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Optimizing flocculation of digestate to increase circularity in manure treatment

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ABSTRACT

The flocculation of (co-)digested cattle and pig manure has rarely been investigated, leading to a rather intuitive use of flocculants in manure treatment processes, resulting in overdosing and increasing costs. Here, we investigate the effect of molecular weight, charge density and branching of reference and commercially available flocculants by establishing the optimal flocculant dosage and the corresponding maximum organic matter removal. Higher molecular weight flocculants show increased turbidity removal as result of their long chains corresponding to a higher amount adsorption sites. Results presented show that polymers with an increased cationic charge density give moderate and unstable flocculation due to the low amounts of non-charged parts essential for the hydrophobic interactions and hydrogen bonding. Further, the results show that a linear high molecular weight flocculant with a nonionic or a low anionic charge density is the most effective as it reached the highest organic matter removal at a low dosage.

1. Introduction

Manure surplus is a well-known challenge for the agricultural sector due to more strict legislation on the utilization of manure in Europe and particularly in the Netherlands (Hou, 2016). The Netherlands aims to lower the agricultural nitrogen emission by farm housing, nutrition and manure processing by 10 kt/yr. in 2030 to protect the so-called Nature 2000 areas through an “integrated approach to nitrogen” plan (Programma Aanpak Stikstof, PAS) (de Heer et al., 2017). As stated in these regulations, manure processing is becoming increasingly important. Most of all, the pig industry has difficulties to meet the legislation as they often do not own land for crops and thus lack the convenience of direct manure application for fertilization. This increases the need for manure processing. Therefore, this sector aims for the valorization of pig manure into separate nutrient-rich fractions for precision fertilization while limiting the emission of nitrogen in the form of ammonia and nitrogen oxide and (climate-driven) CO₂ to meet the imminent legislation (Aguirre-Villegas et al., 2017; Hou, 2016; Velthof, 2015). The valorization treatment, see Fig. 1 for a schematic overview, often involves co-digestion of manure, various mechanical and membrane separation technologies and polishing steps to produce biogas, dischargeable water and nutrient-rich fractions (Aguirre-Villegas et al.,

2017; Hoeksma and De Buissonjé, 2015; Velthof, 2015).

A typical pig-manure treatment process starts with the digestion of manure in combination with energetic co-products like food and agricultural waste and can be enhanced by the addition of glycerol to increase the production of biogas (Astals et al., 2012). The digestion leaves a residual stream known as digestate. This stream contains a large amount of water and nutrients like phosphorus, nitrogen and potassium useful for crop growth. Hence, the digestate is separated into a phosphor-rich solid fraction and a liquid stream with techniques like a sieve belt press and/or dissolved air flotation. Further separation is applied to the liquid streams by extraction of water using reverse osmosis (RO) installations to produce a mineral concentrate and dischargeable water, which simultaneously lowers the transportation costs of the nutrient-rich mineral stream. The solid fraction rich in phosphorus and the mineral concentrate containing nitrogen and potassium are used as basic fertilizers in fertilization where the nutrient ratio is adjusted for the specific crop.

The mechanical solid-liquid separation step is often improved by addition of polymeric flocculants to improve the dewatering of the manure slurry and to increase the organic matter removal efficiency. This consequently increases the recovery of the phosphorus-rich solid fraction (Aguirre-Villegas et al., 2017; Luo et al., 2018). The liquid

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fraction is subsequently cleaned from the suspended particles, after which a high-quality liquid stream containing nitrogen and potassium species is obtained that is further treated by reverse osmosis (Aguirre-Villegas et al., 2017). However, so far particularly this dosage of the polymeric flocculant in the digestate solid-liquid separation step is not well studied. Dosing is done rather intuitively in the current treatment facilities. When the flocculation does not perform well, more is added. As removal of added flocculant is not possible this intuitive dosage often results in an overdosage of the polymeric flocculant. This unnecessarily increases the costs and the amount of chemicals used and has even an opposite effect on the intended solid-liquid separation.

Moreover, the excess polymer accumulates in the treatment system due to the recycle loops present in the installation and inevitably ends up in the RO system. The presence of polymer in the RO system results in fouling of the membranes and increases the operational costs (Luo et al., 2018). Hence, the importance to design an accessible method to find a suitable flocculant and determine its optimal dosage to increase the efficiency in the solid-liquid separation.

In this study, we investigate the effect of the molecular weight (MW), charge density (CD) and branching of polymeric flocculants on the flocculation performance of co-digested animal manure digestate. As polyacrylamide (PAM) type of polymers are frequently used as flocculant in manure and digestate treatment because of its settling performance and low production costs (Heviánková et al., 2018; Nasser and James, 2006), it is also selected for this study. PAM polymers with a similar chemical structure but different charged or noncharged functional groups are used to investigate the influence of MW and CD. In addition, linear and branched chemical structures are compared.

1.1. Background

To increase the efficiency of solid-liquid separations often flocculation with polymers or coagulation is used. The characteristics of the polymers, mainly MW and CD, influence the flocculation performance in terms of floc formation which leads to a certain turbidity removal from the liquid stream and corresponding flocculant dosage. Flocculants are known for their high Mw ranging from 10^4 to 10^8 g/mol (SNF Floerger, 2014). Based on charge, flocculants are divided in two subclasses 1) Anionic and non-ionic flocculants containing often a negative carboxylic group and 2) Cationic flocculants containing a positive ammonium functionality (SNF Floerger, 2014). Table 1 indicates the classification of the flocculants in terms of structure, MW and CD.

The formation of flocs is based on charge neutralization, patching and/or polymer bridging as shown in Fig. 2. The neutralization of charged particles is generally referred to as coagulation and often achieved by the addition of metal salts like iron (III) sulphate/chloride or aluminum chloride. The highly charged metal ions interfere with the stable colloidal particles according to the DLVO theory (Atkins and de Paula, 2014; Duan and Gregory, 2003; Hyrycz et al., 2022). This theory states that the double layer of counter ions, measured as the zeta potential, around the colloid determines whether the particles are attracted to or repelled from each other. The presence of metal ions

Table 1

Classification of flocculants based on structure, MW and CD (Hyrycz et al., 2022; Lee et al., 2014).

Characteristic	Category	
Structure	Linear	
	Branched	
Molecular weight [g/mol]	Low	$< 3 \cdot 10^6$
	Medium	$3-6 \cdot 10^6$
	Standard	$6-10 \cdot 10^6$
	High	$10-15 \cdot 10^6$
	Very high	$> 15 \cdot 10^6$
Charge class	Non-ionic	
	Anionic	
	cationic	
Charge density [%]	Low	< 10
	Medium	$10-40$
	High	$40-80$
	Very high	> 80

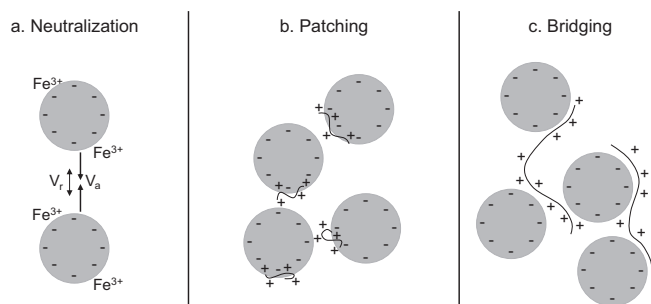


Fig. 2. Various flocculation mechanisms, a) neutralization (coagulation), b) patching c) and bridging are shown schematically for negatively charged particles (representing organic matter) and positively charged flocculants.

destabilizes this double layer which leads to lower repulsion forces (V_r) compared to the attractive forces (V_a) between the particles. As a result of the decrease in repulsion, the distribution of the forces shifts, lowering the energy barrier for the particles to overcome for interaction with one another and therefore increasing the flocculation potential. Hence, small flocs are formed which typically form a good foundation for additional flocculation to produce larger flocs (Dayarathne et al., 2021; Duan and Gregory, 2003; Hjorth et al., 2008).

Another way to increase the attraction between the particles is by the addition and subsequent attachment of relatively short high CD polymers. These polymer chains adsorb patchwise onto the negatively charged particles to form areas of opposite charge (Gregory and Barany, 2011; Hyrycz et al., 2022). This gives the required attractive interaction between the particles to induce agglomeration which occurs when areas of opposite charge align and coincide. The positive and negative sites on two or more different particles induce a large attraction force to form strong bonds between the particles. This subsequently results in floc formation (Gregory and Barany, 2011; Hjorth et al., 2008; Nasser and

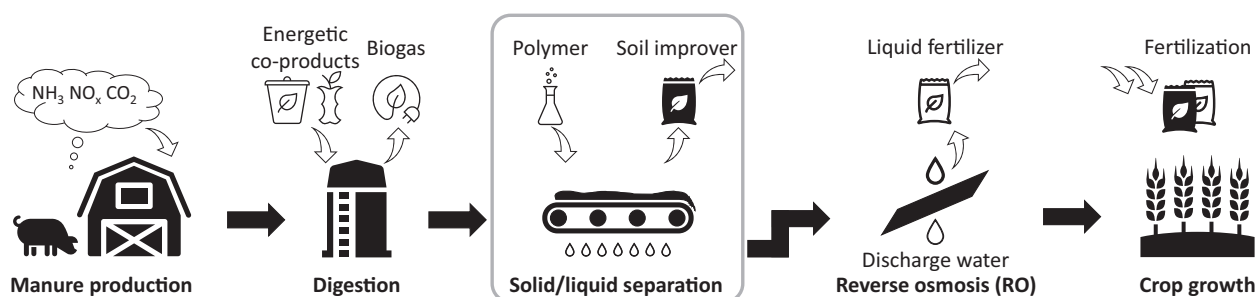


Fig. 1. A schematic overview of general liquid pig manure treatment for fertilizer production.

James, 2006).

High MW polymers on the other hand can form bridges between the particles by adsorption of one polymer chain onto several particles simultaneously. This results in strong flocs capable of withstanding the agitation often used in manure treatment (SNF Floerger, 2014). The long chains contain tails and substantial amounts of adsorption sites that are able to form loops on the surfaces. When such loops and tails extend further than the electrical double layer around the particle, multiple particles can be actively adsorbed on one long polymer chain. Increasing the MW of the polymer increases the number of adsorption sites and flocculation opportunities and thus usually results in higher efficiencies (Dayarathne et al., 2021; Nasser and James, 2006; Petzold et al., 2003). However, this bridging flocculation depends on the particle surface coverage and thus on the polymer concentration (SNF Floerger, 2014).

The attractive interactions required for the formation of aggregates are defined by the physical chemical surface interactions. The interactions are based on the charge, dipole moments and the free energy of particles and polymers (Atkins and de Paula, 2014). These driving forces will result in electrostatic or hydrophobic interactions or hydrogen bond formation facilitating the aggregate development (Atkins and de Paula, 2014; Gregory and Barany, 2011).

The relatively strong hydrophobic interactions can occur between hydrophobic segments of polymers onto hydrophobic parts of particles (Gregory and Barany, 2011). This interaction is based on the entropy and the free energy of water surrounding the components in the system, these are the driving forces for the interaction to occur. The hydrophobic interactions result in an aggregate of non-polar particles in polar solvents (Atkins and de Paula, 2014). However, the organic matter particles in digestate are often more hydrophilic components like humic acids and proteins that rather form hydrogen bonds in the polar solvent (Dayarathne et al., 2021).

Hydrogen bonds are a result of attractive interactions between a partially positively charged hydrogen, attached to an electronegative element, and an electronegative element from another component. These elements are typically oxygen and nitrogen. However, anionically charged species might also contribute to the hydrogen bonding. This interaction is considered a contact like interaction which dominates other intermolecular interactions like van der Waals interactions (Atkins and de Paula, 2014). These hydrogen bonds are often observed for bridging flocculation as the organic matter particles contain the electronegative elements and the long bridging polymers generally contain amide bonds suitable for this hydrogen bond formation (Gregory and Barany, 2011; Hyrycz et al., 2022).

Looking further into the bridging flocculation, high MW polymers with a positive charge are often used to aggregate negatively charged organic matter typically present in digestate (Christensen et al., 2009; Heviánková et al., 2018). Polymers with a high CD easily attach to the negative sites of the particles, forming strong bridges and flocs. However, the amount of charge added with the polymers should be aligned with the charge present on the particles in solution to prevent charge overcompensation (Gregory and Barany, 2011; Hoogeveen et al., 1996; Shin et al., 2002). Such overcompensation occurs in case e.g. the polymer contains significantly more charges compared to the bound particles, resulting in an excess of positive charges attached to the particles. This excess charge from the polymers induces repulsive forces between the partially bridged particles, preventing the formation of additional bridges for the formation of large flocs as presented in Fig. 3 (Hoogeveen et al., 1996). Therefore, for low to non-charged particles the addition of low or non-charged polymers is favorable to induce floc formation by bridging through several loops and tails based on the physical chemical interactions and especially hydrogen bonding rather than on strong charge interactions (Gregory and Barany, 2011).

Next to the MW and CD, the structure of a polymeric flocculant plays a significant role in the flocculation efficiency as well. Flocculants are polymers with a linear or branched chemical structure. Large amounts of branches result in steric hindrance during floc formation, that lowers the

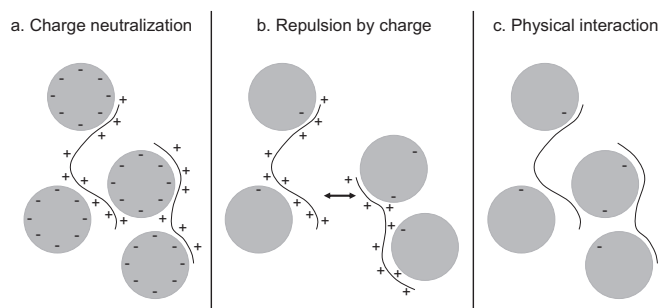


Fig. 3. A schematic drawing of the flocculation mechanisms for a) highly charged particles and polymers, b) charge repulsion present for low charged particles combined with highly charged polymers c) and uncharged polymer for low/non-charged particles.

efficiency (Dayarathne et al., 2021; Hyrycz et al., 2022). This steric hindrance between the polymers reduces the ability of the polymer adsorption sites to reach the particle surface, preventing attachment. Consequently, a higher dosage is required to reach the same organic matter removal as for linear polymers (Hjorth et al., 2008; Hyrycz et al., 2022). Nevertheless, branching can be favorable in case the polymer side chains have certain functionalities like a specific charge or increased hydrophobicity that changes the flocculation interactions (Hyrycz et al., 2022). The charged functional side chain is used to bind particles through charge neutralization to form strong flocs. Flocculation polymers can also be modified by adding hydrophobic groups for hydrophobic interactions and to improve dewatering of the flocs (Hyrycz et al., 2022). In this work, the focus is on the investigation on the interplay of MW, CD and linear or branched structures of various commercial flocculants.

2. Materials and methods

2.1. Chemicals

Nonionic polyacrylamide (nPAM) with MWs of $2.5 \cdot 10^4$, $1.5 \cdot 10^5$ and $2.5 \cdot 10^6$ g/mol (Sigma Aldrich®, Germany), with a medium to standard MW (Table 1), were used to investigate the effect of MW. Commercially available cationic PAM (cPAM) with an MW of 10^6 g/mol and CD values of +0.18, +0.43 and + 1.57 meq/g (SNF Floerger, France), corresponding to the low to medium CD range for flocculants, were investigated for the effect of cationic charge. Additionally, synthetic polymers 5CL, 12AB and 8AL (MW $\cdot 10^6$ g/mol, Cationic/Anionic, Linear/Branched) were used for the performance evaluation of commercial flocculants typically applied in manure treatment processes. The bulk composition of the flocculants consists of polyacrylamide. However, due to the use of commercial products, the exact composition of the monomers of the flocculants is unknown. The MW of the commercial flocculants was measured using a 1 M NaCl (Akzonobel, Denmark), citric acid (VWR, USA) and sodium phosphate dibasic (Sigma Aldrich®, Germany) buffer of pH 7. The CD of the polymers was determined using N/400 potassium polyvinyl sulfate (PVSU) and polydiallyldimethyl ammonium chloride (PDAD) solutions (Fujifilm Wako Chemicals, USA) with pH adjustment by addition of 1 M hydrochloric acid (Sigma Aldrich®, Germany) and 1 M sodium hydroxide (Sigma Aldrich®, Germany).

2.2. Digestate preparation

Real co-digestate was collected after the hygienisation step from the pig manure treatment processing plant Duurzaam Landleven Bernheze, Heeswijk-Dinther (The Netherlands). Before transport the co-digestate was filtered through a screen with a 4 mm mesh to remove coarse impurities. The average characteristics and ion composition of the digestate from three different days over the range of 5 months are shown in

Table 2

The average characteristics and ion composition of the co-digested manure.

Characteristic	Ion composition	
DM feed	85 g/kg digestate	
Turbidity digestate	16,500 NTU	Sodium 2.30 g/L
Turbidity liquid fraction	6000 NTU	Ammonium 5.47 g/L
Particle size	100 to 2000 nm	Potassium 5.17 g/L
pH	8.5	Chloride 3.40 g/L
Conductivity	35 mS/cm	Phosphate 1.86 g/L
Zeta potential	-32 mV	Sulphate 0.07/L
Surface charge density	-32 meq/kg digestate	

Table 2. The amount of dry matter (DM) in the digestate was measured by weight after water evaporation for 24 h at 105 °C under a nitrogen flow. The turbidity values of the digestate before treatment and of the liquid fraction were measured, after a dilution of 200 times using water, with a turbidity meter (Eutech TN-100, Thermo scientific, USA). The particle size of the digestate was measured with an Antonpaar Litesizer 500 with an angle of 175°, 12 to 30 runs at 20 °C repeated three times. This resulted in particle size distribution up to 2000 nm for sample 2 and 3 as visualized in Fig. S1 in the supplementary material. The particle size distribution of sample 1 deviates a little since it also contains some bigger particles. The Litesizer 500 was also used for the zeta potential measurements of 100 runs repeated three times at 20 °C using the Smoluchowski method to calculate the zeta potential of the liquid fractions after flocculation and resulted in a value of -32 mV for the manure digestate. Zeta potential measurements were also performed after titration of the digestate with polycation solution ($2.5 \cdot 10^{-4}$ mol/mL PDAD solution with 1 eq/mol charge) to find the surface charge density of the digestate (Christensen et al., 2009; Hjorth and Jørgensen, 2011). For the pH and conductivity, a pH meter (pocket pro+ multi 2, Hach, France) and a conductivity meter (GMH 3400, Greisinger, Germany) were used. The ion composition was measured with a Thermo Fisher Integrion-Aquion ion chromatography system (Thermo Fisher, Breda, The Netherlands) using an CS12A cation column with a methyl sulfonic acid eluent and an AS12A anion column with a sodium carbonate/sodium bicarbonate eluent.

2.3. Flocculation procedure

A jar tester flocculator system (Velp scientifica, Italy) was used with six simultaneously stirring paddles. Beakers with 250 g of homogenous digestate at room temperature were used for the flocculation. In the first step the digestate was rapidly pre-mixed at 300 rpm for 1 min after which flocculant in mg/g dry matter (DM) was added. The solution was mixed for another minute. The flocculation proceeded with 5 min of slow stirring at 50 rpm for floc formation. The solid-liquid separation was simulated by a centrifuge (Sigma 2-16 KL, Salm en Kipp, the Netherlands) running 45 mL of the flocculation mixtures at 12,000 rpm for 10 min. Next 10 mL of supernatant was removed to represent the liquid fraction. The turbidity of the liquid fraction was measured after a dilution of 200 times with demineralized water (Lenhart et al., 2010). Water was used as the effect of salt concentration from a dilution with a salt solution (neutral pH) on the turbidity was within the error of the measurement, as was tested with NaCl solutions with a conductivity range of 0.005 to 31.5 mS/cm, of which the highest is comparable to the conductivity of the original digestate.

2.4. Polymer structure characterization

The general structure of the commercial flocculants 5CL, 12AB and 8AL were compared to nPAM (MW 10^6 g/mol) through ATR FT-IR (Varian, the Netherlands) and solid-solid NMR (MW of the polymers was too high for liquid NMR). A Varian-cary 3100 FT-IR spectrometer with a golden gate attenuated total reflectance (ATR) was used to produce spectra (resolution 4 cm^{-1} and 50 scans) of the synthetic polymers

at room temperature. The solid-state MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) spectra were obtained using an 11.7 T AVANCE NEO Bruker NMR spectrometer operating at 500 MHz, and 125 MHz for ^1H and ^{13}C respectively. ^1H and ^{13}C MAS NMR experiments were performed using a Bruker triple channel 4 mm MAS probe head spinning at a rate of 8 kHz. A Hahn echo pulse sequence $p_1\text{-}\tau_1\text{-}p_2\text{-}\tau_2\text{-}aq$ with a 90° pulse $p_1 = 5 \mu\text{s}$ and a 180° pulse $p_2 = 10 \mu\text{s}$ was used for ^1H NMR spectra with an interscan delay of 5 s. ^{13}C spectra were measured using a CPMAS pulse sequence with a 2 ms contact time and 5 s interscan delay. NMR shift calibrations of ^1H and ^{13}C were done using tetramethyl silane and solid adamantane, respectively.

2.5. Molecular weight and charge density calculations

The MW was calculated with the Mark-Houwink equation and constants for PAM which involved the intrinsic viscosity as shown in Eq. (1) (SNF Floerger, 2014). The reduced viscosity of several polymer solutions with various concentration in a buffer of pH 7 was determined with a 532 10 Ubbelohde viscometer (SI analytics, Germany) in a water bath of 30 °C. The intrinsic viscosity ($\eta_{intrinsic}$) was extrapolated as the intersection with the y-axis after plotting the reduced viscosity [dL/g] against the polymer concentration [g/dL].

$$\eta_{intrinsic} = 3.73 \cdot 10^{-4} \cdot MW^{0.66} \quad (1)$$

Direct and indirect colloidal titration were used to establish the CD [meq/g] in acidic and alkaline conditions according to Eq. (2). The cationic and anionic titration required the addition of PVSK and PDAD solution with a concentration of $2.5 \cdot 10^{-3}$ M ($M_{titrant}$) and molar equivalent of 1 eq/mol ($Eq_{titrant}$). The amount of PVSK or PDAD in terms of volume in liters ($V_{titrant}$) required for the color change of toluidine from blue to purple violet was determined. The results were used to calculate the equivalent charge per $0.5 \cdot 10^{-3}$ g of polymer ($m_{polymer}$) (Kam and Gregory, 2001).

$$CD = \frac{V_{titrant} \cdot M_{titrant} \cdot Eq_{titrant}}{m_{polymer}} \quad (2)$$

3. Results and discussion

3.1. The effect of molecular weight and cationic charge density

The effect of MW on the flocculation performance is investigated using several nPAM polymers with different MWs (respectively 10^4 , 10^5 and 10^6 g/mol) as flocculants and measuring the turbidity over a range of polymer dosages (Fig. 4).

Fig. 4a shows that initially the turbidity of the supernatant decreases with increasing nPAM dosage. This proves that a higher polymer dosage results in an increased amount of sedimented aggregated particles during floc formation resulting in a lower turbidity (Hjorth et al., 2008; Nasser and James, 2006). However, after a certain dosage point, referred to as the optimal dosage point (ODP), no additional turbidity removal and thus particle attachments, occurs as indicated by the plateau value. At this point, steric stabilization occurs as a result of the high polymer concentration (Hyrycz et al., 2022). This high concentration of polymer adsorbs onto the particles which gives hindrance for bridging formation and thus reaches a maximum removal. That is in agreement with previous findings with bentonite (Gregory and Barany, 2011) and kaolinite (Nasser and James, 2006) particles. Moreover, the addition of high polymer dosages above the ODP results in an excess of polymer that is unbound to the particles which can even slightly increase the turbidity again. Such overdosages will lower the manure treatment performance in the long term due buildup of polymer in the process (Gregory and Barany, 2011). Dosages just below the ODP are thus preferred giving fractional surface covering of flocculant (Gregory and Barany, 2011).

Fig. 4a shows that the plateau region for high MW polymers is

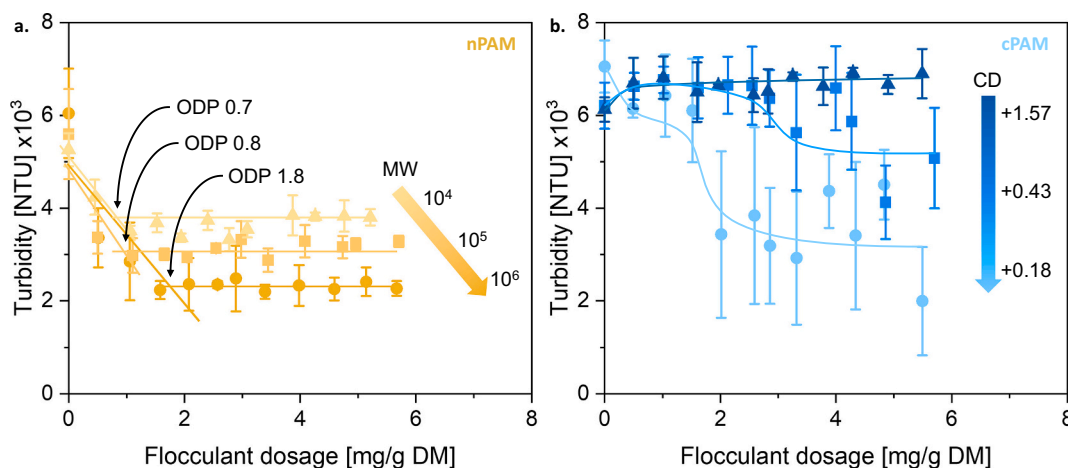


Fig. 4. The turbidity [NTU] of the remaining liquid fraction after flocculant treatment over a range of flocculant dosages [mg/g DM] for a) PAM with an MW of respectively 10^4 , 10^5 and 10^6 g/mol and b) cationic PAM with an MW of 10^6 g/mol and CDs of +0.18, +0.41 and +1.57 meq/g. Lines are provided to guide the eye.

reached at lower turbidity values. This lower turbidity correlates to increased organic matter removal and thus higher flocculation efficiency. This efficiency corresponds to the amount of aggregates that is formed during flocculation as the removal of aggregates in solid-liquid separation is more efficient compared to particles (Hjorth et al., 2008). The formation of these aggregates is for nPAM based on the amount of bridges that is formed between the particles and polymers (Gregory and Barany, 2011). This amount is higher for long chain high MW polymers as these contain a larger amount of amide groups that can adsorb onto the particles through hydrogen bonding (Biggs et al., 2000; Gregory and Barany, 2011; Nasser and James, 2006).

Alongside the MW of the polymers, also the CD of the flocculant plays a significant role in the flocculation of negatively charged organic matter. This flocculation occurs when electrostatic interactions are made when the particles contain negative charges or dipole moments (partial charges) and the polymers contain positive charges. The interaction is based on the coulombic potential energy of interaction between the particle and polymer. The potential energy between a charge and dipole moment reaches zero much faster with increasing distance between the particle and polymer compared to the interaction energy between two charges (Atkins and de Paula, 2014). Therefore the interaction chance for charged particles to form an ionic interaction is much higher compared to partially charged particles forming a van der Waals interaction, which would be the case for patching flocculation (SNF Floerger, 2014).

To understand the flocculation of digestate in more detail, the effect of the amount of cationic charge is investigated by using cPAM with CD values of respectively +0.18, +0.43 and +1.57 meq/g and an MW of respectively 10^6 g/mol (best performing polymer from Fig. 4a). The turbidity of the remaining liquid fraction against the flocculant dosage for cPAM with various CD values is shown in Fig. 4b. The results demonstrate that cationically charged PAMs are not able to reach the same flocculation efficiencies as neutral nPAM for the flocculation of digestate to enhance solid-liquid separation. The graph shows some flocculation for the lower CD values while no floc formation is observed for the polymer with a high CD value of +1.57 meq/L. The flocculation with low CD polymers reaches the plateau region at a dosage comparable to nPAM. However, in comparison, this polymer removes less organic matter and gives unstable flocculation behavior as shown by significant deviations over the whole dosage range. The charge compensation from the cationically charged polymers would be up to 3 % based on the surface charge density of the digestate and polymers (Hjorth and Jørgensen, 2011). However, no organic matter removal is observed at this charge compensation of 3 % whereas at 0.3 % charge compensation a significant drop of turbidity was measured. This

indicates that electrostatic interactions are of minor importance compared to hydrogen bonding and hydrophobic interactions at low flocculant dosages. The removal of turbidity at low cationic CD suggest that the organic matter removed had a low amount of negative charges compared to the high surface charge density of -32 meq/kg of the digestate. In contradiction, as reported in literature, typically a lower surface charge density of around -4 meq/kg manure is found, where the use of cationically charged polymers results in significant organic matter removal indicating the removal of negative charges (Christensen et al., 2009; Hjorth et al., 2008; Hjorth and Jørgensen, 2011). For co-digested manure, it was found that flocculants with a low cationic charge are more effective compared to high cationically charged polymers, showing that the removed organic matter from digestate contains low amounts of negatively charged particles (Heviánková et al., 2018). This further indicates the importance of hydrogen bonding and hydrophobic interactions for the flocculation of digestate. In contradiction, the study from Sievers et al., shows successful flocculation experiments of digested manure with high cationically charged polymers, nevertheless at high optimal dosage values of 150 mg/g DM. However, in their study, the digested manure was diluted with tap water before flocculation whereas we used undiluted manure, being more efficient and in line with reality as added water gives additional costs as it has to be removed and cleaned again before it can be discharged (Sievers et al., 1994).

In this research, more insight was gained with zeta potential measurements which is often used in research concerning model solutions containing e.g. kaolin where the negative kaolin particles are removed with positively charged polymer resulting in increasing zeta potential values with increasing flocculant dosages (Nasser and James, 2006). The zeta potentials of the liquid fractions after flocculation with the cationically charged PAMs showed no significant change over the dosage range as for example for the low cationically charged polymer no addition of cPAM resulted in a zeta potential of -40 mV and dosages of 2.6 (approximately the ODP) and 5.2 mg/g DM resulted in zeta potential values of -40.9 and -42.1 mV. Also the use of high charge density cPAM resulted in a similar zeta potential at the highest dosage of -41.8 mV as the amount of charge compensated would not result in significant zeta potential change. However, as a change in turbidity was observed for the low CD flocculant, the zeta potential measurements confirmed that bridging flocculation based on hydrophobic interactions and hydrogen bonding is dominant and electrostatic interactions are of minor importance in this dosage range. The low CD flocculant, the polymer chain has sufficient non-charged parts for these interactions. Increasing the CD resulted in less change in turbidity as more charge groups would result in less polymer chain suitable for non-electrostatic interactions. As a result, the influence of the high concentration of ions

present in the digestate (Table 2) on the flocculation interaction is limited. Typically the ions influence electrostatic interaction whereas as the bridging flocculation mechanism based on the hydrophobic interactions and hydrogen bonding in the digestate is insensitive to the ionic strength of the solution (Huang and Lapitsky, 2011).

3.2. Efficiency of commercial flocculants

3.2.1. Characterization of commercial flocculants

Typically, commercial flocculants are PAM based polymers, nPAM as used in this study, is thus as a reference material to assess commercial flocculants 5CL, 12AB and 8AL typically used for manure treatment processes (Heviánková et al., 2018; Nasser and James, 2006). First, the characteristics of the commercial flocculants were determined before investigating their flocculation performance. The functional groups and structure of the polymer combined with the MW and CD provide important information on the flocculation performance (Nasser and James, 2006).

The functional groups of the commercial polymers are assigned through ATR FT-IR spectra (see supplementary material Fig. S2). The FT-IR shows that all bonds from the functional groups of nPAM are also present in the spectra of the commercial flocculants. The peaks found in the spectra are assigned to the carbon backbone and the amide group of nPAM (Arinaitwe and Pawlik, 2009; Chiem et al., 2006; Kulicke et al., 1982). The peak at 1100 cm^{-1} , presenting the C—O acyl bond, is more intense in the 5CL spectrum compared to the spectrum of nPAM. The higher intensity suggests the presences of charged groups close to this bond as typically present in amine-based charged flocculants (Lin et al., 2017; Sun et al., 2013).

The solid-state NMR (see supplementary material Fig. S3a and b) shows that the polymer base of all commercial flocculants consists of PAM as the peaks corresponding to the protons and carbons of PAM are found for all flocculants. The additional information from the NMR spectra suggests the presence of charged groups and branching, which can influence the flocculation performance of the polymer. For 5CL an additional peak is found in the ^{13}C spectra at 162 ppm, as shown by the blue dotted line, that represents the presence of a charged group changing the chemical shift of the amide group (Garbow et al., 1989). The ^{13}C NMR spectrum for 8AL shows a small additional peak at 53 ppm, presented by the red dotted line, that shows the presence of a methoxy group indicating that small amounts of electron negative groups is present (Garbow et al., 1989; Neto et al., 1995). The ^1H NMR spectrum of 12AB shows an additional peak in the downfield at 0.1 ppm, as shown by the green dotted line, that indicates the presence of CH_3 at a low chemical shift as a result of alkane branching (Beauchamp, 2016).

The flocculation performance of the polymers is largely devoted to the MW and CD of the commercial flocculants (Dayarathne et al., 2021). The molecular weight of these synthetic polymers, given in Table 3, show a significant difference between the polymers ranging from $4.9 \cdot 10^6$ to $12 \cdot 10^6$ g/mol which are standard values for bridging flocculation (Hyrycz et al., 2022).

These measurements indicate that 5CL contains a low cationic charge whereas very low anionic charge densities for the high molecular weight flocculants 12AB and 8AL compared to nPAM. Literature indicates that high MW polymers with a low anionic CD stretch because of repulsion within the polymer coil. The extension of the polymer increases the formation of loops and leads to higher flocculation efficiencies

Table 3

Experimentally determined characteristics for nPAM (reference), 5CL, 12AB and 8AL.

Flocculant	nPAM	5CL	12AB	8AL
Molecular weight [$\cdot 10^6$ g/mol]	2.5	4.9	12	8.1
Charge density [meq/g]	0	+0.09	-0.02	-0.03
Structure	Linear	Linear	Branched	Linear

(Dayarathne et al., 2021; Nasser and James, 2006).

3.2.2. Flocculation performance

Next, the flocculation behavior of the commercial polymers is investigated and compared to that of nPAM (Fig. 5). All flocculants show the same removal trend where the turbidity lowers with increasing flocculant dosage until a plateau is reached, similar to the performance results of nPAM. Again, the minimum turbidity value is established from the plateau region which correlates to the maximum organic matter removal. The start of the plateau region is the corresponds to the optimal dosage point (ODP). This value can be quantified from the intersection of the stable part of the linear declining slope with the asymptotic line, as presented by the dashed lines drawn in Fig. 5.

Fig. 5 shows that a minimum turbidity of approximately 1200 NTU is reached for the commercially available polymers while a value of only 2200 NTU is obtained for reference polymer nPAM. This confirms that the high MW of all commercial polymers results in lower turbidity values and thus increased organic matter removal. However, the various commercially available flocculants do show different ODP values due to their characteristics influencing the efficiency of the bridging flocculation. These ODP values are significantly lower than those found in literature for digestate (15.8 mg/g DM) and manure (10 mg/g DM) (Heviánková et al., 2018; Hjorth et al., 2008). However, in that case, the initial amount of DM in the digestate and manure was approximately 33 and 56 g/kg and their flocculation procedures were different than the methods used in our study, involving a filter press and gravitational drainage. This makes it thus difficult to directly compare their results with the ones found in our study where we used a feed with a DM of 84 g/kg and a procedure using a centrifuge (Heviánková et al., 2018; Hjorth et al., 2008).

The reference nPAM required an optimal dosage of 2.3 mg/g DM, slightly higher than the ODP value found in the MW investigation as a result of the difference between the digestate batches. 5CL has the highest ODP value (4.2 mg/g DM) due to its low cationic CD and lower MW compared to the other flocculants. The branched high MW flocculant 12AB reaches the minimum turbidity at an ODP value of 1.9 mg/g DM, which is lower compared to the reference nPAM due to its higher MW. Moreover, Synhtofloc required a much lower dosage (0.8 mg/g DM) leading to a high flocculation efficiency as a result of its high MW and linear chemical structure.

The performance of the commercial flocculants also shows a different behavior in terms of flocculation stability. Based on the CD results for cPAM, it was expected that more repulsion would occur for the low cationically charged 5CL as schematically shown in Fig. 3b. Though, only a larger deviation (in terms of larger error bars) is found up to the plateau region, most likely induced by some repulsion before stable flocculation is achieved at the high ODP value. Moreover, 5CL shows a plateau with a small deviation while 12AB gives varying flocculation performances over the whole dosage range. This is explained by the branching of 12AB interfering with the hydrophobic interactions and hydrogen bonding resulting in the polymer adsorption on the particles. This steric hindrance lowers the overall performance of the high MW polymer in terms of stability (Hjorth et al., 2008; Hyrycz et al., 2022). The high MW and very low anionic charge of 8AL results in stable and efficient flocculation, as a low dosage is enough to reach the minimum turbidity. Literature confirms that the flocculation performance for linear polymers with a high MW is high due the large amount of adsorption sites and thus increased bridging capacity (Dayarathne et al., 2021; Gregory and Barany, 2011). In addition, following the studies of Dayarathne and Nasser and James that state that the small anionic charge of 8AL can result in repulsion within the polymer, leading to stretching of the long chain depending on the ion composition of the solution, we hypothesize that a low ion concentration potentially leads to more repulsion between the charges in the polymer chain and thus stretching which would be favorable for the bridging flocculation as shown in Fig. 2c (Dayarathne et al., 2021; Nasser and James, 2006). This

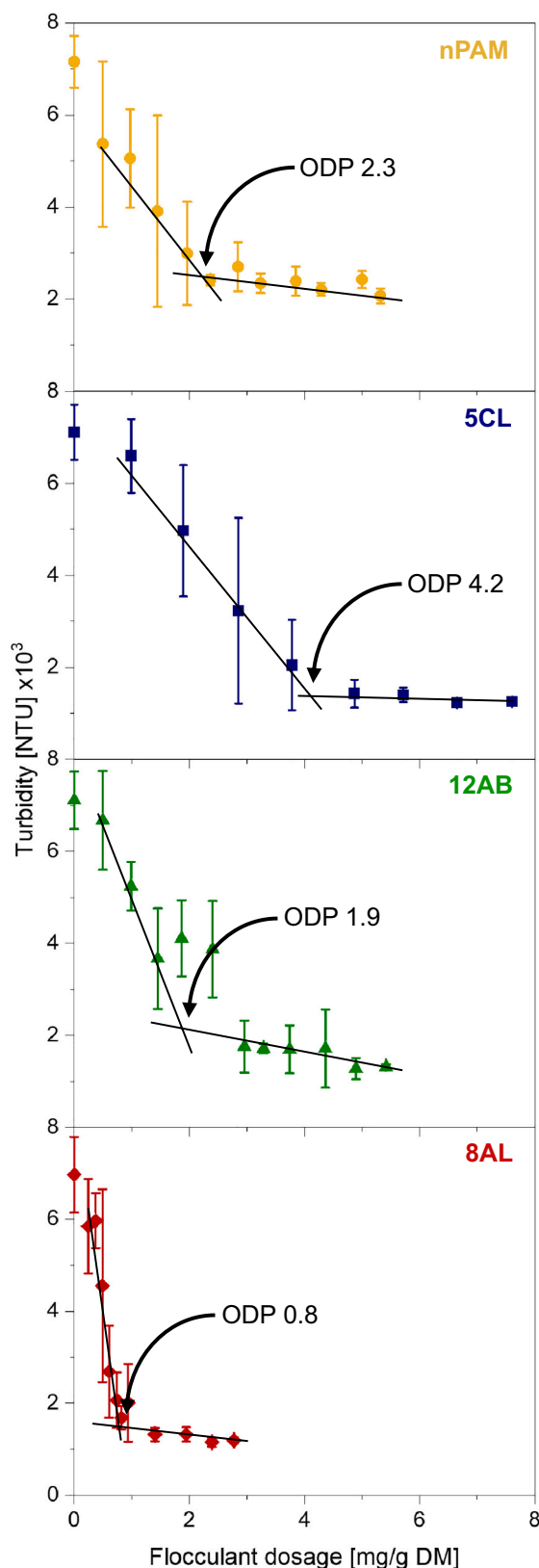


Fig. 5. The liquid fraction turbidity [NTU] against the flocculant dosage [mg/g DM] of nPAM and commercially available flocculants 5CL, 12AB and 8AL.

further increases the amount of adsorption sites and therefore improves the efficiency. The overall results show that a high MW flocculant increases the organic matter removal wherein using a low CD anionic flocculant further increases turbidity removal even at a lower dosage.

4. Conclusion

Various flocculants were investigated to determine the effect of polymer characteristics on the flocculation of animal manure digestate. Turbidity determinations provide insight in the flocculant efficiency and usage in organic matter removal. Cationic high CD flocculants provide moderate and unstable floc formation resulting in lower turbidity removal as the majority of the flocculation interactions are hydrophobic interactions and hydrogen bonding. The best turbidity removal was obtained with linear high MW low CD anionic flocculants. This flocculant reached the lowest turbidity values at small flocculant dosages lowering use of chemicals and costs.

CRediT authorship contribution statement

Marrit van der Wal: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Zandrie Borneman:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition. **Kitty Nijmeijer:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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