Effect of flocculation pre-treatments on membrane nutrient recovery of digested chicken slurry: Mitigating suspended solids and retaining nutrients

Hongzhen Luo[ae], Tao Lyu[d], Atif Muhmood[a], Yong Xue[a], Haotian Wu[a], Eric Meers[e], Renjie Dong[a], Shubiao Wu[abc]*

[a]*College of Engineering, China Agricultural University, Beijing 100083, P. R. China*

[b]*Aarhus Institute of Advanced Studies, Aarhus University, Høegh-Guldbergs Gade 6B, DK-8000 Aarhus C, Denmark*

[c]*Department of Bioscience, Aarhus University, Aarhus 8000C, Denmark*

[d]*School of Animal Rural & Environmental Sciences, Nottingham Trent University, Nottinghamshire NG25 0QF, UK*

[e]*Department of Green Chemistry & Technology, Coupure Links 653, 9000 Gent, Ghent University, Belgium*

**Corresponding author. Tel.: +86-10-62737852; Fax: +86-10-62737885*

E-mail address: wushubiao@gmail.com

Abstract

Use of membrane filtration is attracting increasing attention for nutrient recovery from anaerobically digested slurry. However, the challenge is to reduce membrane fouling by effective solids mitigation, while maintaining valuable nutrients. In this study, the effects of several flocculation pre-treatments using polyaluminium chloride, iron chloride, and flocculant aid at various dosages were investigated. The results showed significant improvement in membrane flux from 0.8 to 27.6 mL/m^2/s due to solid migration (up to 75% removal). Significant loss of PO_4^{3-}-P (99%) and humic acids (40–80 %) was observed. However, the content of NH_4^+-N and indoleacetic acids was largely maintained in the treated slurry. Moreover, toxic metals were significantly removed through flocculation, making the final product risk-free of heavy metals for agricultural application.

Keywords: Anaerobic digestion; membrane filtration; flocculation pre-treatment; heavy metals, organic fertilizer

1. Introduction

Prominent fluxes in livestock breeding have occurred globally, especially over the past six decades. A major consequence of intensive or industrialized livestock production is the generation of a large amount of wastes [1]. Therefore, there is an urgent need for efficient and affordable treatment alternatives to handle excess manure. Anaerobic digestion (AD) is a suitable technology for livestock manure management due to its low maintenance cost and high treatment efficiency [2]. Moreover, AD technology could transform livestock waste into bioenergy (biogas), which eases the fossil energy crisis, as well as greenhouse gas emission [3].

The digestates generated in the AD of livestock manures are often rich in macronutrients, such as N, P, and K, and micronutrients, such as Zn, Fe, Mo, and Mn [4, 5, 6]. According to the sustainable concept of converting waste into useful products that enhance food security [7], these digestates have substantial potential to be used as organic fertilizers and soil amendments in agricultural land. However, the surrounding farmland is not sufficient in many regions to completely consume such large quantities of digestates. Thus, large storage capacity requirements and/or high transportation costs would arise, because a majority of the digestate is presented as liquid digested slurry with high water content and relatively low nutrient concentration [8]. Therefore, a feasible utilization method ought to be adopted to enrich nutrient concentrations and reduce the volume of digested slurry so that the pre-treated digested slurry could be easily transported and applied as a fertilizer in regions of high demand [9]. This nutrient enrichment and mitigation strategy might also help reduce the environmental pollution risk of nutrient run-off and leaching by the surplus application of digested slurry [10].

So far, membrane technology for the enrichment and recovery of nutrients from digested slurry has been attracting increasing interest [11]. However, clogging (or fouling) is well recognized as a major challenge in this membrane concentrating technology, inhibiting its large-scale implementation. Pre-treatment of slurry by decreasing the suspended solids through flocculation has been proposed as a feasible solution to this problem [12]. Due to the advantages of easy-operation and low cost, the flocculation-sedimentation pre-treatment prior to membrane filtration process have added value in decentralized installations of small size anaerobic plants where other expensive technologies are not feasible.

Flocculation involves the destabilization and aggregation of particles in suspension [13], and the efficiency of flocculants is highly dependent on the physicochemical properties of particle suspension in specific wastewaters. Various commonly used flocculants and flocculant aids exist in the industrial sector [14], such as trivalent aluminium salts and iron salts. From a traditional point of view of wastewater treatment, flocculation is fairly effective as a pre-treatment for membrane technology, because it removes not only suspended solids, but also N, P, and organic matter from the water [15]. However, the results from these studies cannot be transferred directly to digested slurry, due to its specific physicochemical properties. Moreover, if we take the recovery of the nutrients from the wastewater and their retention in concentrated liquor as the main target of this technology, removal of suspended solids by flocculation may also result in the loss of nutrients, e.g. nitrogen and phosphate, and plant growth promoters, e.g. phytohormone and humic acids, through floc formation [16]. Considering the value of these nutrients as fertilizers, it is crucial to determine a suitable flocculation strategy that balances the conflict between increasing the membrane flux by the removal of suspended solids and retaining the nutrients.

To address this knowledge gap, various combinations of the two commonly used flocculants, polyaluminium chloride (PAC) and iron chloride ($FeCl_3$), and the flocculant aid, cationic polyacrylamide (CPAM), were selected to evaluate the flocculation effect on digested chicken slurry in this study. The effect of various flocculation strategies on the membrane filterability of digested chicken slurry were initially investigated by determining the content of suspended solid (SS), distribution of particle size, as well as membrane flux. Secondly, the corresponding influence of the flocculation process on the macronutrients (NH_4^+-N and PO_4^{3-}-P), plant growth promoters (phytohormones and humic acids), and metals (Fe, Al, Zn, Ni, Cu, Pb, and Cr) has been evaluated.

2. Materials and Methods

2.1 Experimental Materials

Digested chicken slurry was found to contain more plant growth nutrients than digested mammal manure slurry [17]. Therefore, it was selected as the target slurry to recover nutrients by flocculation pre-treatment in the present study. Anaerobically digested chicken slurry was collected from Deqingyuan biogas plant located in a suburb of Beijing, China. The biogas plant was operated under mesophilic condition (37 °C), with a hydraulic retention time (HRT) of approximately 28 days. The fresh effluent of the anaerobically digested slurry was collected and transported to laboratory within 4 hours. The anaerobically processed chicken slurry was analysed for physicochemical characteristics, nutrients, plant growth promoters and metals prior to the experiment (Table 1).

2.2 Batch Experiments

Polyaluminium chloride (PAC) and iron chloride ($FeCl_3$) were used as flocculants, while cationic polyacrylamide (CPAM) was used as the flocculant aid in this study. According to previous studies [18], as well as industrial practice, the dosage for PAC was determined to be 6, 12, 18, and 24 g/L, while for $FeCl_3$, it was 3, 6, 9, and 12 g/L. For the combined treatment with flocculant and flocculant aid, the dosage of CPAM was kept constant at 0.2 g/L (Table 2). For the flocculation treatment, 0.5 L of digested slurry was placed into a 1-L beaker and treated with various dosages of PAC and $FeCl_3$, with and without the aid of CPAM. Each treatment beaker was stirred rapidly (300 rpm) for 1 min, followed by slow stirring (75 rpm) for 12 min, using an overhead stirrer with four impellers (JJ-4, Baita Xinbao Instruments, China). The same value of slurry, which was stirred without adding flocculants and flocculant aid, was considered as the control after settling. All the treatments and control were conducted in triplicate.

Immediately after stirring, 10 mL of the sample was collected from 5 cm under the surface for particle size distribution analysis. After 24 h of natural settlement, 100 mL of the liquid samples was collected from 10 cm above the flocs. Among them, 10 mL of the sample was used for the particle size distribution analysis, 5 mL was used for membrane filtration tests, and the remaining was used to analyse the value pH, EC, and the concentrations of SS, NH_4^+-N, and PO_4^{3-}-P. The liquid samples collected from the same position from the sample with the highest dosage of PAC (24 g/L), PAC+CPAM (24 g/L + 0.2 g/L), $FeCl_3$ (12 g/L), and $FeCl_3$+CPAM (12 g/L + 0.2 g/L), were used to detect the remaining concentrations of phytohormones, humic acids, and metals. Moreover, flocs settled at the bottom were collected and dried under −40 °C for the elemental composition test for metals.

2.3 Membrane filtration tests

The membrane filtration performance was tested by a suction flask with a cellulose acetate membrane with a pore size of 0.45 μm and a vacuum pump. Five millilitres of the liquid sample, collected after 24 h of settlement, was filtrated through the membrane fixed at the top of the suction flask. The operation pressure was maintained at 0.85 bar. A quantitative tube was used to collect the filtrate. The time required to obtain 3 mL of the filtrate was recorded. The membrane flux (*f*) was defined as:

$$f = \frac{V_f}{t},$$

where f is the membrane flux in mL/s, V_f is the volume of the filtrate in mL, and t is the time required to collect 3 mL of the filtrate liquid in s.

2.4 Analytical Methods

The particle size distribution was determined by a laser particle size analyser (MasterSizer 3000, Malvern, UK) with a detection range of 0.01 to 100000 μm. Values of pH and electrical conductivity (EC) were measured using a portable Orion 5-Star multimeter with both pH and EC electrodes (9172BNWP; THERMO, USA). Suspended solids (SS) were determined by drying the residues on a cellulose acetate membrane (pore size 0.45 μm) to a constant weight (24 h) at 105 °C. Soluble fractions of the liquid samples were obtained by centrifuging at 8000 rpm for 15 min at 4 °C, subsequently filtering the supernatant through a cellulose acetate membrane with a pore size of 0.45 μm. After standard pre-treatment and reagent addition according to the standard methods [19], the concentrations of ammonium (NH_4^+-N/4500-NH_3 F; phenate method) and orthophosphate (molybdenum blue colorimetric method) were measured using a UV-Vis spectrophotometer (Gold S54T; Lengguang Tech, China). Contents of phytohormones like GA_3, IAA, and ABA were analysed using a Dionex Ultimate U3000 system (Dionex, Sunnyvale, CA, U.S.A), equipped with an online solid phase extraction (SPE) column and diode array detector [20]. Humic acid contents were measured in accordance with the Chinese Industry Standard for water-soluble-fertilizer (NY/T 1971-2010). Contents of metals, including Fe, Al, Zn, Ni, Cu, Pb, and Cr, were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Elan 9000, Perkin Elmer, USA). All the parameters were determined in triplicate. The elemental composition of flocs was examined by employing Scanning Electron Microscopy (Hitachi 7700, Japan) at 15 kV, coupled with an Energy Dispersive X-ray (EDX) Spectrometer.

2.5 Statistical Analysis

One-way analysis of variance (ANOVA) was conducted to compare the differences among various parameters (pH, EC, SS, membrane flux, NH_4^+-N, PO_4^{3-}-P, phytohormones, humic acids, and metals) in digested chicken slurry under various flocculation pre-treatments. The significant difference for all comparisons was set at $p<0.05$. Sigmaplot software (version 12.5, Sigma, Inc.) was used for plotting and data analysis.

3. Results and discussion

3.1 Effect of flocculation treatments on membrane filterability

Flocculation is found to be a simple and effective strategy to remove suspended solids and improve membrane filtration performance [21]. Therefore, the effect of various combinations of two commonly used inorganic flocculants, polyaluminium chloride (PAC) and iron chloride ($FeCl_3$), with an organic flocculant aid, cationic polyacrylamide (CPAM), on the membrane filterability of digested chicken slurry were initially investigated by determining the content of suspended solid (SS) and membrane flux. The results from the solid mitigation showed that SS was significantly ($p<0.05$) removed in the flocculation experiment after adding $FeCl_3$ and CPAM (Figure 1a). SS removal was associated with the flocs formed by inorganic flocculants, which were derived from the electrical neutralization of negatively charged colloids by cationic flocculants (Edwards, 2014). Under the same dosage of different flocculants (6 and 12 g/L), $FeCl_3$ showed significantly higher ($p<0.05$) SS removal capability than PAC, regardless of the addition of flocculation aids. It may due to the high hydrolysis rate of iron in liquid, thus increasing the possibility of charge neutralization and particle precipitation [22]. This may also be the reason for increased SS removal (up to 75%) by the increase of $FeCl_3$ dosage from 3 to 9 g/L. However, no significant improvement was observed when the $FeCl_3$ dosage was further increased from 9 to 12 g/L. It might indicate that the extra amount of flocculants could lead to the inhibition of further sedimentation of flocs [23]. The addition of PAC flocculant at a dosage of 6 to 24 g/L showed limited effect on SS removal (~2.1%) in the digested chicken slurry. When PAC was applied in combination with CPAM, the SS removal rate significantly ($p<0.05$) increased to 20.5–23.2%, due to the netting and bridging function of CPAM to increase the floc size and aid the sedimentation [24]. Due to the SS and colloid removal through flocculation pre-treatments (Figure 1a), the viscosity of digested chicken slurry showed a similarly downward trend corresponding to the SS removal (Figure 1b), potentially aiding further membrane filtration.

After the flocculation reactions, particle size (0.1–10000 μm) distribution in the digested slurry was analysed before and after the 24-h settlement. Accordingly, the corresponding particle concentrations of various sizes in the slurry have been calculated and presented in Figure 2. In the original digested slurry, the particles were mainly distributed in the size range of 0.5–200 μm, with one peak at approximately 1 μm (Figure 2a). The flocculation treatment significantly increased their size immediately after the reaction, which can promote the sedimentation of solid particles and colloidal particles [25]. Thus, after the 24-h settlement, all particles larger than 100 μm in the pre-treated slurry were removed with $FeCl_3$ and $FeCl_3$+CPAM treatments (Figure 2b). With the PAC and PAC+CPAM treatments, flocs with particle size >10 μm were also formed immediately after the flocculation reaction (Figure 2a). Even though these large sized flocs were completely (>97%) removed after the 24-h settlement (Figure 2b), the content of fine particles of approximately 1-μm size significantly ($p>0.05$) increased to a level higher than that in the original slurry. This unexpected phenomenon might be caused due to the excess amount of flocculants that can further react with flocs, causing large flocs to disintegrate [26]. This higher concentration of fine particles under PAC and PAC+CPAM treatments also resulted in the lower removal rate of SS compared to the $FeCl_3$ and $FeCl_3$+CPAM treatments (Figure 1a).

The performance of membrane filtration was tested after the 24-h settlement followed by the flocculation treatment (data not shown, but can be seen in E-supplementary material). The results showed that the flocculation pre-treatments of

PAC improved the membrane flux by approximately 400 times, regardless of the variation in dosages. Moreover, the addition of CPAM along with PAC improved the flux up to 600–1100 times, indicating the important role of CPAM in the flocculation process of PAC. Flocculation pre-treatment by $FeCl_3$ shows its advantage on the improvement of membrane flux to over 3000 times higher than the flux of the original slurry. These results are in agreement with previous research on membrane filtration [12, 27], which indicated that the flocculation-sedimentation process can significantly improve membrane filtration performance. However, if we compare the results from the treatments of PAC+CPAM and $FeCl_3$+CPAM, CPAM showed better performance in terms of promotion in the PAC flocculation process than in the $FeCl_3$ treatment process. The reason might be that PAC and CPAM contain a similar polymeric structure, which could enhance their cooperation for flocculation.

3.2 Effect of flocculation treatment on macronutrient recovery

During flocculation pre-treatments, physicochemical properties such as EC, pH values, and nutrient content (PO_4^{3-}-P and NH_4^+-N) in the digested chicken slurry, were altered (Figure 3). The EC value increased through the flocculation treatment to 58 mS/cm at a $FeCl_3$ dosage of 12 g/L (Figure 3a). The increase in EC values was potentially due to the addition of Cl^-, as well as unsettled alum and iron. Moreover, the flocculation treatments resulted in a decrease in the pH value of the digested slurry, which may due to the H^+ generated, along with the hydrolysis of the Al^{3+} and Fe^{3+} from the flocculants.

The influence of various flocculation treatments on the concentration of phosphorus is shown in Figure 3c. All the tested flocculants and their integrations with CPAM in this study showed a strong effect on the reduction of PO_4^{3-}-P content in the digested chicken slurry. As the original concentration of PO_4^{3-}-P was approximately 126.1 ± 2.7 mg/L in the digested chicken slurry (Table 1), a higher loss of PO_4^{3-}-P (over 99%) was observed with the addition of $FeCl_3$, as compared with other flocculation treatments. Phosphorus removal after $FeCl_3$ addition can be the result of either the precipitation of dissolved orthophosphate [16] or the flocculation of suspended phosphorus-containing particles [28]. However, under PAC and PAC+CPAM treatments, the unexpected increase in the loss of PO_4^{3-}-P from 54% to 95% was also found as the applied dosage of PAC increased from 6 g/L to 24 g/L, regardless of SS removal. These results indicated that most of the PO_4^{3-}-P might have been absorbed by PAC with alum, instead of being removed with the suspended particles [28]. The outcomes of the current investigation are in accordance with the results obtained by Ebeling [29], who evaluated chemical flocculants to remove suspended solids and phosphorus from wastewater, finding the performance of both ferric chloride and alum flocculants to be similar. However, the nutrient use efficiency/plant availability of the phosphorus in the settled sludge should be further investigated. Otherwise, as alternative future perspective, the potential use of Ca- or Mg-salts in substitution of the current used Fe- and Al-flocculants should be discussed.

The influence of various flocculation treatments on the nitrogen dynamics (in the form of ammonium) is shown in Figure 3d. A slight reduction in the ammonium concentration was found in the treated digested slurry, as compared to the original slurry. However, it was not significant by the statistical analysis ($P>0.05$). A similar result was also reported in a previous study, which also detected only a small fraction of ammonium reduction through the flocculation treatment in digested swine manure slurry [30]. This might be due to the highly soluble nature of ammonium ion in the solution and the limited adsorption capacity of negatively charged colloidal particles [31].

3.3 Effect of flocculation treatment on the content of plant growth promoters

Humic acids and phytohormones, including gibberellin III (GA_3), indoleacetic acid (IAA), and abscisic acid (ABA), have been proved to be functional plant growth promoters [32-33]. In general, the level of these substances should be maintained during the treatment of digested slurry if the goal is to produce value-added fertilizer. Therefore, this study investigated the effect of flocculation pre-treatments (12 g/L of $FeCl_3$ dosage and 24 g/L of PAC dosage) on the contents of phytohormones (GA_3, IAA, and ABA) and humic acids (Figure 4).

There is no significant ($p>0.05$) influence of flocculation pre-treatments on the content of IAA, which varied in the range of 40–60 mg/L in both the original and treated slurry. However, high loss of GA_3 and ABA was recorded, with a maximum reduction of 76% for GA_3 under the PAC+CPAM treatment, and 75% for ABA under the $FeCl_3$

treatment. The difference in the influence on IAA as compared to GA_3 and ABA might be due to their chemical constitutions and characteristics. Compared to IAA, there are more active groups, e.g. hydroxyl and alkenyl groups, in the structure of GA_3 and ABA, which might increase the possibility of reaction with inorganic flocculants. However, the information required to explain these results might still be insufficient, requiring more detailed investigation in the future.

Humic acids are a series of macromolecular organic substances whose chemical structures are dominated by phenol groups and long carboxylic fatty acids [34]. They tend to react with cationic flocculation [35]. This might be the reason for the higher loss of humic acids under PAC+CPAM and $FeCl_3$+CPAM treatments, compared with PAC or $FeCl_3$ applied individually (Figure 5b). The humic acid loss is mainly through floc formation, which can be shown by the high rates of C, N, and O in flocs through EDX spectra analysis (Figure 5b and 5d). Moreover, humic acids are also regarded as one of the main components of membrane fouling pollutants [36], which should be maintained at a low concentration before membrane filtration. Therefore, in this case, further optimization of flocculation pre-treatment to balance the membrane fouling prevention and valuable fertilizer component recovery continues to be very challenging.

3.4 Effect of flocculation treatment on metal content

The heavy metal content in the digested chicken slurry may accumulate in the agricultural soil after long-term application [37-38], which has been a global agricultural challenge. Therefore, the influence of various flocculation treatments on the heavy metal content was investigated here (Figure 6). Results show that the content of Zn, Cu, Ni, Pb, and Cr in chicken slurry before flocculation treatments were 8.91 ± 0.4, 1.61 ± 0.08, 0.82 ± 0.06, 0.08 ± 0.02, and 0.03 ± 0.01 mg/kg, respectively (Table 1). After the flocculation treatment, approximately 95%, 21%, 84%, and 72% of Zn, Ni, Cu, and Pb were removed with the combined application of PAC+CPAM and $FeCl_3$+CPAM. Meanwhile, the sole application of $FeCl_3$ resulted in 100% removal of chromium from the chicken slurry (Figure 6). The high removal efficiencies of metals were mainly due to the binding effect of the flocs through the flocculation treatment. However, the removal of Cu, Zn and Ni seems to be less critical as the removal of Pb and Cr, since they are also plant essential micro-nutrients [39].

The content of aluminium and iron in the original digested chicken slurry were detected to be 4.52± 0.5 and 25.4 ± 2.6 mg/kg, respectively. Their content increased in the treated slurry due to the use of PAC and $FeCl_3$. Nevertheless, the metal content after the flocculation treatment was still within the safety limits set by the agricultural application regulations of biosolids in China, Europe, and US. Thus, in addition to the high improvement of membrane filterability, our study shows that optimized flocculation can also achieve a fertilizer product without the risk of heavy metals.

4. Conclusion

Chemical flocculation was demonstrated to be a promising pre-treatment strategy to improve membrane flux for membrane nutrient recovery from digested chicken slurry. High SS removal can be achieved with $FeCl_3$ flocculation, resulting in a significant improvement of membrane filterability. The NH_4^+-N content was maintained after the pre-treatment process, while PO_4^{3-}-P, some humic acids, and phytohormones were lost by floc absorption. However, flocculation has the additional benefit of providing a final product free of heavy metals, thus showing superior value in future agricultural implementation.

E-supplementary data of this work can be found in online version of the paper.

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Captions

Table 1. Characteristics of anaerobically digested slurry from digestion of chicken manure (n=4).

Table 2. Application levels of dosage for flocculation pre-treatment (unit: g/L)

Figure 1. Effect of various flocculation treatments on (a) suspended solid (SS) removal and (b) viscosity reduction, in digested chicken slurry.

Figure 2. Effect of various flocculation treatments on size distribution of particle concentration (a) before and (b) after the 24-h settlement in digested chicken slurry.

Figure 3. Effect of various flocculation treatments on the fertilizer value of digested chicken slurry. (a) Electronic conductivity, (b) pH value, (c) PO_4^{3-}-P concentration, and (d) NH_4^+-N concentration.

Figure 4. Effect of various flocculation treatments on the contents of phytohormones (Gibberellin III (GA_3), indoleacetic acid (IAA), and abscisic acid (ABA)) and humic acids in the digested chicken slurry. The various letters above the bar for each parameter represent the significant difference (Flocculation dosage: $FeCl_3$-12 g/L, PAC-24 g/L, CPAM-0.2 g/L).

Figure 5. EDX spectra of flocs from digested chicken slurry treated by (a) PAC, (b) PAC with CPAM, (c) $FeCl_3$, and (d) $FeCl_3$ with CPAM at a magnification of ×50000 (Flocculation dosage: $FeCl_3$-12 g/L, PAC-24 g/L, CPAM-0.2 g/L).

Figure 6. Effect of various flocculation treatments on the metal content of digested chicken slurry. The various letters above the bar for each parameter represent the significant difference (Flocculation dosage: $FeCl_3$-12 g/L, PAC-24 g/L, CPAM-0.2 g/L).