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## **Improvement of pig slurry mechanical separations using chitosan and biochar**

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### **Abstract**

## 1. Introduction

Solid-liquid separation of pig slurry results in production of dry matter, nutrient and energy rich solid fraction low in volume, and large amounts of nutrient poor liquid fraction (but rich in ammonia). Separation methods proved to be useful practice when export of surplus slurry from the farm to areas without livestock production (higher nutrient inputs needed) is desired. Solid –liquid separation is usually performed using centrifugation or screw press (mechanical separation).

Screw press is a simple mechanical separation where slurry is pressured and effluent is transported into cylindrical screen with a screw, while liquid will pass through the screen and be collected in a container around the screen. This type of mechanical separation is usually characterized with high dry matter removal to solid fraction (20-25%), high flow rate (approx.  $18 \text{ t h}^{-1}$ , varying from  $6\text{-}25 \text{ t h}^{-1}$ ), relatively low costs (approx. 34 000 euro and 5000 euro installation costs) and with energy consumption of  $0.4 \text{ kWh m}^{-3}$ . Therefore, it is one of the separators most commonly in use. Screw press has very low separation efficiency for small, nutrient rich particles, thus it is often needed to be improved by polymer flocculation in order to meet most of separation objectives (Hjorth et al., 2010).

Centrifugation is a type of mechanical separation based on increased settling of manure particles by centrifugal force. The centrifugal force separates solids and liquids into an inner layer with a high dry matter content, and an outer layer consisting of a liquid containing a suspension of colloids, organic components and salts (Hjorth et al., 2010). The flow rate of centrifuge is somewhat lower than for screw press ( $12 \text{ t h}^{-1}$ , ranging from  $6\text{-}25 \text{ t h}^{-1}$ ) with higher energy consumption (approx.  $3.7 \text{ kWh m}^{-3}$ ) (Provolo G.,

2012) and higher investment costs (approx. 100 000 euro for stationary unit and 15 000 euro for installation costs, and approx. 150 000 euro for mobile unit where no installation costs are needed). Despite its high costs and energy consumption, centrifuge is often found as a good solution for farmers, mostly due to its high separation efficiency in removing small, nutrient rich particles, thus producing nutrient rich solids.

Addition of flocculants to manure will cause small manure particles to bind together in larger particles (flocs) that can be easily retained in solid separation fraction. These small particles are nutrient rich (Masse et al., 2005; Hjorth et al., 2010) so their increased retention in solid fraction of low volume is favourable when nutrients should be taken away from the farm. Polymer flocculants are macromolecules of various molecular weight, charge density and structure that after being added, destabilize the solution (suspended charged particles) by building bridges among particles (polymer bridging), neutralizing charges and by electrostatic patch flocculation (Hjorth et al 2010). According to Garcia et al., (2009) flocculants can be divided into 3 groups a) inorganic flocculants; b) organic synthetic high-polymer flocculants and c) naturally occurring flocculants. The most frequently chosen flocculant (in the literature) for application with manure is organic synthetic high polymer-polyacrylamide (PAM). There is a wide variety of PAM formulations with different polymer chain length, structure, number and kinds of functional groups etc (Entry et al., 2002). Previous research (Hjorth et al., 2008, 2009; 2013) showed that the optimal polymer for manure is cationic, very large, linear and had medium charge density (20-30%) based on polymer bridging and patch flocculation as main processes. Despite high effectiveness in manure separation, and relatively low costs of polyacrylamides, naturally occurring flocculants should receive more attention as they are usually biodegradable, non-toxic and derived as by-products from naturally occurring sources, with multiple application in food and medical industry. In this study we have tested the effectiveness of chitosan

in improving mechanical separation of pig slurry. Chitosan is a linear copolymer of randomly distributed  $\beta$ -(1-4)-D-glucosamine and N-acetyl-D-glucosamine. It is a polycationic polymer that has one amino group and two hydroxyl groups in repeated glucosidic residue (Dash et al., 2001) and it is amino group on the molecule that provides sites for a variety of side group attachment, and gives chitosan cationic character in acidic media (at low pH (< 6) amine groups are protonated while at high pH (> 6) they are deprotonated, lost their charge and thus insoluble. Chitosan is usually produced by deacetylation of chitin, a polysaccharide widely distributed in nature (second most common biopolymer after cellulose). For these reasons we wanted to test how chitosan would affect separation efficiency when compared to PAM.

Pig slurry is usually diluted (2-6%DM) and as efficiency of mechanical separators mainly depends on dry matter content of the feedstock (raw slurry) being lower for diluted slurry, increase of feedstock dry matter can be a promising solution. Biochar is a product of gasification-thermal decomposition of organic matter under controlled amount of oxygen and steam, at high temperatures (>700 °C) but without combustion. The resulting gas mixture (syngas) is used as a fuel and the power from gasification is regarded as a renewable energy, whereas biochar is a by-product. Biochar usually contains about 99% of dry matter (Reference) so its addition to manure in order to increase dry matter content and thus increase mechanical separation efficiency sounded like a pleasant idea. Moreover, due to its chemical characteristics (large surface area, high CEC etc.) it is likely that biochar can be used as for capturing more N, P, Cu and Zn in solid fractions after mechanical separation. However, biochar application to manure prior solid-liquid separation followed by spreading of separated fractions to the arable land has received surprisingly little systematic investigation to date. So, we evaluated if separation efficiency (with respect to DM, N, P, K, Cu and Zn) of

mechanical separators is affected when biochar was added to the raw slurry. We also tested the effect of biochar addition on efficiency of separation system which already includes chemical-pre-treatment (flocculant addition).

Main hypothesis was to test if addition of polymers and biochar and their combination will improve efficiency of screw press and centrifuge separation for dry matter, N, P, K, Cu and Zn.

## 2. Material and methods

### 2.1. Raw slurry

Fresh pig slurry (from fattening pigs) was sampled on 5<sup>th</sup> November 2012 at Bonetto farm, Racconigi, Piedmont, Italy. Around 750 L of raw slurry was collected from agitated pre-tank over a period of 30 minutes. Slurry was collected and transported in 1m<sup>3</sup> plastic container to the laboratory, where it was transferred to a tank placed into the freezer room at +5° C for the time of experiment duration. All separation tests were performed at the laboratory of the “Waste management group” at the Department of Agriculture, Forest and Food Sciences, University of Turin, Italy.

Prior to separation treatment, representative samples were taken from the tank after vigorous mixing with two manual mixers for 5 minutes. In each separation treatment around 20 L of slurry was processed. After separation, produced fractions were subsampled into 1L plastic containers and stored at -18° C for further analyses. Prior to subsampling, solid samples were thoroughly mixed by hand for 10 minutes, while liquid samples were mixed with rod for 2 minutes.

### 2.2. Experimental set-up

Six separation treatments were applied to collected slurry, at laboratory scale (Table 1).

>>>Insert Table 1.

Screw press treatment was performed using a machine usually used to produce tomato juice at small scale (production for one household) that works based on the screw press principle with a capacity of 200 kg/h of tomato and auger rotation of 180 rpm (for more information about the machine see: [www.imperia.com](http://www.imperia.com)). The machine was applied to



approx. 20 kg (per treatment) of raw slurry as a simplified model for a screw.

Centrifugation (CENT) treatment was performed by transferring around 200 mL slurry to a centrifugation tube, centrifuging for 30 seconds at maximum speed (with additional 15 seconds for acceleration and 20 seconds for deceleration) at 3500g, and carefully collecting the supernatant by suction. A decanting centrifuge is typically running with this retention time. Centrifugation was applied as a simplified model for a decanter centrifuge (Moller et al. 2007).

Flocculation treatments were performed by adding optimal dosage of two flocculants (PAM and chitosan) to raw and biocharred slurry and co-digestate (Table 1). PAM- synthetic polymer; 0.2% polyacrylamide (superflock C-2260, cationic, linear, high molecular weight, 40% charge density, Kemira Kemwater, Finland) was dissolved in water. Chitosan - a natural flocculant; 0.45% chitosan (Sigma-Aldrich Inc.) was dissolved in 2% acetic acid (Garcia et al., 2009). The optimal flocculant dosage was determined using multiple trial-and-error flocculations. For PAM different polymer rate treatments were applied in the increment of 50 ml/L in a dosage range of 200-400 ml/L. For chitosan the increment was of 120 ml/L in a dosage range of 240-480 ml/L.

Polymers are added slowly to manure, mixed for 5 minutes and let for 20 minutes to rest. After flocculation took place, samples were drained by gravity (for 20 minutes) through a 1 mm mesh size screen. Obtained fractions were analyzed for dry matter content, and mass separation was calculated (Table 1). Optimal flocculants dosages were chosen based on visual characterisation of the floc size, solid and liquid fraction DM, turbidity of liquid fraction and mass separation. When chitosan was used as polymer, foam formation was included in optimal dosage determination.

Optimal PAM dosage for raw slurry was 350 mlPAM/L, while for biocharred slurry was 300 mlPAM/L. Chitosan optimal dosages for raw and biocharred slurry were 240 mlChitosan/L slurry.

### 2.3. Biochar characteristics

Biochar selected for this study was produced in gasification process using wood chips as a feedstock (GEM CHIMICA SNC DI Cerutti G.&C.). Gasification was performed on a 3m<sup>3</sup>/h capacity gasifier, using an down draft (biomass from the top, air collected from the bottom). The average steady state temperature was 1300°C. Biochar was collected bulk under the gasifier, cooled under air and stored in big bags.

Chemical characteristics of biochar were determined by D.M. 13/09/1999 GU n° 248 21/10/1999 method, while ash content was determined by REG CE 152/2009 27/01/2009 method. Produced biochar contained 0.22%, 0.42% and 1.09% of nitrogen, phosphorus and potassium, respectively. It contains 25.8% of ash and 4.15% of water. The pH value was 11.7, while C:N ratio was 226, and organic carbon content was 49.75%.

In this study, biochar was applied in amounts so dry matter content is increased for 1%. Based on preliminary results (data not published) on time application of biochar, we have added biochar approximately 16 hours prior to separation. Biochar was carefully added to manure barrel, and slowly mixed, and left overnight at the room temperature (with tighten lid on). Before polymer was added, biochar and slurry were mixed vigorously for 2 minutes.

## 2.4. Chemical analysis and calculations

Dry matter (DM) was determined by drying the fresh samples to constant weight (24h) at 105° C and is presented as percentage of wet weight. Volatile solids content (VS) was determined on dried samples as loss on ignition at 550° C for 5h (VDI 4630, 2006) and presented as percentage of dry matter. Dry matter and volatile solids were measured using (Kern, mod. ABS 220-4) limiting on 4 trustful digits. The pH was measured directly in slurry and liquid samples, while for solids it was measured in diluted samples (de-ionized water). Solid samples were shaken for 45 minutes and left for settling for 15 minutes, prior to pH measurements (Jorgensen and Jensen 2009). Total N and NH<sub>4</sub>-N were measured by Kjeldah method. Total phosphorus was measured by M.U. 2252:08 method, total potassium, by EPA 3015A 2007 + EPA 6010C 2007 while copper and zinc were measured by EPA 3015A 2007 + EPA 6020C 2007 method.

Calculation of mass recovery for each treatment was based on the measured mass of input slurry and masses of produced solid and liquid fractions, using a balance (Orma mod. BC) with 2 trustful digits. Mass separation was calculated based on the concentration of dry matter in separation fractions for all performed treatments.

Separation indices were calculated based on the calculated mass separation for each separation treatment and the measured concentrations of dry matter and elements N, P, K, Cu, and Zn (mass ratio of a solute transfer from raw slurry to the solid separation fraction). Simple ( $Et$ ) and the Reduced separation index ( $Et'$ ) were used to compare efficiency of separation treatments for dry matter, N, P, K, Cu and Zn. For further details, see (Peters et al., 2011; Popovic et al., 2012). In brief,  $Et$  indicates the relative

proportion of the component which ends up in the solid fraction. It can be calculated using following formula (eq. 1):

$$E_t(x) = \frac{m(x)_{solid}}{m(x)_{slurry}} \quad (\text{eq.1})$$

where  $m$  is the mass of the compound  $x$  (DM, N, P, Cu, or Zn). Simple separation states the distribution of  $x$  between solid and liquid separation fractions, and ranges from 0-1, where e.g.  $E_t(x) = 0.70$  indicates that 70% of  $x$  is present in the solid fraction.

Reduced separation index ( $E_t'$ ) indicates the degree of upconcentration of the component, with a positive value indicating upconcentration in the solid fraction and a negative value indicating upconcentration in the liquid fraction. It can be calculated using following formula (eq. 2):

$$E_t'(x) = \frac{E_t(x) - \frac{m(solid)}{m(slurry)}}{1 - \frac{m(solid)}{m(slurry)}} \quad (\text{eq.2})$$

where  $m(slurry)$  is the total mass (g) of separated slurry and  $m(solid)$  the total mass (g) of solids produced. The reduced separation index ranges from -1 to 1, with positive values indicating an increase in the concentration of  $x$  in the solid fraction compared with the raw slurry, and negative values indicating an increase of the concentration of  $x$  in the liquid fraction.

## 2.5. Statistical analysis

Differences in chemical characteristics in all solids and liquids within the fraction were tested by one-way ANOVA. One-way ANOVA was also used when assessing the difference between  $E_t$  and  $E_t'$  values.

### 3. Results and Discussion

#### 3.1. Characterisation of raw slurry

The measured chemical composition (**Table 2**) of raw slurry used in this study was similar to that previously found in the literature (Sommer and Husted 1995-referenca za italijanski stajnjak).

>>> Insert Table 2

In following paragraphs increase/decrease in terms of elemental content of produced fractions would refer to comparison between elemental content in produced fractions with pre-treatment and fraction produced by its respectable simple mechanical separation (screw press or centrifuge).

#### 3.2. Characterization of separated fractions

Solids produced after centrifugation contained more water (approx. 15% of dry matter) when comparing to solids produced with screw press (approx. 25% of dry matter) (Table 2), mostly due to the separator performances on both, farm and laboratory scale. When screw pressed, at the end of the axle, solid are pressed against the plate, so even more liquid is forced out of solids. On the other hand, centrifugation has high potential in dewatering the slurry when volumetric feed rate is reduced, which increase retention time, thus increasing dewatering zone and dry matter content in solids. However, increased retention time will lead to poorer economic performance of the centrifuge making these adjustments difficult to be implemented on the farms.

In general, pre-treatments (P, C and B) were more efficient prior to screw press than to centrifuge with respect to all analysed chemical characteristics. Given the fact that centrifuge (decanting) is one of the most efficient mechanical separation (at reduced volumetric feed rate) for retaining P and dry matter in solid fraction mainly due to its selectivity for small-nutrient rich particles, it was expected that treatments based on flocculation will have less effect on efficiency of centrifugation than on screw press.

When PAM was added (P+SP and P+CENT) to manure, smaller manure particles, to which P, Cu and Zn are attached (**Popovic et al., 2012**), were agglomerated into bigger flocs and retained in the solid fraction, while dissolved Cu and Zn were not captured and thus remained in the liquid. When biochar was added in combination with PAM (B+P+SP and B+P+CENT) both, dissolved and sorbed Cu and Zn were able to be retained in the solid fraction. Thus we have observed lowest Cu and Zn content in liquids from P+B+SP and P+B+CENT when compared to their respective P and B treatments. On the other hand, biochar decreased chitosan flocculation with respect to P, Cu and Zn, most probably due to the P, Cu and Zn association to biochar particles which lowered amount of free charges (CEC) on biochar particles, unabling chitosan to flocculate them (main flocculation mechanism of chitosan flocculation at pH 6.5 is charge neutralization (**Reference**)).

### 3.2.1. Screw press

Treatment B+SP produced liquids with significantly increased dry matter content (**Table 3**), and it did not show the expected increase in dry matter of produced solids, as most probably smallest biochar particles followed liquid fraction for which screw press

has low selectivity. For that reason the respectable liquid fraction had significantly higher dry matter content when compared to SP liquid fraction. In B+SP solids, biochar addition significantly lowered P, and significantly increased NH<sub>4</sub>-N content. Capability of biochar, to adsorb organic compounds (Oen et al., 2006 and Brandli et al., 2008) and remove heavy metals from waste-waters (Mohan et al., 2007) has been shown. Due to its high CEC, biochar is very suitable for removing metals (Cu, Zn, Ni, Cd, Pb and As) from contaminated soils. The study of **Lehman et al 2002** when biochar (wood from black locust (*Robinia pseudoacacia*)) was added to cow manure showed phosphate and ammonium being adsorbed readily by biochar/manure mixture. , but the share of NH<sub>4</sub>-N in total N increased due to NH<sub>4</sub>-N adsorption onto biochar particles. Smaller-sized particles generally adsorbed more nutrients than larger ones, due to their high surface area. Most of dry matter in solid fraction after screw press is consistent from particles larger than 250 µm, while in liquid fraction particles are mostly lower than 25 µm (**Popovic et al., 2012**). Addition of biochar increased the amount of small particles that compete for P, Cu and Zn with large slurry and biochar particles, and due to small particles high CEC outcompete large once. Therefore, we believed dissolved phosphorus was adsorbed to small biochar particles that after screw press separation followed liquid fraction. This resulted in producing solid fraction with decreased content of phosphorus (on dry matter basis) and liquid fraction with increased P content (on dry matter basis) from B+SP treatment when compared to SP.

>>> Insert Table 3.

Solids produced in C+SP treatment contained significantly lower total N, Cu and Zn concentration (dry matter basis) when compared to solids from SP (**Table 3**). Decrease was observed also for P, but has not been significant. Chitosan addition prior to screw

press did not increase retention of the smallest particles in solid fraction, therefore, we observed significant decreased of N, P, Cu and Zn content in C+SP solids compared to their content in SP solids (dry matter basis) while their content in liquids was similar to SP liquids content. In our study, we have activated chitosan in 2% acetic acid, and when adding optimal dose to the slurry, we lowered raw slurry pH for almost one unit (at 6.5) creating acidic conditions. Failure of chitosan flocculation could be due to the flocculent nature, as previous study (**Huang et al., 2000**) showed that when pH of solution is below 7, chitosan becomes more extended chain (with more charges on the surface) and thus produce smaller and looser flocs. These loose flocs can be damaged when separated applying pressure (using screw press).

When PAM was combined with screw press (P+SP) total N content was significantly increased, whereas P, Cu and Zn content of solid fraction were also increased but not significantly. Increase in total N content of P+SP solid fraction when compared to its content in SP solids, could be due to the shift of organic N to solid fraction. However, there is still a significant amount of N present in the liquid fraction as dissolved ammonium N (**Table 2**). Surprisingly, PAM did not affect P content in solid fraction, despite the fact that most of P is associated to smaller particles (**Masse et al., 2005, Meyer et al., 2007**) and should follow the same pattern during separation as dry matter and organic N. Previous studies (Legros et al., 2010; L'Herroux et al., 1997; Popovic et al., 2012) showed that most of Cu and Zn are bound to organic matter smaller than 25  $\mu\text{m}$  and are also present in liquid phase of manure. Therefore, increased content of Cu and Zn in P+SP solids were expected. Based on the above stated arguments we can conclude that removal of small particles to solid fraction plays an important role in producing solid fraction with high N, P, K, Cu and Zn content. This treatment produced the cleanest liquid fraction (lowest dry matter content) in group of screw press based



separations, with low Cu and Zn content (**Table 3 and 4**), but it did not show any effect on liquids N and P content.

When chitosan was accompanied with biochar (B+C+SP) as a pre-treatment to screw press, concentrations of N, P, Cu and Zn were lower when compared to solid from SP treatment, but not statistically. Treatments where PAM was in combination with biochar (B+P+SP) significantly increased dry matter content, while lowering P concentration in solids. In liquids dry matter, Cu and Zn content was significantly lowered.

### 3.2.2. Centrifugation

After biochar addition, increase in dry matter content was observed for solids produced in B+CENT treatment (**Table 4**).

Total N content was significantly decreased in liquids from C+SP and significantly increased in liquids from C+CENT. Chitosan addition lowered Cu and Zn contents in produced liquids being significantly lower only in liquids from C+CENT treatment. Main mechanism by which chitosan flocculates is based on destabilization of negative colloidal suspension by adsorption of particles (charge neutralization), followed by polymer bridging. Chitosan can also flocculate based on precipitative coagulation, electrostatic patch and aggregation phenomenon, but the mechanism that will take the major role in flocculation depends, on chitosan dosage and pH. The effect of pH can be attributed to differences in the protonation of chitosan's amine groups, changes in the conformation of the macromolecule chain (chain repulsion) and the structure of the flocs., while they could be more resistant to application of centrifugal force, as liquids

from C+CENT treatment contained lower Cu and Zn content than CENT liquids (**Table 4**).

>>> Insert Table 4.

All treatments with polymers and centrifugation (P+CENT and C+CENT) produced liquid fractions with significantly lower amount of Cu and Zn, and treatments including PAM (P+CENT and P+B+CENT) produced liquid fractions with P concentration below detection limit. On the other hand, solids chemical characteristics were not strongly affected by PAM addition. When PAM was added to slurry prior centrifuge, the increase in solid fraction N, P, K, Cu and Zn content was only for couple of percent (**Table 3**) when compared to their content in CENT solids, due to already high selectivity of centrifugation for small, nutrient rich particles. As P+CENT and P+SP produced the clearest liquid fractions it was to expect that their liquids will contain very low P, Cu and Zn content (**Table 4**). All pre-treatments significantly lowered K content of solids when compared to its content in solids produced by centrifugation only.

### 3.3. Separation efficiency of all treatments

Separation efficiency with respect to all examined chemical parameters (dry matter and elemental content) (Figure 1, 2 and 3), as reflected by the simple separation index  $Et_{(x)}$  was generally higher for centrifugation treatments when compared to screw press. As it was mentioned,  $Et_{(x)}$  calculation takes into account elemental concentration and mass separation, so higher separation efficiency (based on  $Et_{(x)}$ ) observed for centrifugation when compared to screw press was to be expected. The exceptions are two treatments with PAM (P+SP and P+CENT), having similar efficiency with respect to all determined parameters, regardless of the type of mechanical separation that followed.

This exception may be due to increased mass separation (Table 1) and elemental content in solid fraction of P+SP and P+B+SP treatment, when compared to SP solids.

All separation treatments performed rather poor separation of potassium, and the highest  $Et_{(K)}$  (33%) was achieved with CENT treatment, while lowest (5%) with C+B+CENT treatment.

Biochar addition to raw slurry (B+SP and B+CENT), 16 hours prior to mechanical separation, increased dry matter of input slurry for approx 1%, thus increasing efficiency of both mechanical separators for 2-3% with respect to the mass (**Table 1**).

### 3.3.1. Screw press group

Screw press separation (SP) of raw pig slurry produced small mass (11%) present in the solid fraction (Table 1). Only P+SP; B+SP and P+B+SP treatments increased mass balance to 13; 13 and 15%, respectively, while the rest of the treatments did not affect mass separation. In the SP group, both PAM treatments (P+SP and P+B+SP) significantly increased separation efficiency (**Figure 1, 2 and 3**) and up-concentrated (**Table 5**) dry matter and total N, P, Cu and Zn in solid fraction.

The treatment with chitosan and biochar (C+B+SP) significantly decreased separation efficiency of screw press with respect to dry matter (**Figure 1**) and lowered transfer of dry matter content to solid fraction (**Table 5**). As indicated by  $Et$  and  $Et'$  (Figure 2, 3, and 4, Table 5) chitosan and biochar (alone or in combination) did not significantly change the efficiency of mechanical separators with respect to N, P, Cu and Zn to solids, most probably due to increased amount of small particles introduced by biochar addition and loosen flocs formed when chitosan was applied.

### 3.3.2. Centrifugation group

In contrast to screw press, centrifugation produced large mass (34%) present in the solid fractions, but with high water content. Pre-treatments involving polymers lower mass balance (up to 22%) of centrifuge, while only B+CENT treatment increased mass of solid fraction to 37%.

In the CENT group, addition of PAM alone or in combination with biochar significantly reduced  $Et_{(DM)}$ , as well as up-concentration of dry matter in solids (**Figure 1 and Table 5**), while other treatments did not significantly affect it. All treatments from CENT group showed high separation (**above \_\_\_**) efficiency for total N, but most N was upconcentrated in solid fraction from P+CENT treatment. No pre-treatment had an effect of separation efficiency of  $NH_4-N$ , indicated by very low (and even negative) values of  $Et'_{(NH_4-N)}$ . In general, all treatments from CENT group showed high separation efficiency for P, Cu and Zn, but no effect was statistically significant (**Figure 2 and 3 and Table 5**).

>>> Insert Table 5.

Treatments with PAM alone and in combination with biochar, produced solids in small volume with high P, Cu and Zn content making it feasible for transporting off from the farm and for possible utilization of solid fractions as organic fertilizers.

Liquid fractions produced when PAM is used alone or in combination with biochar, are with low dry matter content and thus more suitable for land application (less clogging of spreader tubes, better spreading through soil profile etc.). Moreover, due to the low P,

Cu and Zn level in liquids produced in PAM treatments there is a potential in lowering their build-up in soils when applying liquid fraction as N fertilizer.

## **Conclusion**

Pre-treatments (P, C and B) showed more effect on screw press than on centrifuge, with respect to all analysed parameters.

Addition of biochar, chitosan and their combination did not improve separation efficiency of SP and CENT, and did not increase elemental content of produced solid fractions.

PAM+SP was effective in removing P, Cu and Zn to solid, and in producing liquid fraction with lowest dry matter and elemental content. In combination with biochar, liquid fraction with increased total N, and low P, Cu and Zn content was produced.

PAM+CENT produced liquid fraction with P content lower than detection limit.

## References

- Dash, M., Chiellini, F., Ottenbrite, R.M., Chiellini E., 2001. Chitosan—A versatile semi-synthetic polymer in biomedical applications. *Progress in Polymer Science* 36, 981–1014.
- Garcia, M.C., Szogi, A.A., Vanotti, M.B., Chastain, J.P., Millner, P.D., 2009. Enhanced solid–liquid separation of dairy manure with natural flocculants. *Bioresource Technology*. 100, 5417–5423.
- Entry, J.A., Sojka, R.E., Watwood, M, Ross, C., 2002. Polyacrylamide preparations for protection of water quality threatened by agricultural runoff contaminants. *Env. Pollution* 120, 191–200.
- Hjorth, M., Christensen, K.V., Christensen M.L., Sommer S.G., 2010. Solid–liquid separation of animal slurry in theory and practice. A review. *Agron. Sustain. Dev.* 30, 153 – 180.
- Hjorth, M., Nielsen, A.M., Nyord, T., Hansen, M.N., Nissen, P., Sommer S.G., 2009. Nutrient value, odour emission and energy production of manure as influenced by anaerobic digestion and separation. *Agronomy for Sustainable Development*. 29, 329-338.
- Hjorth, M., Christensen, M.L., 2008. Evaluation of methods to determine flocculation procedure for manure separation. *Transactions of the Asabe*. 51, 2093-2103.
- Masse, L., Masse, D.I., Beaudette, V., Muir, M., 2005. Size distribution and composition of particles in raw and anaerobically digested swine manure. *Transactions of the Asae*. 48, 1943-1949.
- Sommer, S.G., Husted, S., 1995. A simple model of pH in slurry. *The Journal of Agricultural Science*. 124, 447–453.

## Acknowledgment

Table 1. Treatments IDs and details of separation methods applied

<u>Treatment ID</u>	<u>Biochar</u>	<u>Separation method</u>		<u>Mass separation (%)</u>
		<u>Polymer dosage (ml/0.5L manure)</u>	<u>Mechanical separation</u>	
<b>SP</b>				11
<b>P+SP</b>		175 ml of PAM		13
<b>C+SP</b>		120 ml of Chitosan		10
<b>B+SP</b>	0.5 g		Screw press	13
<b>P+B+SP</b>	0.5 g	150 ml of PAM	(SP group)	15
<b>C+B+SP</b>	0.5 g	120 ml of Chitosan		11
<b>CENT</b>				34
<b>P+CENT</b>		175 ml of PAM		22
<b>C+CENT</b>		120 ml of Chitosan		27
<b>B+CENT</b>	0.5 g		Centrifugation	37
<b>P+B+CENT</b>	0.5 g	150 ml of PAM	(CENT group)	29
<b>C+B+CENT</b>	0.5 g	120 ml of Chitosan		34

*Table 2. General characterisation of raw slurry. The concentrations of all parameters are calculated and presented on dry matter basis.*

Raw slurry	DM %ww	VS %DM	pH	tot N mg/g	NH <sub>4</sub> -N % tot N	Tot P mg/g	Tot K mg/g	Tot Cu µg/g	Tot Zn µg/g
	4.81	69	7.38	68	76	36	52	117	763



Table 3. Characterisation of solid fractions produced by different screw press separation of raw slurry. The concentrations of all parameters are calculated and presented on dry matter basis.

	Treatments	DM	VS	pH	tot N	NH <sub>4</sub> -N	Tot P	Tot K	Tot Cu	Tot Zn
Solid		%ww	%DM		mg/g	% tot N	mg/g	mg/g	µg/g	µg/g
	SP	20 <sub>a</sub> <sup>*</sup>	84 <sub>a</sub>	8.14 <sub>a</sub>	29 <sub>a</sub>	35 <sub>a</sub>	47 <sub>ac</sub>	11 <sub>a</sub>	80 <sub>ab</sub>	591 <sub>ac</sub>
	P+SP	20 <sub>a</sub>	74 <sub>a</sub>	8.06 <sub>a</sub>	43 <sub>bc</sub>	35 <sub>b</sub>	51 <sub>ab</sub>	10 <sub>b</sub>	197 <sub>b</sub>	1542 <sub>a</sub>
	C+SP	21 <sub>a</sub>	81 <sub>b</sub>	8.49 <sub>a</sub>	23 <sub>c</sub>	45 <sub>a</sub>	34 <sub>c</sub>	5 <sub>a</sub>	70 <sub>d</sub>	389 <sub>b</sub>
	B+SP	20 <sub>a</sub>	84 <sub>a</sub>	8.45 <sub>a</sub>	24 <sub>ab</sub>	49 <sub>b</sub>	29 <sub>b</sub>	8 <sub>ac</sub>	59 <sub>b</sub>	341 <sub>a</sub>
	<b>P+B+SP</b>	26 <sub>b</sub>	70 <sub>b</sub>	7.45 <sub>b</sub>	27 <sub>ab</sub>	43 <sub>ab</sub>	32 <sub>b</sub>	9 <sub>ad</sub>	102 <sub>ac</sub>	799 <sub>c</sub>
	C+B+SP	20 <sub>a</sub>	84 <sub>a</sub>	8.24 <sub>a</sub>	24 <sub>ab</sub>	49 <sub>b</sub>	41 <sub>abc</sub>	6 <sub>bc</sub>	71 <sub>b</sub>	394 <sub>a</sub>
Liquid										
	SP	2.8 <sub>a</sub>	60	7.16	106 <sub>a</sub>		18 <sub>a</sub>	70 <sub>ac</sub>	115 <sub>ac</sub>	755 <sub>ac</sub>
	P+SP	1.0 <sub>b</sub>	52	7.33	187 <sub>a</sub>	89	47 <sub>a</sub>	257 <sub>a</sub>	76 <sub>b</sub>	482 <sub>bcd</sub>
	C+SP	2.9 <sub>c</sub>	57	6.42	90 <sub>c</sub>	84	21 <sub>a</sub>	41 <sub>bc</sub>	67 <sub>bc</sub>	403 <sub>ce</sub>
	B+SP	3.9 <sub>d</sub>	67	7.21	82 <sub>a</sub>	83	34 <sub>a</sub>	41 <sub>a</sub>	146 <sub>a</sub>	979 <sub>ac</sub>
	<b>P+B+SP</b>	1.5 <sub>b</sub>	52	7.17	146 <sub>b</sub>	83	11 <sub>a</sub>	155 <sub>c</sub>	30 <sub>b</sub>	161 <sub>d</sub>
	C+B+SP	2.9 <sub>a</sub>	67	6.42	83 <sub>a</sub>	91	33 <sub>a</sub>	42 <sub>a</sub>	131 <sub>ac</sub>	842 <sub>c</sub>

\* Means (n=3) within each parameter (vertical), followed by different letters are significantly different from each other (P<0.05)

Table 4. Characterisation of solid fractions produced by different centrifugation separation of raw slurry. The concentrations of all parameters are calculated and presented on dry matter basis.

	Treatments	DM %ww	VS %DM	pH	tot N mg/g	NH <sub>4</sub> -N % tot N	Tot P mg/g	Tot K mg/g	Tot Cu µg/g	Tot Zn µg/g
Solid	CENT	12.5 <sup>ac*</sup>	67	7.43	39 <sub>a</sub>	57 <sub>a</sub>	50 <sub>a</sub>	19 <sub>a</sub>	117 <sub>a</sub>	960 <sub>a</sub>
	<b>P+CENT</b>	15.2 <sub>bc</sub>	70	7.5	40 <sub>a</sub>	48 <sub>a</sub>	51 <sub>a</sub>	11 <sub>b</sub>	152 <sub>a</sub>	1211 <sub>a</sub>
	C+CENT	13.7 <sub>ad</sub>	76	7.36	37 <sub>a</sub>	41 <sub>a</sub>	30 <sub>a</sub>	7 <sub>b</sub>	139 <sub>a</sub>	936 <sub>a</sub>
	B+CENT	14.1 <sub>bd</sub>	71	7.64	32 <sub>a</sub>	57 <sub>a</sub>	39 <sub>a</sub>	12 <sub>b</sub>	107 <sub>a</sub>	756 <sub>a</sub>
	P+B+CENT	15.9 <sub>e</sub>	71	7.31	33 <sub>a</sub>	41 <sub>a</sub>	42 <sub>a</sub>	12 <sub>b</sub>	146 <sub>a</sub>	796 <sub>a</sub>
	C+B+CENT	12.0 <sub>c</sub>	78	7.08	35 <sub>a</sub>	49 <sub>a</sub>	42 <sub>a</sub>	9 <sub>b</sub>	179 <sub>a</sub>	1270 <sub>a</sub>
Liquid	CENT	1.6 <sub>a</sub>	57 <sub>a</sub>	7.49 <sub>a</sub>	161 <sub>a</sub>	81 <sub>a</sub>	18 <sub>a</sub>	148 <sub>ab</sub>	148 <sub>a</sub>	759 <sub>a</sub>
	<b>P+CENT</b>	0.8 <sub>b</sub>	53	7.43	191 <sub>bc</sub>	96 <sub>a</sub>	nr	268 <sub>b</sub>	15 <sub>b</sub>	71 <sub>b</sub>
	C+CENT	0.9 <sub>b</sub>	39	6.09	196 <sub>b</sub>	102 <sub>a</sub>	41	122 <sub>a</sub>	12 <sub>b</sub>	60 <sub>b</sub>
	B+CENT	1.4 <sub>a</sub>	58	7.36	168 <sub>ac</sub>	79 <sub>a</sub>	11 <sub>ac</sub>	155 <sub>ab</sub>	155 <sub>a</sub>	747 <sub>a</sub>
	P+B+CENT	0.8 <sub>b</sub>	52	7.54	201 <sub>b</sub>	90 <sub>a</sub>	nr	245 <sub>ab</sub>	27 <sub>b</sub>	121 <sub>b</sub>
	C+B+CENT	1.0 <sub>b</sub>	57	6.63	178 <sub>abc</sub>	108 <sub>a</sub>	39 <sub>d</sub>	199 <sub>ab</sub>	28 <sub>b</sub>	172 <sub>b</sub>

\* Means (n=3) within each parameter (vertical), followed by different letters are significantly different from each other (P<0.05)

Table 5. Reduced separation index (for ID explanations see Table 1).

Treatment ID	DM	VS	N	NH <sub>4</sub> -N	P	K	Cu	Zn
SP	0.39 <sub>bc</sub> *	0.03 <sub>a</sub>	0.09 <sub>ab</sub>	-0.02 <sub>a</sub>	0.53 <sub>a</sub>	-0.02 <sub>a</sub>	0.22 <sub>a</sub>	0.27 <sub>a</sub>
P+SP	0.45 <sub>ab</sub>	0.01 <sub>a</sub>	0.23 <sub>b</sub>	0.03 <sub>a</sub>	0.72 <sub>a</sub>	-0.04 <sub>a</sub>	0.87 <sub>b</sub>	1.08 <sub>a</sub>
C+SP	0.36 <sub>bc</sub>	0.02 <sub>a</sub>	0.06 <sub>a</sub>	-0.01 <sub>a</sub>	0.35 <sub>a</sub>	-0.06 <sub>a</sub>	0.18 <sub>a</sub>	0.14 <sub>a</sub>
B+SP	0.35 <sub>bc</sub>	0.03 <sub>a</sub>	0.07 <sub>ab</sub>	-0.01 <sub>a</sub>	0.35 <sub>a</sub>	-0.05 <sub>a</sub>	0.16 <sub>a</sub>	0.13 <sub>a</sub>
B+P+SP	0.59 <sub>a</sub>	0.00 <sub>a</sub>	0.21 <sub>ab</sub>	0.04 <sub>a</sub>	0.70 <sub>a</sub>	0.00 <sub>a</sub>	0.67 <sub>ab</sub>	0.84 <sub>a</sub>
B+C+SP	0.28 <sub>c</sub>	0.03 <sub>a</sub>	0.06 <sub>a</sub>	-0.01 <sub>a</sub>	0.46 <sub>a</sub>	-0.06 <sub>a</sub>	0.18 <sub>a</sub>	0.14 <sub>a</sub>
CENT	0.83 <sub>a</sub>	-0.01 <sub>a</sub>	0.25 <sub>a</sub>	0.06 <sub>ab</sub>	1.35 <sub>a</sub>	-0.02 <sub>a</sub>	0.83 <sub>ab</sub>	1.18 <sub>a</sub>
P+CENT	0.60 <sub>c</sub>	0.00 <sub>a</sub>	0.25 <sub>a</sub>	0.05 <sub>ab</sub>	1.00 <sub>a</sub>	-0.09 <sub>a</sub>	0.88 <sub>ab</sub>	1.15 <sub>a</sub>
C+CENT	0.68 <sub>abc</sub>	0.03 <sub>a</sub>	0.20 <sub>a</sub>	-0.06 <sub>a</sub>	0.50 <sub>a</sub>	-0.22 <sub>a</sub>	0.88 <sub>ab</sub>	0.92 <sub>a</sub>
B+CENT	0.79 <sub>ab</sub>	0.02 <sub>a</sub>	0.21 <sub>a</sub>	0.01 <sub>a</sub>	1.29 <sub>a</sub>	-0.20 <sub>a</sub>	0.99 <sub>ab</sub>	1.12 <sub>a</sub>
B+P+CENT	0.66 <sub>bc</sub>	0.01 <sub>a</sub>	0.15 <sub>a</sub>	-0.05 <sub>a</sub>	1.16 <sub>a</sub>	-0.11 <sub>a</sub>	1.28 <sub>b</sub>	1.01 <sub>a</sub>
B+C+CENT	0.52 <sub>abc</sub>	0.06 <sub>a</sub>	0.15 <sub>a</sub>	-0.08 <sub>b</sub>	1.01 <sub>a</sub>	-0.30 <sub>a</sub>	0.98 <sub>a</sub>	1.12 <sub>a</sub>

\* Means (n=3) within each parameter (vertical) separately for screw press \* of raw slurry and for screw press \*\* of raw co-digestate, followed by different letters are significantly different from each other (P<0.05)

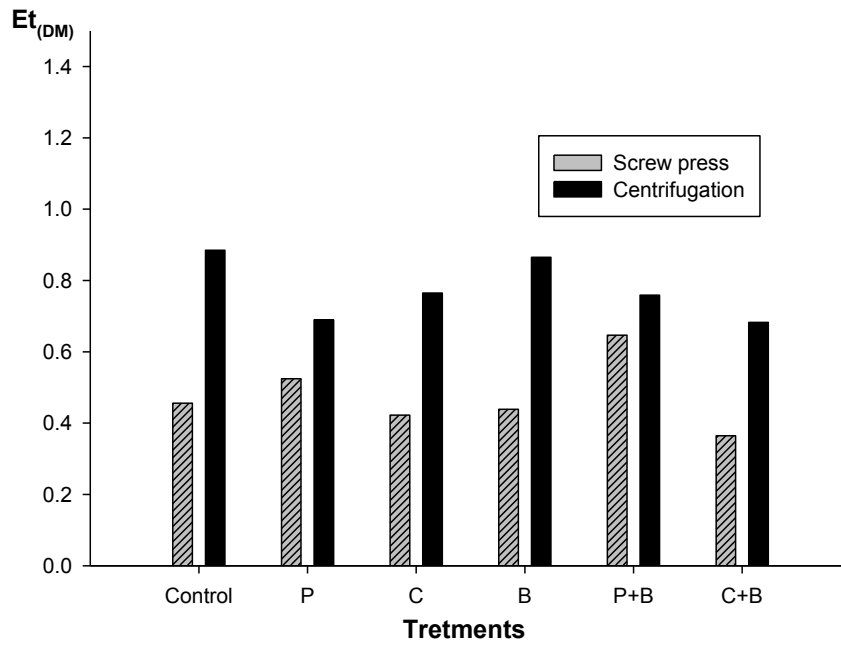


Figure 1. Simple separation index (Et) calculated for dry matter. Means (n=3) within each of bar groups representing one mechanical separation type followed by different letters are significantly different from each other (P<0.05)

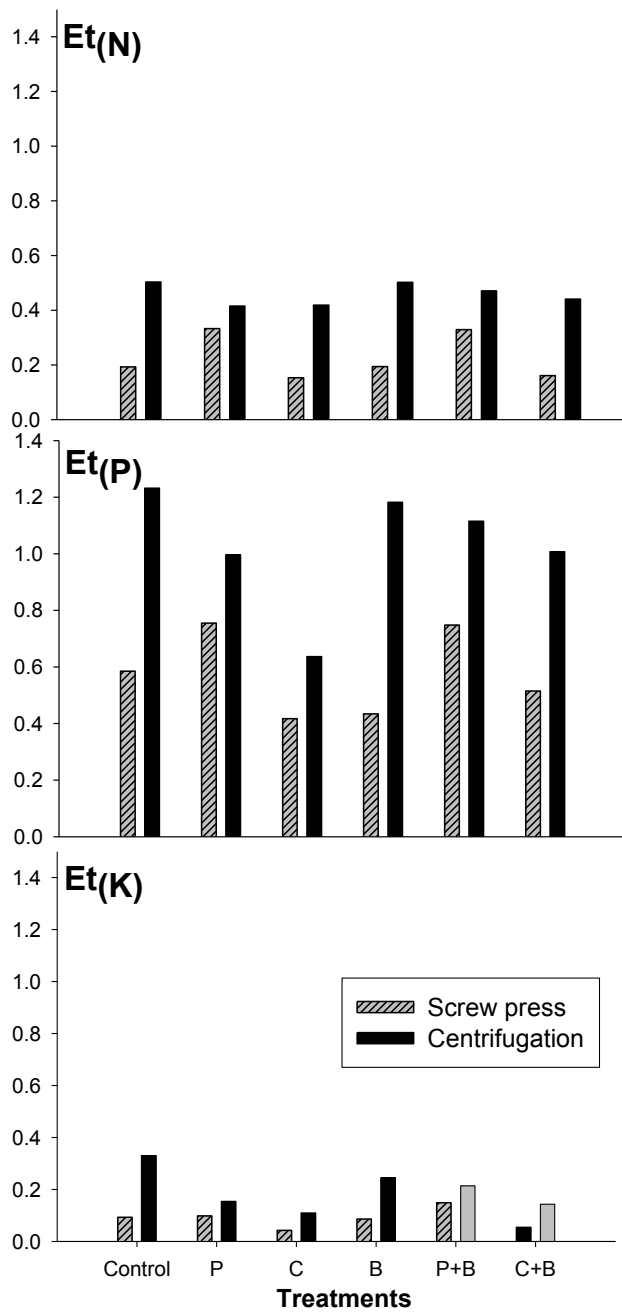


Figure 2. Simple separation index (Et) calculated for total nitrogen phosphorus and potassium. Means (n=3) within each of bar groups representing one mechanical separation type followed by different letters are significantly different from each other (P<0.05)

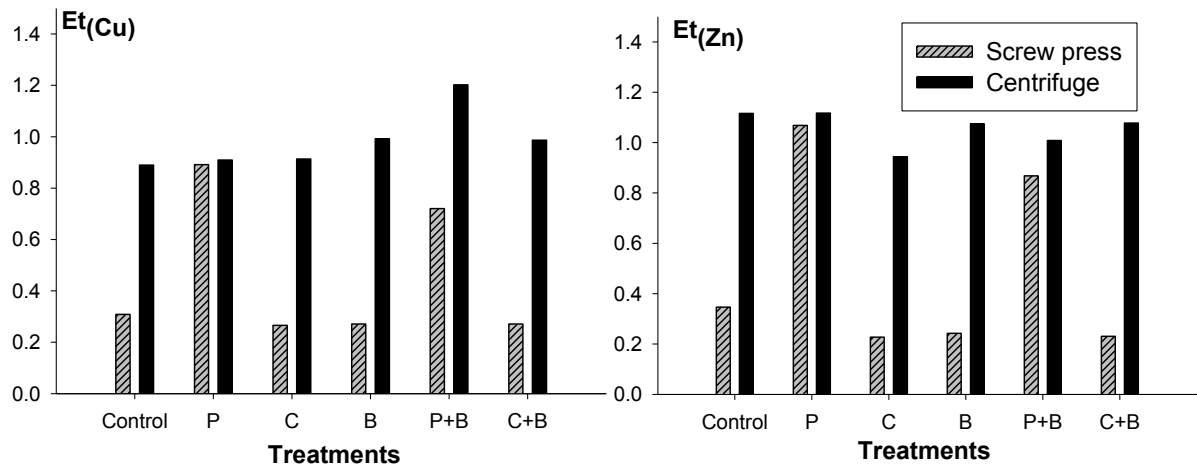


Figure 3. Simple separation index (Et) calculated for total copper and zinc. Means (n=3) within each of bar groups representing one mechanical separation type followed by different letters are significantly different from each other ( $P < 0.05$ )