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THE APPLICATION OF BIODEGRADABLE FLOCCULANTS DERIVED FROM POTATO STARCH FOR NUTRIENT RECOVERY IN PIG MANURE

Juliana Rolf [1,2], Tobias Weide [1,2], Elmar Brügging [1,2], Christof Wetter [1,2]
[1] *Faculty of Energy·Building Services·Environmental Engineering, Münster University of Applied Sciences, Stegerwaldstr. 39, 48565 Steinfurt, Germany*
[2] *Institute network "Resources, Energy and Infrastructure", Münster University of Applied Sciences, Stegerwaldstr. 39, 48565 Steinfurt, Germany*

ABSTRACT*: In the domain of wastewater treatment, flocculation and coagulation are widely utilized. In search of an ecologically-friendly approach, the flocculation and coagulation properties of starch-based flocculants are analyzed herein. The investigation was conducted using flocculants derived from potato starch. The goal was to evaluate the removal of particles and nutrients, such as phosphorus. The trials were undertaken using two different cationic and three different anionic flocculants. Pig manure was treated by means of separation with a fine filter and flocculation. Separation and flocculation using the cationic flocculants resulted in a separation of 79% phosphorus, as well as a reduction in dry matter by 69%. Trials were carried out that included separation and flocculation with cationic and anionic flocculants, which achieved a separation of 86% phosphorus, as well as a dry matter diminution of 75%.*

KEYWORDS*:* Wastewater treatment; starch-based flocculation; pig manure; nutrient recovery; solid–liquid separation

INTRODUCTION

Current discourse on the nutrient situation in Germany and the need for action to be taken against excess buildups has fostered increased agricultural research in this area. The European Environmental Agency notes that 80% of European bodies of water have good or high standards of water quality, but that when such bodies become polluted, it is often due to the excessive use of agricultural fertilizers (European Environment Agency, 2018). For instance, phosphorus (P) contained in runoff from agricultural land can induce eutrophication in bodies of water (Timby et al., 2004). In accordance with the EU Nitrates Directive, in most EU countries, only 170 kg/ha N is permitted to be used (EEC, 1991). Adequate solid–liquid separation prevents nutrients from being washed off of agricultural land, simplifies manure-handling and reduces the cost and environmental impacts of manure transportation by decreasing its overall volume (Hjorth et al., 2009; Jørgensen and Jensen, 2009). Moreover, the nutrient value of the solid phase is increased (Burton, 2007).

Different methods of solid–liquid separation have been evaluated in the literature, and include sedimentation, flocculation and mechanical separation, such as centrifugation, screen separation, and mechanical pressing techniques (Møller, 2000; Westerman and Bicudo, 2000; Burton, 2007; Jørgensen and Jensen, 2009; Vanotti et al., 2009; Hjorth et al., 2011; and Peters

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et al., 2011). Solid–liquid separation techniques can yield liquids for on-farm usage that contain high contents of potassium (K) and mineral nitrogen (N), and solids with high organic solid and phosphorus contents (P) (Zhang and Westerman, 1997; Vanotti and Hunt, 1999; Møller et al., 2007; and Jørgensen and Jensen, 2009). Fertilizer prices have also recently increased, and so there is interest in developing technologies to recover and recycle nutrients from manure (Vanotti et al., 2020).

Hjorth et al. (2011) pointed out that the efficiency of separation depends on the chemical and physical composition of the substrate, the desired end products, and the technology or combination thereof used. Investigations into the different techniques for mechanical liquid–solid separation have revealed differences in separation efficiency and costs, with the decanter centrifuge inducing the highest values for the removal of dry matter and phosphorus but also entailing the highest costs (Møller, 2000). Additionally, the efficiency of the separations process is dependent on the particle size, as most nutrients are suspended in particles that are small in size (Zhang and Westerman, 1997; Jørgensen and Jensen, 2009; and Peters et al., 2011). Vanotti et al. (2002) demonstrated that 80.4% of the total suspended solids (TSS) and 93% of the P fractions in flushed pig manure, which can potentially be removed by separation, were contained in particles less than 0.3 mm in size (Vanotti et al., 2002). As mechanical solid–liquid efficiencies are insufficient, further dry matter (DM) and P removal can be accomplished by means of flocculation.

With respect to coagulation and flocculation, many studies have been conducted using metal oxides such as aluminum sulfate ($Al_2(SO_4)_3$) or ferric chloride ($FeCl_3$) for coagulation, as well as synthetic polymers based on polyacrylamides (PAMs) for flocculation. PAMs are long-chained and soluble organic polymers (Vanotti et al., 2020). The long polymer molecules destabilize charged particles by adsorbing into and building bridges between them (Gregory, 1989; Vanotti et al., 2020).

The use of these coagulants and flocculants has raised health concerns (Salehizadeh et al., 2017) and their lack of biodegradability, environmental ones (Sharma et al., 2006). Therefore, some research has been undertaken using natural flocculants such as chitosan (Ravi Kumar, 2000; Garcia et al., 2009; Fragoso et al., 2015; and Wang et al., 2019), sodium alginate, tannin (Grenda et al., 2020), starch (Khalil and Aly, 2001; Pal et al., 2004), and cellulose (Grenda et al., 2017). Bio-based flocculants have the advantages of being nontoxic, biodegradable, thermo-stable (to some extent) and shear-stable (Yang et al., 2016). Many studies have been conducted using wastewater, resulting in a lack of data on the flocculation of pig manure. A review of the production, purification modification, characterization, and applications of these was performed by Salehizadeh et al. (2018).

Starch is a linear, biodegradable, inexpensive polysaccharide polymer obtained from plants (Salehizadeh et al., 2017). Depending on the source, its amylose and amylopectin content varies from 25%–95% (Salehizadeh et al., 2017). Research on the preparation of starch-based flocculants or grafted starch has been undertaken (Khalil and Aly, 2001; Wei et al., 2008; Kolya et al., 2017; Liu et al., 2017; and Maćczak et al., 2020), as well as on the flocculation characteristics of silica or kaolin suspension (Pal et al., 2004; Wei et al., 2008; and You et al., 2009), the treatment of wastewater (Pal et al., 2004; Anthony and Sims, 2013; and Kolya et al., 2017), and the sedimentation of harbor sludge (Shirzad-Semsar et al., 2007).

The goal of this study is to evaluate the two-step treatment of pig manure using a starch-based flocculant. This treatment includes a solid–liquid separation through a fine filter, followed by flocculation, whereby the solid–liquid separation is performed by means of sedimentation. The main objectives were therefore: (1) to determine the effect on nutrient removal of N, P, K, and other chemical properties; and (2) to investigate the flocculation efficiency of starch-based flocculants as a solid–liquid separation technique for pig manure.

METHODOLOGY

Experimental procedure

The experimental procedure was divided into two phases (see Fig. 1).

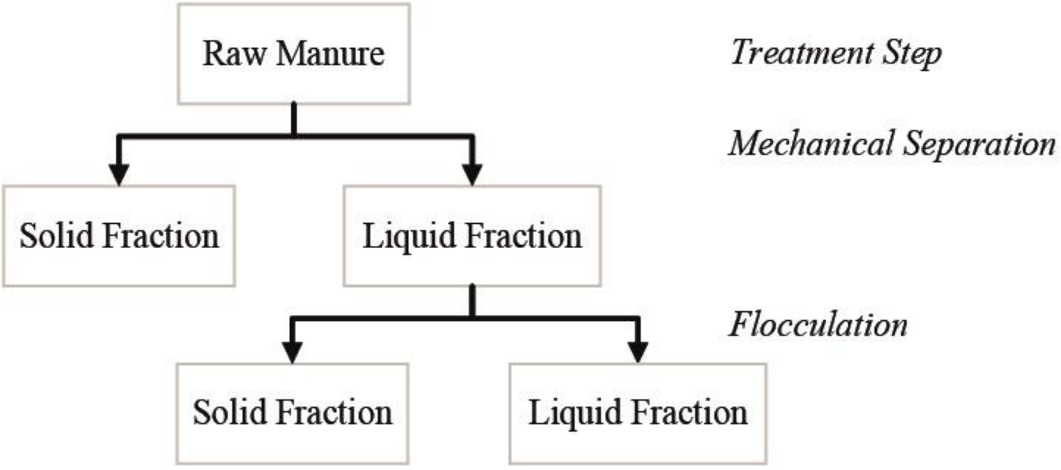

Figure 1. Experimental procedure.

In the first step, the manure was separated by means of a fine filter with a mesh size of 100 µm. During this treatment, solids were removed. Additionally, the reduced solid content meant that less flocculant was required, thus reducing the cost of the treatment. In the second step, flocculation was conducted using starch-based flocculants. Two different types of flocculation were performed. In one, monoflocculation, only the cationic flocculant was added. In the other, dual flocculation, the cationic flocculant was added first, followed by the anionic one.

Materials

Pig manure: The pig manure used for this research was obtained from a farm in Greffen, Germany. The pigs were fed nitrogen- and phosphorus-reduced feed and phytase was included. Immediately prior to the test, the sample was stirred. The properties of the manure used are displayed in Table 1. The manure was stored for three weeks at 10°C –15°C prior to treatment. This was done in order to prevent possible chemical and physical alterations of the sample. *Starch flocculants:* The flocculants used were derived from potato starch. The flocculants, Emfloc KCG 750 (K1) and Emfloc KC 750 (K2), are cationic and were provided with a dilution ratio of 1:5. Emfloc KA 3 (A1), Emfloc KA 10 (A2), and F 11034 (A3) are anionic flocculants, and were prepared as 0.5% solutions. The flocculants were obtained from Emsland-Stärke GmbH (Germany).

Experimental setup

Fine filter

The first step of the treatment entailed separating the liquid and solid phase through a fine filter with a mesh size of 100 µm. Fig. 2 shows the filter's design.

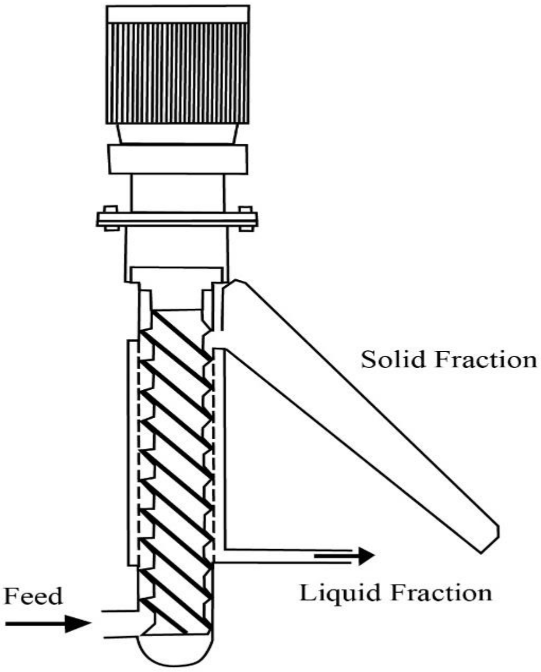

Figure 2. **Experimental design of the fine filter.**

The sample (V = 1,000 l) was pumped into a receiver tank, which was equipped with level gauges. When a suitable level was reached, the manure was pumped into a spiral from below. The spiral was located in a cylinder equipped with a screen whose mesh size was 100 µm. The liquid passed through this screen and was collected in a separate tank. The solids were then pushed upwards and entered another tank.

Flocculation

Monoflocculation: The flocculation test was conducted in a Jar Tester. The sample was placed beakers (V = 0.5 l) and the stirring speed set to 100 rpm. After adding the flocculant, the stirring speed was held for 10 s and then reduced to 30 rpm for 120 s. The beakers were then left to stand without stirring for 15 min in order to allow the flakes to settle. Different dosages (1, 2, 3, 4, and 5 $ml \cdot l^{-1}$) were tested, and a reference sample was utilized for visual comparison. Following flocculation, a 100 µm sieve was used to separate the solid fraction from the supernatant.

Dual flocculation: This test was also conducted using a Jar Tester and, as in the case of the monoflocculation, until the cationic flocculant had been added. The K1 flocculant was added at a dosage of 2 ml·l^{-1}. The stirring speed was maintained for 10 s and then reduced to 30 rpm for 120 s. The anionic flocculant was then added at four different dosages (4, 8, 12, and 16 g·l^{-1}) and the sample was stirred for a further 120 s. The beakers were then left to stand without being stirred for 15 min to allow the flakes to settle. A sample that had only been flocculated with K1 was utilized for visual comparison.

Analytical methods

The DM content was determined in accordance with ordinance DIN EN 12880.

The nutrient values of N, NH_4-N, P, and K were measured in accordance with ordinances: VDLUFA Bd. II 1, 111.5.1; DIN 38406-5 (E 5–1/E 5-2), 1983–10; DIN 38414-7; and DIN EN ISO 11885.

The COD of the pig manure was analyzed by means of cuvette tests (LCK014, Hach Lange, Germany). The samples were prepared in accordance with the standards for the LCK014 cuvette tests, and the COD content was then measured using a photometer (DR 2800, Hach Lange, Germany).

The pH value was determined by an electrode in accordance with DIN 38404-5.

The amount of solids and liquid following separation, as well as in the initial sample, was then balanced.

Calculations

The separation efficiency was calculated as shown in Equation 1, below. In order to take the divided streams into account, the reduced separation efficiency was calculated as shown in Equation 2 (Burton, 2007).

Equation 1. Formula for simple separation efficiency index (Burton, 2007):

$$\frac{S}{F} \cdot \frac{X_S}{X_F} = E_t$$

Symbol meanings:

S: Solid Stream

F: Feed Stream

X_S: Concentration of X in Solid Stream

X_F: Concentration of X in Feed Stream

E_t: Simple Separation Efficiency Index

Equation 2. Formula for reduced separation efficiency index (Burton, 2007):

$$\frac{S}{F} \cdot \left(\frac{X_S}{X_F} - 1\right) = E_t'$$

Symbol meanings:

S: Solid Stream

F: Feed Stream

X_S: Concentration of X in Solid Stream

X_F: Concentration of X in Feed Stream

$E_t^{'}$: Reduced Separation Efficiency Index

RESULTS AND DISKUSSSION

The properties of manure affect its handling (Landry et al., 2004). The manure samples collected for this research and their physical and chemical properties are comparable to those used in other studies (Federolf et al., 2016). The composition of manure can vary due to factors such as feeding, animal husbandry, storage, species, and water supply (Møller, 2000; Zhang and Westerman, 1997). The solids contained in manure can be classified as fiber (> 5 mm), coarse solids (1–5 mm), fine solids (20 µm–1 mm), colloidal particles (1–20 µm), and dissolved solids (< 1 µm) (Burton, 2007).

Fine Filter Separation

The results of the separation using the fine filter are shown in Table 1. These results indicate that the DM content of the raw manure was 2.5 times higher compared to that in the liquid phase following mechanical separation. It follows that the DM content in the solid phase was 3.6 times higher than in the raw manure, confirming that solids were removed by the treatment. The comparison of the total N and P revealed that the values were 1.3 and 1.4 times higher, respectively, for the raw manure. In the case of K and ammonium nitrogen (NH_4-N), no corresponding removal from the raw manure could be detected. These results can be compared to a study performed by Møller et al. (2000), in which a screen size of 0.5–3 mm was employed. This led to the raw manure having a 1.3–5.6 times higher DM content, a 1.1–2.4 higher TP content, and a 1.0–1.45 higher TN content than the liquid fraction (Møller et al., 2002). The nutrient distribution lay within the intervals of those presented in this study.

Table 1. Results of the fine filter separation (100 µm)

Parameter	Raw Manure	Liquid Fraction	Solid Fraction	Unit
DM – Dry Matter	5.9	2.4	21.5	wt%
pH	8.05	8.02	-	-
TN – Total Nitrogen	4.21	3.32	7.83	$g \cdot kg^{-1}$
NH_4-N – Ammonium Nitrogen	2.08	2.07	2.08	$g \cdot kg^{-1}$
P_2O_5 – Phosphorus	0.39	0.27	0.64	$g \cdot kg^{-1}$
K – Potassium	2.01	2.01	2.02	$g \cdot kg^{-1}$
COD – Chemical Oxygen Demand	18.7	12.0	-	$g \cdot l^{-1}$

To determine the removal efficiency, the percentage of nutrients removed from the solid fraction was calculated. The results of this are shown in Table 2. After treatment, the manure was divided into 9.9% solid and 90.1% liquid fractions. K (9.92%) and NH_4-N (9.94%) were correspondingly removed into the solid fraction. 20.6% of P was removed, as was 20.5% of the total nitrogen (TN). In the case of N, approximately 70% was found to be dissolved and the rest was bound to particles (Christensen et al., 2009). The P and TN content removed were bound to particles > 100 µm. By comparison, using a decanter centrifuge, Møller et al. achieved a removal of 60.5% for TS, 62.3% for TP, and 29.3% for TN (Møller et al., 2002). This result confirms other research findings stating that mechanical separation, except for when a decanter centrifuge is used, is inefficient (Masse et al., 2005). Møller et al. (2002) concluded that a normal separator removes particles > 1 mm in size from the manure, whereas a decanter centrifuge removes particles that are > 0.02 mm (Møller et al., 2002).

In outlining the efficiency of solid–liquid separation technologies, it is important to take the particle size affecting nutrient distribution into account. Masse et al. (2005) determined that most standard solid–liquid separation technologies, with the exception of those utilizing decanter centrifuges, are unable to efficiently separate nutrients. The study stated that 64% of dry matter has a particle size < 10 µm, 20% of P is soluble, 50% of P is associated with particles between 0.45 and 10 µm in size, and 30% of P is associated with particles > 10 µm. Furthermore, 95% of the organic N is associated with particles in the size range between 0.45 and 10 µm (Masse et al., 2005).

Table 2. Removal into the solid fraction, simple separation efficiency index, and reduced separation efficiency index

Method	Removal into the Solid Fraction (%)					U/Q (%)	Reduced Separation Efficiency Index			Simple Separation Efficiency Index	Source
	TS	P	N	NH_4-N	K		TS	N	P	DM	
Fine filter	49.6	20.6	20.5	9.9	9.9	9.9	0.33	0.03	0.06	0.42	Own Results
Tilted plane screen						30	0.41	0.08	0.17		(Møller, 2000)
Pressing screw (1)						5.0	0.26	0.02	0.12		
Pressing screw (2)						7.3	0.25	-0.01	0.11		
Two-stage separator						24	0.55	0.04	0.14		
Belt press separator						17.5	0.5	0.1	0.2		
Screw Press	27.3	7.1	6.6			4.2					(Møller et al., 2002)
Centrifugation	60.5	62.3	29.3			13.1					
Sedimentation							0.68	0.1	0.77	0.60	(Peters et al., 2011)
Centrifugation							0.62	0.13	0.7	0.27	
Pressurized filtration							0.38	0.03	0.15	0.14	

DM: Dry matter; P: Phosphorus; N: Nitrogen; K: Potassium; U/Q: solid fraction/manure.

Meyer et al. (2007) observed that particles smaller than 125 µm contain 86% of N, 85% of P, and 99.8% of K, and account for 46% of TS. The use of a common mechanical separator with a 2 mm screen enabled the removal of 19% of TS, 5% of N, 5% of P, and 0.07% of K. By employing a double screen separator (between 1 and 2 mm), 31% of TS, 7% of N, 7% of P, and 0.09% of K were removed (Meyer et al., 2007).

Both the simple and reduced separation indexes were calculated to evaluate the effectiveness of the separation process (Møller, 2000). The simple separation index was reliable for calculating TS separation (Møller, 2000). For nutrient distribution, the reduced separation index was used to permit better indication of the separation (Burton, 2007). For instance, if the feed F results, after treatment, in a 10% solid content and the nutrient X is also separated to 10%, this is not an effective separation of nutrient X. In this case, the reduced separation index is equal 0. In this study, the reduced separation index for NH_4-N and K was 0. Therefore, no effective separation was achieved for NH_4-N and K. The reduced separation indexes for TS, N, and P were 0.33, 0.03, and 0.06. The results for TS and N can be compared to the results for a pressing screw (Møller, 2000) and pressurized filtration (Peters et al., 2011). The reduced separation index for P was lower than the other results from other research and the mechanical separation was successful in removing DM content. This meant that less flocculant was required for the second treatment step.

Flocculation

The second treatment step was carried out by flocculating the separated manure (liquid fraction). In this study, the efficiency of starch-based flocculants, in contrast to the more widely studied metal oxides and synthetic polymers based on polyacrylamide, will be determined. The data presented in Table 3, below, exhibit the removal efficiency of TS, TN, NH_4-N, P, and K as a function of the dosage of the respective flocculant. The first flocculants used were both cationically-charged and based on potato starch. First, a cationic flocculant was used, as the organic particles in manure often have a negative charge and are therefore best suited for flocculation (Garcia et al., 2007). The difference between the two flocculants lies in their modification, with K2 forming the pre-stage of K1.

K2 resulted in flocculation after a dosage of only 4 $ml\cdot l^{-1}$, whereas K1 featured flocculation at a dose of 1 $ml\cdot l^{-1}$. K1 reached the highest removal efficiency for P (73%), with a dosage of 2 $ml\cdot l^{-1}$. The removal efficiencies for TS (0 %) and TN (13 %) were slightly higher with a dosage of 1 $ml\cdot l^{-1}$, which can be attributed to the higher U/Q ratio. Therefore, K1 with a dosage of 2 $ml\cdot l^{-1}$ was used for the further experiments.

Table 3. Removal rates of nutrients from separated manure via monoflocculation

Flocculant	Dosage (ml·l^{-1})	U/Q (%)	Removal Efficiency (%)				
			TS	P	N	NH_4-N	K
K1	1	7.6	41	70	24	10	8
	2	3.8	40	73	13	5	4
	3	3.8	41	71	14	7	4
	4	4.2	39	71	13	6	5
	5	3.9	36	69	11	5	4
K2	1	-	-	-	-	-	-
	2	-	-	-	-	-	-
	3	-	-	-	-	-	-
	4	17.8	12	68	9	4	2
	5	4.7	37	73	14	7	5

DM: Dry matter; P: Phosphorus; N: Nitrogen; K: Potassium; U/Q: solid fraction/manure.

The data presented in Table 4 show the removal efficiency of separated manure following dual flocculation. Dual flocculation was found to increase the removal efficiency of TS and P, with the highest results being achieved with A3. The highest removal efficiency of TS and P was 50% and 87%, respectively. NH_4-N and K remained in the liquid fraction during flocculation.

The results of this work correspond to those of previous studies. The tests reveal that aniotically charged flocculants, when used alone, do not lead to flocculation. This result corresponds to various studies that have dealt with cationically- and aniotically charged PAM flocculants (Garcia et al., 2007).

The use of metal oxides and PAM flocculants applied to pig manure has been widely investigated. By comparison, when polyacrylamide-based, cationic flocculants were used, removal levels of 76.1% and 78% TS, respectively, have been achieved (González-Fernández et al., 2008; Rico et al., 2012). González-Fernández et al. (2008) attained removal rates of 28% for Total Kjeldahl Nitrogen (TKN), 38% for soluble P, and no changes for ammonium when 200 ppm PAM was used. In turn, Rico et al. (2012) achieved removal rates of 59.1% for TKN and 87.4% for TP in the solid phase (29.1%) by using cationic PAM (Rico et al., 2012). Katers and Pelegrin (2012), achieved removal rates of 69% for TS, 87% for TP, 89% for dissolved P, 44% for TKN, and 23% for TK (Katers and Pelegrin, 2012). In the case of precipitation with metal oxides, Ndegwa et al. (2001) found that the use of 1,500 mg/l of aluminum sulfate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$) increased phosphorus removal by sedimentation from 42% to 78% and 86%, respectively (Ndegwa et al., 2001). DeBusk et al. (2008) employed $FeCl_3$ and $AlCl_3$ to remove solids and phosphorus, attaining a TS removal of 52% for $FeCl_3$ and 62% for $AlCl_3$. In the case of P, removal rates of 82% for $FeCl_3$ and 94% for $AlCl_3$ were achieved. The combined use of $FeCl_3$ and PAM flocculants affected a P removal of 80% (DeBusk et al., 2008).

Table 4. Removal rates of nutrients from the separated manure via dual flocculation

Flocculant 1	Dosage (ml·l^{-1})	Flocculant 2	Dosage (g·l^{-1})	U/Q (%)	Removal Efficiency (%)				
					TS	P	N	NH_4-N	K
K1	2	A1	4	3.8	44	77	15	6	4
	2		8	3.7	41	82	13	5	4
	2		12	3.9	40	80	14	6	4
	2		16	4.4	42	83	13	6	5
K1	2	A2	4	3.6	36	75	11	5	4
	2		8	4.3	44	83	17	7	4
	2		12	4.1	44	78	16	6	4
	2		16	5.3	43	81	19	8	7
K1	2	A3	4	3.4	41	84	14	6	4
	2		8	4.4	50	87	17	7	5
	2		12	4.3	51	86	17	6	4
	2		16	4.4	49	85	18	7	5

TS: Total Solids; P: Phosphorus; N: Nitrogen; K: Potassium; U/Q: solid fraction/manure.

As a biodegradable flocculant alternative, chitosan can also be used for flocculation. Garcia et al. (2009) reported removal rates of 95.3% for TSS, 92.3% for VSS, 86% for TKN, and 61.9% for TP using a 540 mg/l polymer and 1 mm screen for solid–liquid separation (Garcia et al., 2009) to flocculate pig manure. Fragoso et al. (2015) compared the application of chitosan to the commonly-utilized coagulant, $Al_2(SO_4)_3$. In that study, the use of $Al_2(SO_4)_3$ enabled removal rates of 49% for TS and 94% for P. The use of chitosan saw removal rates of 38% for TS and 70% for P. The authors surmised that chitosan is an interesting alternative to conventional agents, as it fosters a higher fraction of biodegradable liquid (Fragoso et al., 2015).

Water Quality of the Treated Manure

In order to present comparable results, the overall nutrient removal level was determined. Table 5 shows the nutrient contents following the treatments. Separation and monoflocculation produced removal rates of 69% for TS, 31% for TN, 14% for NH_4-N, 79% for P, and 14% for K in the solid fraction, which amounted to 13% from the original phase. With the help of further flocculation from the anionic flocculant, the removal rates increased to 75% for TS, 34% for TN, and 86% for P. In addition, COD was reduced by 55% (monoflocculation) and 82% (dual flocculation), respectively. In the case of K and NH_4-N, no differences were observed. These results show similar removal rates compared to more commonly-used flocculants.

Table 5. Nutrient contents of the treated manure

Parameter	Raw Manure	Post-Treatment Liquid Fraction			Unit
		Separation	MF	DF	
DM – Dry Matter	5.9	2.4	0.7	0.6	wt%
pH	8.05	8.02	7.83	7.67	-
TN – Total Nitrogen	4.21	3.32	2.2	2.05	$g \cdot kg^{-1}$
NH_4-N – Ammonium Nitrogen	2.08	2.07	1.84	1.82	$g \cdot kg^{-1}$
P_2O_5 – Phosphorus	0.39	0.27	0.057	0.052	$g \cdot kg^{-1}$
K - Potassium	2.01	2.01	2.07	1.98	$g \cdot kg^{-1}$
COD – Chemical Oxygen Demand	18.7	12.0	5.8	2.2	$g \cdot l^{-1}$

MF: Monoflocculation; DF: Dual flocculation

CONCLUSIONS

In this study, mechanical separation was used to remove many solids and a small amount of P and N. Subsequent flocculation increased the removal of these elements. A comparison with the literature demonstrates that starch-based flocculants constitute an interesting alternative to flocculants that are in current common used. Further test series should be conducted to improve the efficiency, and thereby the applications, of available resources.

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