.0	NS
		NH_4	9	3.4+0.5·x	0.6	*	NA	NA	NA
		P	7	80.9	0.2	NS	NA	NA	NA
8 Swine Centrifugation	No	DM	46	29+0.5·x	0.48	*	29.3+0.5·	0.61	*
		N	45	16.1+0.2·x	0.15	**	15.4+0.1·x	0.21	*
		NH_4	17	18.1-0.02·x	0.0	NS	NA	NA	NA
		P	45	54.1+0.3·x	0.24	*	53.4+0.3·x	0.37	*
	Yes	DM	12	29.6+0.5·x	0.05	NS	49.7+0.5·x	0.07	NS
		N	12	16.2+0.1·x	0.05	NS	33.7-0.1·x	0.00	NS
		NH_4	0	NA	NA	NA	NA	NA	NA
		P	12	53.4+0.3·x	0.07	NS	60.1+0.7·x	0.12	NS

a) b_0 and b_1 are equations' coefficients: $y=b_0+x\cdot b_1$, where x is DM concentration of the input slurry and y is the separation efficiency for a specific component (DM, N, N-NH_4 or P).

b) Significant at $p<0.05$ or $p<0.01$: * $p<0.01$, ** $p<0.05$.

NS= Not Significant; NA= Not Available.

5.3.4. Model validation

After model definition, regressions were validated using plots and error calculation. In particular, the errors RMSE and RRMSE were calculated only for significant regressions (Table 5.3). In most cases, the RRMSE values are below 50% for both random and cross-validation methods. Moreover, for group 7, the model for the N-NH_4 separation efficiency was not validated because of the lack of data in the validation dataset.

Table 5.3. RMSE and RRMSE values for significant equations.

Group	**Additive**	**Efficiency (%)**	**RMSE**		**RRMSE (%)**	
			Random	**Cross-Val.**	**Random**	**Cross-Val.**
1 Cattle Filtration	No	DM	17.29	14.26	53.60	44.20
	Yes	P	17.73	12.19	26.52	18.23
2 Cattle Pressurised Filtration	No	DM	15.66	12.38	38.98	30.82
		N	8.65	9.06	50.14	52.52
3 Cattle Settling	Yes	DM	7.29	NS	10.63	NA
		P	13.52	NS	27.80	NA
4 Cattle Centrifugation	No	P	15.93	14.00	24.38	19.49
6 Swine Pressurised Filtration	No	DM	15.60	15.22	50.31	49.08
		N	4.87	6.94	52.14	74.30
7 Swine Settling	Yes	DM	22.02	15.68	33.13	23.91
8 Swine Centrifugation	No	DM	7.67	9.69	15.80	19.97
		N	5.83	6.47	27.98	31.05
		P	8.52	10.73	12.80	16.12

NS= Not Significant; NA= Not Available

Finally, the two methodologies were compared graphically. The following plots (Figure 5.4 and Figure 5.5) show the linear regressions for the two methods and the data of the entire database. Only groups with significant regressions for both random and cross-validation methods are displayed.

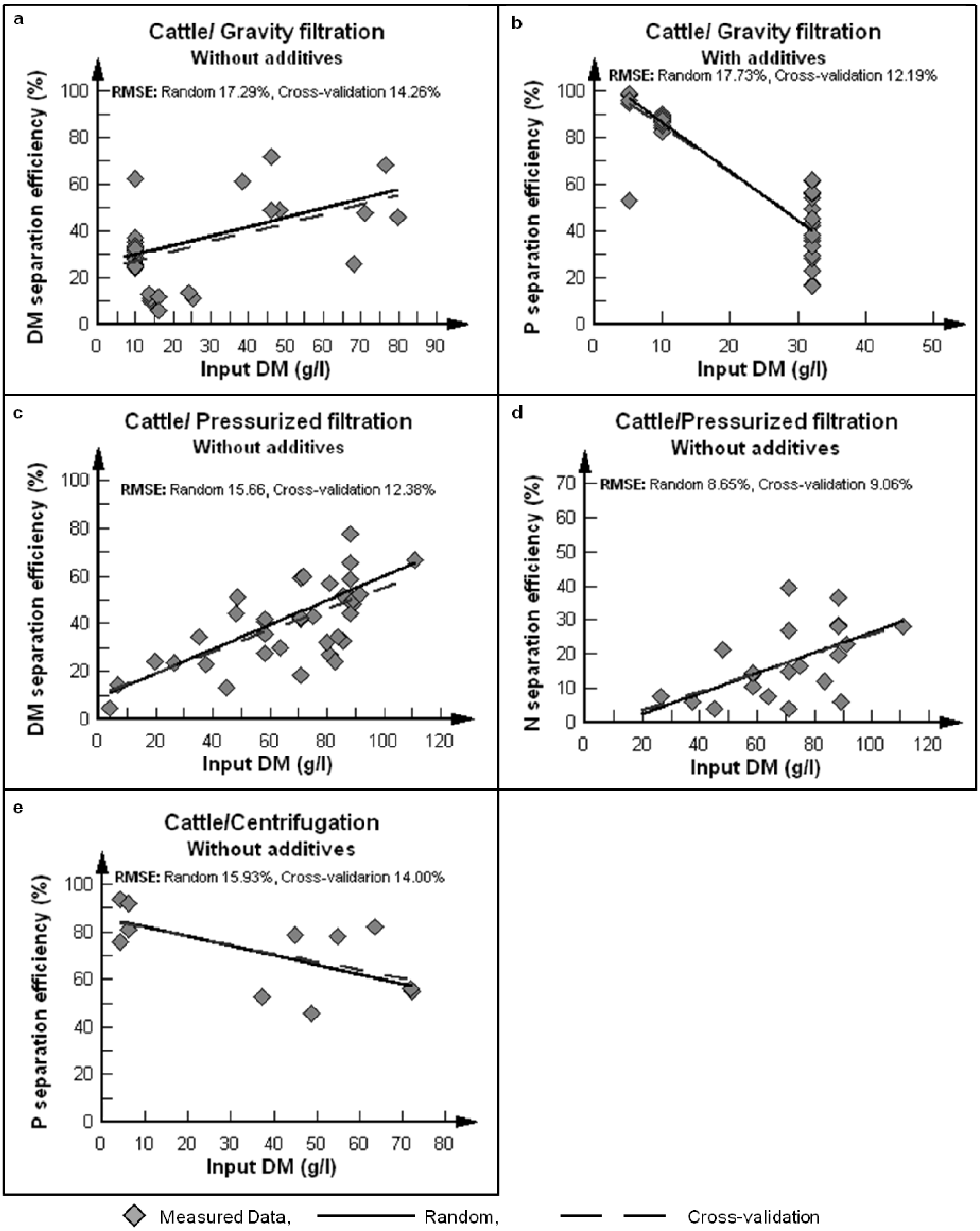

Figure 5.4. Validated models for cattle slurry. The plots are DM separation efficiency for gravity settling (a), P separation efficiency for gravity settling with flocculants (b), DM separation efficiency for pressurized filtration (c), N separation efficiency for pressurized filtration (d) and P separation efficiency for centrifugation (e).

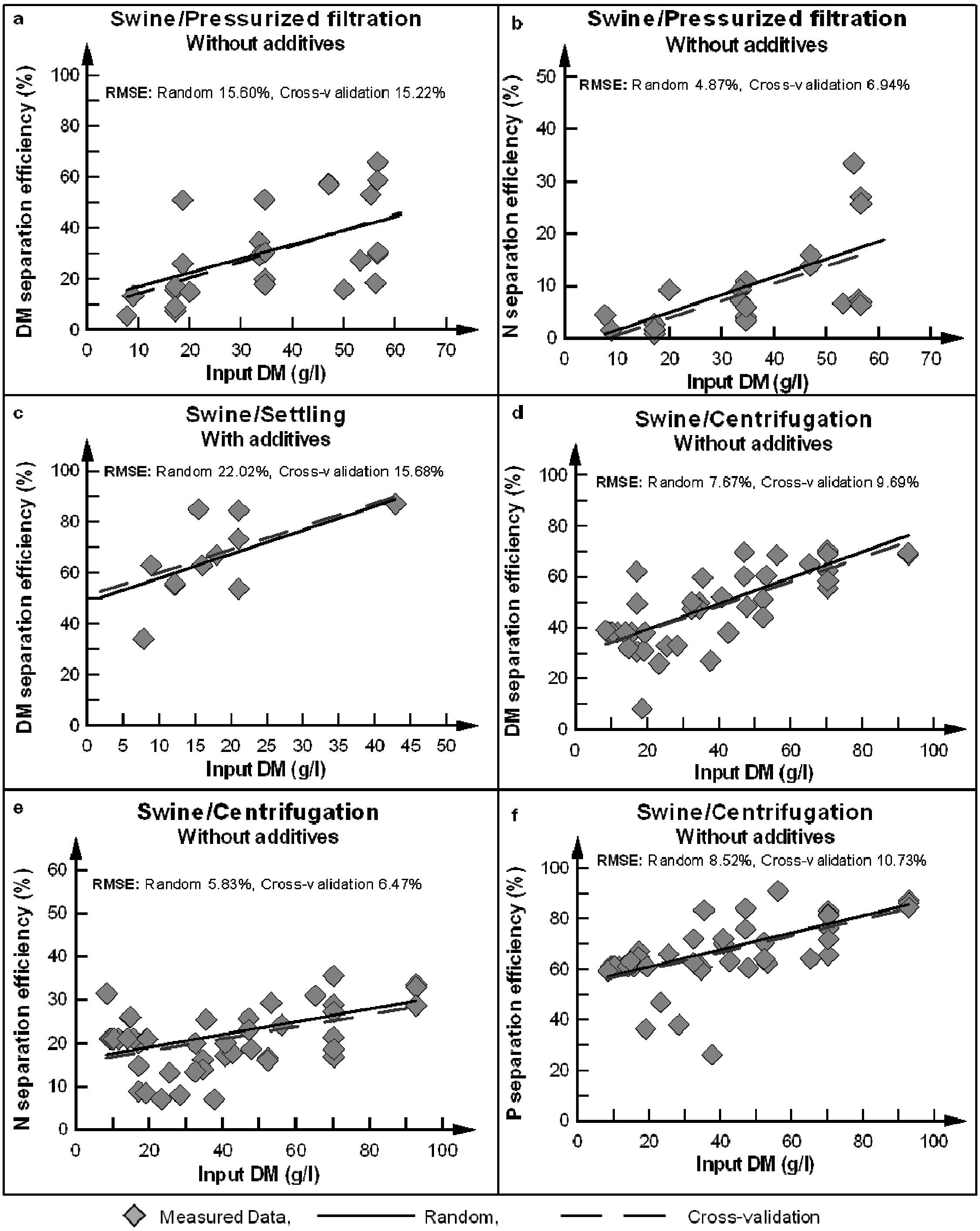

Figure 5.5. Validated models for swine slurry. The plots are DM separation efficiency for pressurized filtration (a), N separation efficiency for pressurized filtration (b), DM for settling using flocculants (c), DM separation efficiency for centrifugation (d), N separation efficiency for centrifugation (e), P separation efficiency for centrifugation (f).

For solid liquid separation of cattle slurry by gravity filtration without using chemical additives, only the models for the DM separation efficiencies were significant (Figure 5.4a). In this case, the measured values present a high variability and thus, the RRMSEs are large for both random and cross-validation models.

Using additives, only the regressions for the separation efficiency of P were significant (Figure 5.4b). The random and the cross-validation models showed a decreasing trend, matching the trend of the data.

Overall, for cattle manure treated by pressurized filtration without the addition of chemicals, the Random and the Cross-validation regressions were significant only for DM and N separation indexes (Figure 5.4c and d). In particular, models for the prediction of the DM separation efficiency (Figure 5.4c) matched the trend of the data well. Hence, the RRMSE values are low.

The separation efficiency for total nitrogen (Figure 5.4d) data has high variability, as shown by descriptive statistics (Table 5.1). For this reason, the RRMSE values are higher.

There are few and variable measured data related to the P separation index for the separation of cattle slurry by centrifugation without chemicals (Figure 5.4e). As for the P separation efficiency for cattle slurry using flocculants, the models for the P separation efficiencies present a decreasing trend.

As for cattle slurry, only the separation efficiencies for DM (Figure 5.5a) and N (Figure 5.5b) present significant regressions for swine slurry separated with pressurized filtration without additives. Separation efficiencies of DM data are very variable, and so, even though the random and cross-validation models are similar, the predicted values diverge more from the observed ones.

The separation efficiency for N presents few data, but the two models fit the trend of the data better than models of separation efficiency for DM, except for high DM concentrations.

The separation efficiency for DM of the solid liquid separation of swine manures by sedimentation using flocculants present few data, which have a clear tendency (Figure 5.5c). This one is well-fitted by the two models.

For the separation of swine slurry with centrifuges, only the separation efficiencies for DM (Figure 5.5d), N (Figure 5.5e) and P (Figure 5.5f) without the addition of flocculants present significant regressions. In general, there are more available data, even if it is possible to notice the presence of anomalous values, such as various separation efficiencies corresponding to the same value of DM concentration (78.3 $g \cdot l^{-1}$). Separation efficiencies for DM, N and P present very similar models. In particular, the two models fit the trend of the data well for the separation indexes of DM and P, while for separation efficiency for N data are more variable.

5.3.5. Models discussion

For model definition, some regressions were not achieved or were not significant because of the lack of available data. In other cases, regressions were not calculated despite the large number of observed data (e.g., group 3). This is due to the DM concentration of the input slurry, which presented only one or a few values and thus was considered a constant. In these instances, model definition and validation should be supported by a larger number of experiments.

The separation efficiency for DM for cattle slurry using gravity filtration (group 1) is not entirely correlated to the input's DM concentration. Hence, a larger number of experimental data could allow us to achieve multiple linear regression lines depending not only on the DM concentration of the input slurry, but also on other criteria that affect the separation efficiency, such as mesh size.

The separation efficiency of DM and N for screw press, roller press and belt press separation of cattle and swine slurry (groups 2 and 6) are both correlated to the DM content of the input slurry. Of all the separator types, these pressurized filtration separators cause the fewest of the minor particles to be retained in the solid fraction, which may cause the simplicity of the correlation and thus the significant relationship.

The significant P separation efficiencies without chemical additives (group 4 and 8) are shown not to be entirely linear functions. Phosphorus is contained in the small particles (60% in 1-25 µm diameter particles) (Peters et al., 2010; Masse et al., 2005), thus inclusion of the small particles in the solid fraction causes a large increase in the separation efficiency. Hence, the use of smaller pores in gravity filtration can result in a large effect on the P separation though a small effect on the DM separation.

For cattle slurry, the P regressions display decreasing trends (Figure 5.3b and Figure 5.4). That is, more DM in input causes less P in the solid fraction. This may be because an increase in DM content is typically dominated by an increase in the largest particles such as straw, which has very low P content.

Generally, significant equations for separation efficiencies were not obtained for flocculants additions, except for groups 1 and 7. The first one regards the P separation index for cattle slurry using gravity filtration, while group 7 concerns the separation efficiency for DM of swine manure by settling. In general, correlations may be complicated by the applied flocculation treatments, which are very different in the various experiments. Thus, it is necessary to take into account the applied chemical and the added dosage relative to the optimal chemical dose.

Since the values of coefficients are similar and RMSEs are relatively reasonable for the majority of the variables, both the random and the cross-validation methods are applicable for model definition and validation. However, for the random method, the model's accuracy is based on the characteristics of regression and validation datasets, which have been constituted randomly. Therefore, as the database presents some anomalous values, in some cases the available data did not allow the definition of useful regressions or, in other cases, a trustworthy validation of the identified equations.

5.4. Considerations

The graphical analysis allowed us to distinguish several technological and operational conditions that affect separation efficiency. However, more parameters could be taken into account with more data.

Furthermore, for 7 of the 14 subgroups it was possible to define and validate the predictive models. These present RRMSEs lower than 50% thus can be implemented in a decision support tool, enabling the identification of the most effective treatment option.

The model should be improved, in order to better support the identification of the separation system to insert in a manure treatment plant, taking into consideration the characteristics of the input manure and the aim of the treatment plant. E.g. the definition of the more suitable separation technique for the biological nitrogen removal (Section 2), may be directly performed through modeling.

6. CONCLUSIONS

The results gathered through the experiments described in the previous sections allow us to better evaluate the different solid-liquid separation technologies. In particular, the required characteristics of the resulting liquid and solid fractions may differ according to the whole treatment scheme and its primary scope. In this context, the available separation techniques present different separation efficiencies and, thus, lead to the production of liquid and solid fractions that have different concentrations of dry matter and nutrients. Separation performances are also affected by operative conditions, such as manure type, pre-treatments and the flow rate of the input slurry. As demonstrated by previous studies, the manure type is affected by animal species and category, the type of housing and the diet. Therefore, different manure types would have different physico-chemical characteristics, which can affect the separation performances. Manure characteristics are also affected by manure pre-treatments, which could modify physical, electrochemical and chemical properties of the input manure and, thus, influence the separation efficiency. E.g. slurry separation lead to a quicker drainage of the liquid from the solid. This causes an increase of the wash-out of the solid particles in the liquid and, thus, to a decrease of the separation efficiency. Therefore, the resulting liquid fraction will be characterized by a higher dry matter and nutrient content compared to a non-acidified liquid fraction.

According the results described above, the performances of the Agroenergie Bergamasche treatment plant (section 2) could be improved by a correct evaluation of the more suitable separation systems. Since during the anaerobic digestion process the manure is co-digested with different biomasses, the resulting digestate present a high dry matter content. Therefore, a pressurized filtration system (e.g. screw press) allows to remove only larger particles and could be used as primary separation step. It could be also replaced by more efficient separation techniques, such as centrifugation or mechanical separation combined to flocculation.

Natural polymers enable to improve the separation efficiency for dry matter and nutrients. Furthermore, the optimal dosage is highly dependent to the characteristics of the treated manure, therefore it is difficult to define guidelines that could give indication of the optimal dosage according to manure properties such as the dry matter content. More data should be gathered in order to identify direct correlations between manure characteristics (e.g. the DM or the VS content) and the optimal additive type and dosage.

During the combination of physical or mechanical separation with coagulation and/or flocculation pre-treatments, the selection of the optimal dosage and the more suitable type of chemical is strongly affected by manure characteristics. Therefore, the performances of a determined separation process may be negatively affected by the utilization of the wrong additive type. Previous laboratory scale analyses (i.e. jar test) could help in the definition of the optimal polymer type.

The identification of the more suitable separation process could be supported by a predictive model that could estimate the separation efficiency of a defined separator under different operative conditions. An empirical predictive model could give good indications for the separation systems more affected by the dry matter concentration of the input slurry (e.g. filtration or pressurized filtration), but the result less precise for other separation systems. In particular, an empirical model does not take into consideration the operating principles of the different mechanical separation or the type and the dosage of chemical additive used during a chemical separation process. Therefore, a more accurate and physical-based model could allow identifying better the separation system more appropriate for a determined treatment plant.

6.1. Future Perspectives

Solid-liquid separation treatments could be improved in order to enhance the removal efficiencies not only for the dry matter, but also for nutrients such as nitrogen and phosphorus. This might allow the transportation of a larger amount of nutrients to fields that are not vulnerable to high nitrogen loads and, thus, minimize the contribution of slurry management to eutrophication and acidification processes.

Solid-liquid separation treatments should be studied in combination to other manure treatments, in order to better understand how the combination of separation techniques and other treatment could minimize the environmental impact related to manure management.

Predictive models could be improved, not only by the addition of information related to the operating principles of the different devices, but also by taking in to consideration the environmental impact of the different solutions. For this reason, Life Cycle Assessment of the different separation systems and of the combination of these ones with other treatment technologies should be developed.

Natural polymers could be used in solid-liquid separation of animal slurry, in order to recycle organic wastes and reduce the toxicity problems related to the application of iron and aluminum salts and of synthetic polymers. However, more studies are necessary in order to improve the application of these products to animal slurries.

The effect of different pre-treatments on the efficiencies of different separation technologies needs to be studied in more detail, in order to improve the performances of the entire treatment system within a farm.

Natural polymers could be used in solid-liquid separation of animal slurry, in order to recycle organic wastes and reduce the toxicity problems related to the application of iron and aluminum salts and of synthetic polymers. However, more studies are necessary in order to improve the application of these products to animal slurries.

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