Removal of Suspended Solids in Anaerobically Digested Slurries of Livestock and Poultry Manure by Coagulation Using Different Dosages of Polyaluminum Chloride

P Li, C J Zhang, T K Zhao and H Zhong

Institute of Plant Nutrition and Resources, Beijing Academy of Agriculture and Forestry Sciences, No. 9 in Shuguang Garden Mid Road, Haidian District, Beijing, RR China

tkzhao@126.com

Abstract. In this study, anaerobically digested slurries of livestock and poultry manure were pretreated by coagulation–sedimentation using an inorganic polymer coagulant, polyaluminum chloride (PAC). The effect of different PAC dosages on suspended solids (SS) removal and pH in the biogas slurries was assessed to provide reference values for reducing the organic load of biogas slurry in the coagulation–sedimentation process and explore the feasibility of reducing the difficulty in subsequent utilization or processing of biogas slurry. The results showed that for the pig slurry containing approximately 5000 mg/L SS, the removal rate of SS reached up to 81.6% with the coagulant dosage of 0.28 g/L PAC. For the chicken slurry containing approximately 2600 mg/L SS, the removal rate of SS was 30.2% with the coagulant dosage of 0.33 g/L PAC. The removal rate of SS in both slurries of livestock and poultry manure exhibited a downward trend with high PAC dosage. Therefore, there is a need to control the PAC dosage in practical use. The pH changed little in the two types of biogas slurries after treatment with different PAC dosages and both were in line with the standard values specified in the “Standards for Irrigation Water Quality”.

1. Introduction

The large-scale intensive livestock and poultry industry has developed rapidly in recent years in China. The gross output value of the livestock industry was 16.27 billion yuan in Beijing in 2011, an increase of 63.8% over 2001. This development has been accompanied by the production of a large amount of animal manure and sewage, among other wastes. Livestock and poultry wastes have become a major source of nonpoint source pollution in rural areas in China [1]. According to China’s first national census of pollution sources [2], the national production of livestock and poultry wastewater was 1.321 billion m³, 57.3% of which was processed and used; the production of livestock and poultry wastewater in Beijing was 4.7774 million m³, only 56.0% of which was processed and used—lower than the national level. The pollutant emissions from agricultural sources have a significant impact on the aquatic environment. Specifically, the chemical oxygen demand (COD) emissions from agriculture reached 13.2409 million t; that is, 43.7% of the total COD emissions across the country. The COD emissions from livestock and poultry industry accounted for 95.8% of the total emissions from agricultural sources, leading to prominent pollution problems in the livestock and poultry industry. Anaerobic fermentation processing technology (i.e., biogas production) plays a major role in the disposal of large amounts of livestock and poultry manure [3], and it has become an important...
measure of waste treatment processes in livestock and poultry farms [4]. In China, the number of biogas users reached $3.0 \times 10^7$ in 2009, ranking first in the world [5]. Additionally, there were more than 4700 large- and medium-sized biogas plants on large-scale farms in 2010, which produced 3 billion t of biogas slurry and residue [6].

Anaerobically digested slurry produced after biogas production by anaerobic fermentation, also known as biogas slurry, contains abundant nitrogen, phosphorus, and potassium, among other major elements; meanwhile, biogas slurry contains large amounts of trace elements (e.g., iron, zinc, and copper), organic matter, many amino acids and vitamins, as well as various beneficial bacteria [7-10] and it can be returned to farmland as fertilizer [11]. Despite the particular benefits obtained from the use of biogas slurry in agriculture worldwide [12-13], the direct discharge of biogas slurry with high pollutant load into farmland can cause detrimental effects to the environment [14-16]. COD and heavy metals are major obstacles that affect the emission and utilization of biogas slurry [12, 17, 18]. Moreover, the application of biogas slurry is limited by arable land resources, storage and transportation costs [19], and crop demand, among various factors [20]. Thus, biogas slurry needs to be effectively processed to ensure the convenience and environmental safety of resource reuse.

Anaerobically digested manure slurry has significantly high concentrations of suspended solids (SS) and COD even after long-term standing and precipitation [21]. Once high-COD effluent is discharged into farmland, the organic matter contained in it will be decomposed; the intermediates can cause crop yield losses, while methane, a greenhouse gas, can also be produced, posing a threat to the atmosphere. The COD of biogas slurry is mainly composed of insoluble organic matter [21] that is unfavorable for subsequent use and processing. Removal of high concentrations of SS can markedly reduce the organic pollution load of biogas slurry, thereby facilitating the subsequent processing. The most simple, effective, and relatively low-cost method of SS removal is coagulation–sedimentation [22]. An important factor that affects the coagulation effect is the dosage of coagulant and coagulant aids [23]. There were no researches for assessing the effect of SS removal on anaerobically digested slurries of pig and chicken manure. In the present study, anaerobically digested slurries of pig and chicken manure were used to assess the effect of different dosages of cheap coagulation agent (i.e., polyaluminum chloride, PAC) for removal of SS. The results will provide a reference for reducing the organic load in biogas slurries of livestock and poultry manure.

2. Materials and methods

2.1. Materials
Anaerobically digested slurry of pig manure (hereinafter referred to as pig slurry) was obtained from the waste effluent tank of a biogas plant in a medium-sized pig farm in Yanqing District, Beijing, China. Anaerobically digested slurry of chicken manure (hereinafter referred to as chicken slurry) was obtained from the waste effluent tank of a biogas station in Yanqing District, Beijing. To prevent degradation at room temperature, the test samples were immediately stored at 4°C upon arrival at the laboratory. The test slurries were passed through a 60-mesh standard sieve to remove coarse impurities before use. The SS content and pH of the test slurries are shown in Table 1. The coagulant was commercially available PAC (an inorganic macromolecular polymer of aluminum salt).

| Table 1. Pollutant content in biogas slurries tested in the study |
|---------------------------------------------------------------|
| Pig slurry | 5080 | 7.84 |
| Chicken slurry | 2693 | 7.85 |

2.2. Methods
2.2.1. Experimental design. In this experiment, a 1000-mL PVC beaker was used as the reaction vessel and a jar test mixer was used for agitation. First, a preliminary experiment was conducted to determine the coagulant dosage for the formation of alumen ustum. Briefly, 400 mL of sieved slurry was added into the beaker and placed on the mixer platform. The mixer was agitated slowly at 60 rpm. When the agitation speed stabilized, the coagulant was added at 0.02 g PAC each time until the appearance of alumen ustum during agitation. The cumulative amount of PAC added was recorded as the minimum coagulant dosage for the formation of alumen ustum, $x_1$ (g/L). The experiment was performed three times and the mean value of $x_1$, $x_2$, and $x_3$ was calculated.

Based on the minimum coagulant dosage for the formation of alumen ustum, $x$ (g/L), we chose $x/3$ as the coagulant dosage for Beaker #1, $2x/3$ as the coagulant dosage for Beaker #6, and the coagulant dosage was successively and equally increased for Beakers #2–5. The coagulant was added into Beakers #1–6 simultaneously and the rates of the coagulant dosage are shown in Table 2. Next, 800 mL of sieved slurry was added into the reaction vessel on the mixer platform. The mixer program was run as follows: rapid agitation at 250 rpm for 1 min with coagulant addition, intermediate agitation at 120 rpm for 10 min, slow agitation at 30 rpm for 10 min, and then agitation was stopped. The water sample was allowed to stand and precipitate for 10 min. The supernatant was collected from the reaction vessel using a 50 mL syringe and used to measure the SS content and pH.

2.2.2. Analytical methods. The SS content of slurry samples was determined by the gravimetric method (GB11901-89). The samples were filtered through a 0.45-μm pore size membrane filter. The filter membrane was dried at 105°C to constant weight and then weighed. The slurry pH was measured using the glass electrode method.

The experimental data were statistically analyzed using SPSS Statistics 19.0 (SPSS Inc., Chicago, IL, USA). The results were plotted using Origin 8.5 (OriginLab Corp., Northampton, MA, USA).

3. Results and discussion

3.1. Effect of coagulation pretreatment on SS in pig slurry

According to the results of the preliminary experiment, 0.83 g/L PAC was the minimum coagulant dosage to form alumen ustum in the pig slurry during coagulation treatment. Therefore, the PAC dosages for the pretreatment of pig slurry were 0.28, 0.55, 0.83, 1.11, 1.39, and 1.66 g/L.

With the PAC dosage in the range of 0.28–0.83 g/L, the SS content of pig slurry pretreated by coagulation–sedimentation was lower than 1000 mg/L and the removal rate of SS remained higher than 80% (Figure 1). With a continued increase in PAC dosage, the SS content of pretreated pig slurry showed an upward trend, while the removal rate of SS dropped to below 80%, varying from 75.9% to 66.4%. With different PAC dosages, the pH of pretreated pig slurry varied between 7.85 and 8.03 (Figure 2), which was slightly but not significantly increased compared with the original slurry; all pH values were in line with the standard values (5.5 to 8.5) specified in the “Standards for Irrigation Water Quality”. With an increase in PAC dosage, the slurry pH showed a slight increase followed by a progressive decrease. The highest pH value was observed with the coagulant dosage of 0.55 g/L PAC.
In the coagulation–sedimentation process, we can preliminarily and intuitively determine the result of coagulation treatment through the formation, size, and sedimentation rate of alumen ustum. There are multiple influencing factors: in addition to the hydraulic conditions and raw water quality, the type and dosage of coagulants strongly influence the formation, size, and sedimentation rate of alumen ustum. If the coagulant dosage is insufficient, it is difficult to form alumen ustum and the effluent is turbid; if the coagulant dosage is too high, the size of alumen ustum decreases and the effluent is also turbid. When the coagulant dosage is within a suitable range, the best results can be obtained with regard to the formation, size, and sedimentation rate of alumen ustum [24]. Han et al. [25] treated the biogas slurry of cattle manure (hereinafter referred to as cattle slurry) with PAC. It was found that with an increase in PAC dosage, the removal rate of cattle slurry turbidity first increased and then decreased, with the highest removal rate obtained with the dosage of 320 mg/L PAC. In the current study, the highest removal rate of SS was obtained in the pig slurry with the dosage of 0.28–0.55 g/L PAC, in agreement with previous results [25].

3.2. Effect of coagulation pretreatment on SS in chicken slurry
According to the results of the preliminary experiment, approximately 0.25 g/L PAC was the minimum coagulant dosage to form alumen ustum in the chicken slurry treated by coagulation–sedimentation. Therefore, the PAC dosages for pretreatment of chicken slurry were 0.08, 0.17, 0.25, 0.33, 0.42, and 0.50 g/L.

With an increase in PAC dosage, the SS content of chicken slurry pretreated by coagulation–sedimentation showed a slight decrease followed by an increase (Figure 3). With the PAC dosage in the range of 0.33–0.42 g/L, the SS content of pretreated chicken slurry was lower than 1900 mg/L and the removal rate of SS remained higher than 30%. With a continued increase in PAC dosage, the SS content of pretreated chicken slurry markedly decreased, while its removal rate decreased to 10.9%. The slurry pH varied between 7.89 and 7.91 after pretreatment with different PAC dosages (Figure 4).
The pH value increased slightly, but not significantly, compared with the original slurry, and all pH values were in line with the standard values specified in the “Standards for Irrigation Water Quality”. The slurry pH was almost constant with the increase in PAC dosage, and relatively high pH was detected with the PAC dosages of 0.08 and 0.25 g/L.

Han et al. reported that when cattle slurry was treated with PAC, the highest removal rate of slurry turbidity was obtained with 320 mg/L PAC; however, the removal rate of slurry turbidity declined when the PAC dosage reached 640 mg/L [25]. In the present study, the highest removal rate of SS was obtained in the chicken slurry with the PAC dosage of 0.33 g/L; the removal rate of SS significantly decreased when the dosage reached 0.50 g/L. The trend of SS removal rate in the chicken slurry was consistent with that reported by Han et al. in cattle slurry [25]. The inorganic macromolecular polymer of aluminum can provide a large number of complex ions, which strongly adsorb colloidal particles and also aggregate colloids through adsorption bridging. The simultaneous chemical and physical changes neutralize the surface charge of the colloidal particles and reduce the zeta potential, resulting in unstable micelles and causing floc formation and sedimentation [26]. With insufficient PAC dosage, impurities in the water do not receive adequate reverse charges for destabilization or coagulation to occur. With excessive PAC dosage, the opposite charge on the colloid surface allows the slightly destabilized colloids to regain stability. According to a domestic study on the removal of organic compounds in chicken slurry by coagulation [27], the pollutant content was relatively low in the chicken slurry tested in the present study. Thus, a comparably good rate of SS removal was obtained with low coagulant dosage of PAC. With a further increase in PAC dosage, the particles in the biogas slurry are surrounded by too much coagulant and thus lose the opportunity to combine with other particles, making coagulation unlikely to occur and thereby affecting the removal of SS [27].

Figure 3. The content and removal rate of suspended solids (SS) in chicken slurry pretreated by coagulation–sedimentation with different coagulant (polyaluminum chloride) dosages.

Figure 4. The pH in chicken slurry pretreated by coagulation–sedimentation with different coagulant (polyaluminum chloride) dosages.

4. Conclusions
With the coagulant dosage in the range of 0.28–0.83 g/L PAC, the removal rate of SS reached more than 80% in the anaerobically digested pig slurry containing approximately 5000 mg/L SS; the highest removal rate was obtained with the PAC dosage of 0.28 g/L. With the coagulant dosage in the range of 0.33–0.42 g/L PAC, the removal rate of SS was higher than 30% in the anaerobically digested chicken slurry containing approximately 2600 mg/L SS; the highest removal rate was obtained with the PAC dosage of 0.33 g/L. High PAC dosage resulted in a decrease in the removal rate of SS in both slurries of livestock and poultry manure, making it necessary to control the PAC dosage in practical use. The pH changed little in the two types of biogas slurries after treatment with different PAC dosages and both complied with the standard values specified in the “Standards for Irrigation Water Quality”.

Acknowledgments
This work was supported by the National Science & Technology Pillar Program during the 12th Five-Year Plan period (2012BAD15B02) and the Technological Innovation Team Development of BAAFS (JNKYT201605).

References
[1] Zhang J, Zhang M X, Shan S D, et al 2009 Journal of Agro-Environment Science. 28(10): 2005-2009
[2] Compilation committee of the data of the first national census of pollution sources 2011 Data collection of the first national census of pollution sources vol 4 (Technical report of pollution sources census vol 2) (Beijing: China Environmental Press) pp 42-47
[3] Li S and Deng L W 2008 Swine Industry Science. (1): 70-72
[4] Zhu J, Qiu Y Q, Zhang C P 2010 Journal of Safety and Environment. 10(5): 24-28
[5] Zhang J F, Yuan H R, Zou D X, et al 2012 Journal of Anhui Agri. Sci. 40(19): 10246-10250
[6] Xie J J, Xu F H, Qi J Y, et al 2012 China biogas. 30(5): 14-18
[7] Zeng G K, Xie J, Yin F 2005 Renewable Energy. (1): 38-40
[8] Ren N Q, Wang A J, Ma F 2005 Microbial physiological ecology of acid producing biogs microorganism (Beijing: Science Press)
[9] Tani M, Sakamoto N, Kishimoto T, et al 2006 International Congress Series. 1293: 331-334
[10] Marcato C E, Pinelli E, Pouech P, et al 2008 Bioresource Technology. 99: 2340-2348
[11] Matsunaka T 2006 International Congress Series. 293: 242-252
[12] Liu X L, Liu J W, Liu B 2012 Journal of Anhui Agri. Sci. 40(2): 968-971
[13] Xu Q X, Guan X F, Qian L, et al. 2015 Environmental Engineering. 33(1): 72-76
[14] Noykova N, Müller T G, Gyllenberg M, et al. 2002 Biotechnol Bioeng. 78(1): 89-103
[15] Mahmoud N, Zeeman G, Gijzen H, et al. 2004 Water Research. 38(9): 2348-2358
[16] Myint M, Nirmalakhandan N, Speece R E. 2007 Water Research. 41(2): 323-332
[17] Ge X, Li B Q, Ding Y Q, et al. 2012 Journal of Anhui Agri. Sci. 40(30): 14897-14898, 15058
[18] Christos M, Christos S, Nikolaos R, et al. 2012 Journal of Agricultural Science and Technology. A2: 149-154
[19] Waeger F, Delhaye T, Fuchs W 2010 Separation and Purification Technology. 73: 271-278
[20] Bai X F, Li Z F, Cheng S K, et al. 2014 Environmetal Engineering. 32(6): 153-156
[21] Tang L Q, Zhu H G, Chen J, et al. 2010 China Biogas. 28(6): 7-12
[22] Xiong H J and Liu S R 2011 Environmental Protection of Oil & Gas Fields. 21(2): 30-33
[23] Ahmad A L, Ismall S, Bhatia S 2005 Environmental Science and Technology. 39(8): 2828-2834
[24] Zhou L Y, Wang S, Ni J 2008 Shanghai Water. (4): 14-17
[25] Han M, Feng C H, Liu K F, et al. 2014 Tianjin Agricultural Sciences. 20(9): 96-101
[26] Zhu H G, Wang D Y 2012 Transactions of the Chinese Society for Agricultural Machinery. 43(4): 93-99, 118
[27] Zhao Y 2006 Research on removal of phosphorus and turbidity in municipal wastewater by PACI, (Wuhan: Central China Normal University)