Distribution of heavy metals in pig farm biogas residues and the safety and feasibility assessment of biogas fertilizer

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Abstract: The presence of high levels of heavy metals in anaerobic fermentation residues is a major obstacle to the resource utilization and urgent research for removal of heavy metals in the biogas slurry is needed. The handling of large-scale residue slurry and safely returning to field urgently needed constructive suggestion. The contents of heavy metal elements in the residue of anaerobic digestion processes of the wastewater and waste of the piggery were mainly investigated. The contents of heavy metals in the original fluid and the centrifugal solution were determined in this study. They included elements, such as Cu, Zn, Cr, Cd, Pb, As, Ni, Mn, and Se, which were compared with the existing standard including the irrigation water quality standards (GB5084-2005), comprehensive discharge standard of sewage (GB8978-1996) and water-solubility humic acid fertilizer quality standards (NY1106-2010). The preliminary data suggested that both the heavy metals before and after centrifugation were in excess of the standards to some degree and the exceeding standard rate declined significantly after centrifugation. The absolute contents of heavy metals after centrifugation declined significantly compared with that before centrifugation. Those ratios are 91.8%, 73.2%, 47.6%, 94.5%, 93.5%, 59.4%, 95.8%, 100% for Zn, As, Cd, Cr, Cu, Ni, Mn, Pb, respectively. A descriptive statistics as well as a correlational analysis showed that there existed strong correlation among Cu, Pb, and the total suspended solids (TS). Meanwhile, significant correlation was found among TS, Cd, Zn, As, Cr, Ni, and Mn at 0.01 level. The data and the analysis above provided the theoretical and experimental support for the removal of heavy mental mainly characterized by the removal of TS. According to the comparison between contents of heavy mental conversed from large amount nutrients and corresponding standard (NY1110-2006), only as was found beyond standard. It was feasible to apply biogas residues after centrifugation as water-solubility fertilizer due to the fact that As had low accumulation efficiency in soil and plants.

Keywords: fluid biogas residue, heavy metals, distribution, correlation, fertilization

DOI: 10.3965/j.ijabe.20130604.005

Citation: Ma J Q, Zhu H G, Fan M. Distribution of heavy metals in pig farm biogas residues and the safety and feasibility assessment of biogas fertilizer. Int J Agric & Biol Eng, 2013; 6(4): 35－43.

1 Introduction

Intensive livestock farm biogas is a kind of clean energy which has huge potential and can reduce environmental pollution[1]. In recent years, as the increasing investment has been given to national projects, the number of “Eco-energy” biogas constructions on rural farms increases every year and returning to field is a main way for most biogas liquid[2] .

It is widely reported domestic and abroad that residue slurry contains heavy metals and its content increases along with the decomposition of organic matter in the anerobic digestion process[3,4]. The safety issues of fertilization have been taken seriously by scholars gradually. Previous study showed that heavy metals in

Received date: 2013-11-10 **Accepted date:** 2013-12-15

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pig farming biogas mainly include Zn, Cu, As, Pb, Cd, Cr, Hg, Ni[5].

Lidia and Agata[6] studies have shown that it is the great amount of zinc oxide (ZnO) and copper sulfate ($CuSO_4$) added to the fodder and some other factors that lead to an increase content of heavy metal in the animal manure and biogas anaerobic fermentation broth now. The issue of the heavy metals in biogas slurry has been a factor constraining the biogas slurry residue returning to field on a large scale.

Other researchers have previously done a lot of safety assessment on biogas slurry residue returning cropland, while no conclusion was drawn till now. The study by Zhang[7] showed that Cu, Zn, Pb, Cd, As and other heavy metals appear certain growth on topsoil by continuous application, but will not exceed the limits for the National Soil Environmental Quality Standards and the accumulation of heavy metals in the soil is of lower risk. While Liu et al.[8] claims that the proportion of manure in raw material of anaerobic digestion should be controlled properly or make some pre-process to remove heavy metals. Liang et al.[9] considered that the irrigation of pure biogas residues or mixing it with fertilizer could both improve soil fertility, and in this way the heavy metals and other harmful elements were removed to meet the national soil environmental quality indicators. However, further studies are needed when it comes to the long-term impact of biogas residues irrigation on soil quality. Virtually, few scholars have studied and put forward constructive suggestions about biogas residues safely returning to field.

The issue of removing heavy metals of anaerobic fermentation residues was studied by some researchers. With xanthate adsorbent which was gained from wheat straw as raw materials, Li et al.[10] has successfully reduced the concentrations of heavy metals to industrial wastewater discharge standards, but the operating procedures were complicated, time-consuming, and difficult to achieve large-scale applications. Although traditional chemical methods can be used to remove heavy metals obviously, the processing costs are relatively high; hence it is difficult to apply chemicals on the removal of heavy metals in the biogas slurry[11]. Further study is needed for the application of biogas slurry. Urgent research on removal of heavy metals in the biogas slurry is needed.

The study aims for returning large-scale biogas residues to field and putting forward constructive suggestions for it on the basis of other researches. The changes of heavy metals concentration before and after centrifugation were gained; the total suspended solids (TS)-removal-oriented method for removing heavy metal was given. The correctness and feasibility of this method were proved in theory and practice; the feasibility and safety of centrifugation solution as fertilizer were evaluated on this basis.

2 Materials and methods

2.1 Test water samples

Test samples were collected from biogas project point which was located in the east Chongming County, Shanghai, China. Test time is from March to June, 2013. Biogas basically maintained neutrality skew alkaline character. A total of 20 samples were collected.

2.2 Index test

Twelve metals (Cu, Zn, Cr, Cd, Pb, As, Ba, Ni, Co, Mn, Pt, Sb and Se) both in the original fluid and the centrifugal solution were investigated. Other parameters chosen to be tested include potassium (K), ammonia (NH_4^+), total phosphorus (TP) and TS. Heavy metals are characterized by atomic emission spectroscopy (ICP) measurement[5,12].

2.3 Data analysis

Comparative analysis was made among standard value and biogas slurry heavy metals concentration and the exceeding ratio was determined, metal standard limits were shown in Table 1. Besides testing the heavy metal concentration of original fluid, we also tested the heavy metal concentration of centrifugal solution. The test results were compared and analyzed; the corresponding distribution law of heavy metals in solid-liquid two phase was summarized.

In accordance with the appropriate standards to determine the feasibility of biogas as a water- solubility fertilizer, the limit values of As, Cd, Pb, Cr were shown in Table 2; Data analysis software of IBM SPASS

Statistics 19.0 was applied to analyze the results.

Table 1 Limits for integrated wastewater discharge standard and irrigation water quality standards (mg/L)

	Cd	Cu	Pb	Zn	As	Se	Cr	Ni	Mn
Integrated wastewater discharge standard (GB8978-1996)[13,14]	0.1	2	1	5	0.5	0.5	1.5	1	5
Irrigation water quality standards* (GB5084-2005)	0.01	1	0.1	2	0.1	0.02	-	-	-

Note: *Carve irrigation water quality standards take the maximum reined upland, water and vegetables to make.

Table 2 Heavy metal standard of soluble fertilizers

Project	Index (mg/kg)
Arsenic (As) (elemental dollars) ≤	10
Cadmium (Cd) (elemental dollars) ≤	10
Lead (Pb) (elemental dollars) ≤	50
Chromium (Cr) (elemental dollars) ≤	50

Note: Standard was quoted from the water-soluble fertilizer containing humic acid (NY1106-2010), water-soluble fertilizer mercury, As, Cd, Pb, Cr limit its determination (NY1110-2006)[15,16].

3 Results and analysis

3.1 Results and analysis of heavy metal concentration of original fluid and centrifugal solution

The charactistics of nine kinds of heavy metal elements (Cd, Cu, Zn, As, Se, Cr, Ni and Mn) were analyzed. The results (Table 3) showed that after removing most of the suspended solids, five metals (Pb, As, Se, Cr and Ni) no longer exceed the standard; Zn was out of the maximum permission level in four samples. The absolute contents of heavy metals after centrifugation declined significantly compared with that before centrifugation. Those ratios are 91.8%, 73.2%, 47.6%, 94.5%, 93.5%, 59.4%, 95.8%, 100% for Zn, As, Cd, Cr, Cu, Ni, Mn, Pb, respectively. These provided experimental basis for the TS-removal-oriented method for removing heavy metals.

The principle of discreteness of the heavy metals content of the original fluid and the centrifugal solution did not significantly change. They were Zn > Cu > Mn > Sb > Cr > Pt > Ba > Ni > As > Pb > Se > Cd and Sb> Zn> Cu> Pt> Mn> Ba> Ni> Cr> As> Se> Cd> Pb, respectively (Table 4 and 5).

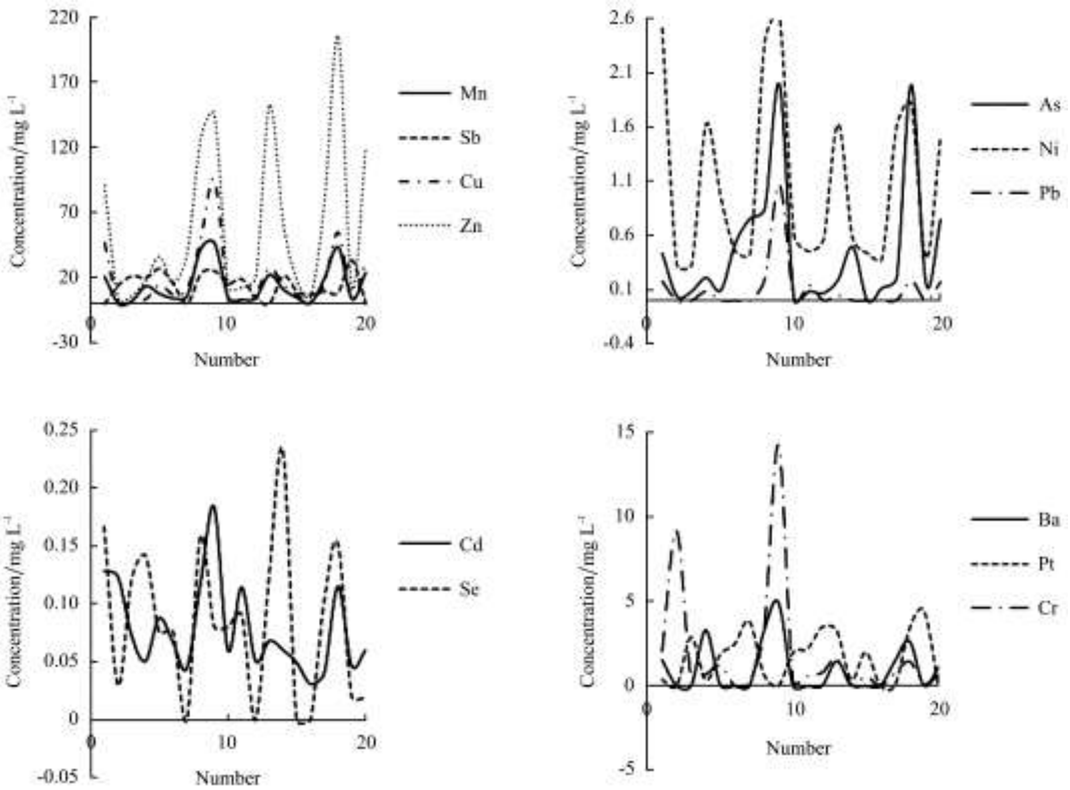


Figure 1 Test results for twelve types of heavy metals in original fluid

Table 3 Exceeding ratio of the heavy metals in centrifugal solution (total of 10 points)

Element / Standard	Cd	Cu	Pb	Zn	As	Se	Cr	Ni	Mn
Over sewage discharge standards/%	10	10	0	40	0	0	0	0	10
Over irrigation water quality standards/%	100	50	0	70	50	80	-	-	-

Table 4 Descriptive statistics of heavy metals in original fluid

	Cd	Cu	Pb	Zn	As	Se	Cr	Ni	Mn
Average	0.079	20.120	0.104	58.918	0.453	0.084	1.896	1.079	14.189
Median	0.064	9.281	0.000	28.031	0.200	0.081	0.662	0.585	6.715
SD	0.039	24.519	0.239	60.740	0.589	0.067	3.537	0.802	14.837
Min	0.031	0.364	0.000	3.010	0.000	0.000	0.000	0.321	0.182
Max	0.184	94.839	1.068	205.430	1.993	0.232	14.209	2.619	46.440

Table 5 Descriptive statistics of heavy metals in the centrifugal solution

	Cd	Cu	Pb	Zn	As	Se	Cr	Ni	Mn
Average	0.041	1.304	0.000	4.811	0.121	0.120	0.104	0.438	0.601
Median	0.025	0.713	0.000	3.566	0.099	0.094	0.048	0.384	0.017
SD	0.035	2.049	0.000	3.885	0.081	0.102	0.152	0.154	1.598
Min	0.023	0.173	0.000	1.576	0.000	0.000	0.000	0.308	0.000
Max	0.133	6.983	0.000	13.943	0.268	0.286	0.491	0.798	5.132

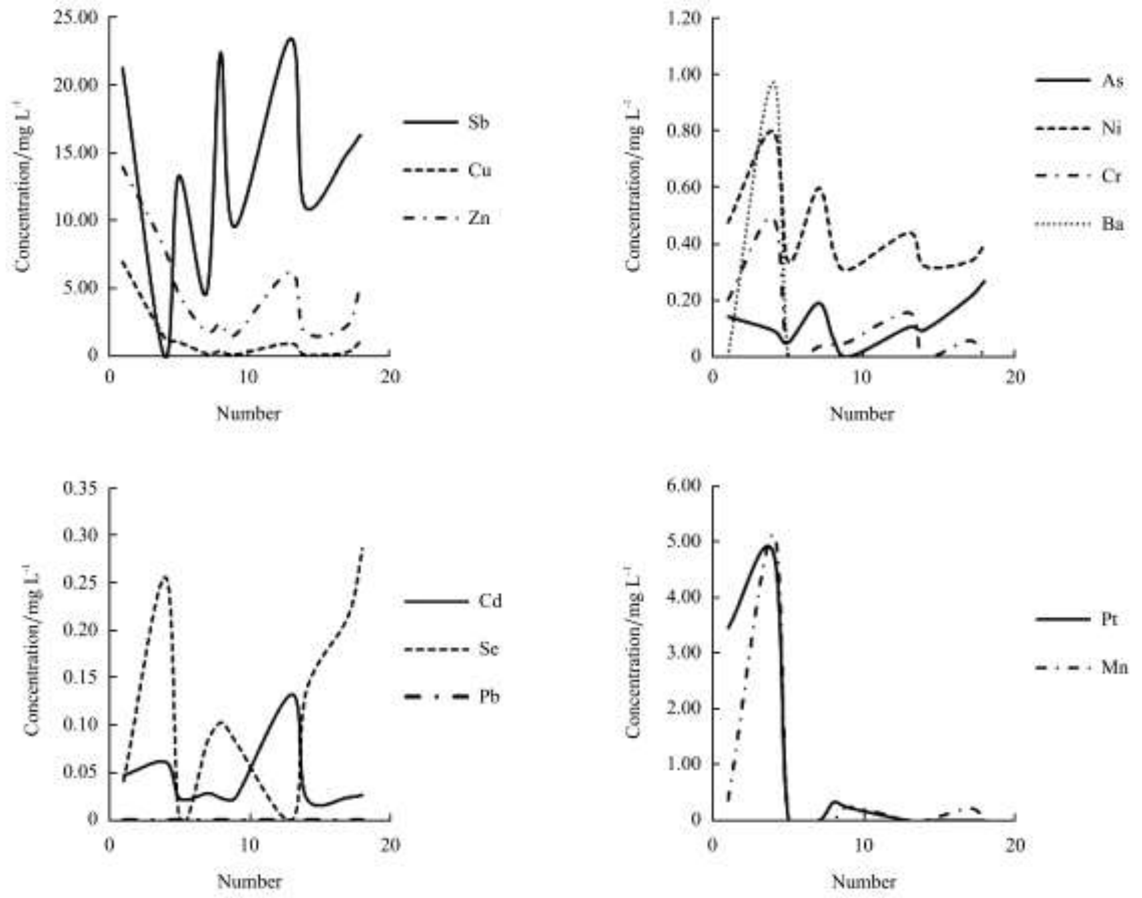


Figure 2 Test results for twelve types of heavy metals in the centrifugal solution

3.2 Correlation analysis

3.2.1 Correlation analysis of heavy metals with ammonia nitrogen, potassium (K), and total phosphorus (TP)

To analyze the fertilizer efficiency changes before and after centrifugal, a correlation analysis of metal elements with NH_3-N, K and TP was made.

The original fluid analysis (Table 6) showed that there was a significant correlation among Cu, Zn and TP at the 0.01 level (bilateral), stronger correlation among As, Se and TP at the 0.01 level (bilateral). The results indicated that the removal of TS would also take away a lot of P, which was a disadvantage in terms of fertilization. This provided the direction for further research in recovery and extraction of phosphorus.

The centrifugal solution analysis (Table 6) showed that there were correlation in the following series: (1) significant correlation: Cu & NH_3-N; Zn & K; Zn, Cr & TP (0.01 level); (2) stronger correlation: Cu, Ni, Mg & TP; Cu & K Zn & NH_3-N (0.05 level).

Table 6 Correlation of original fluid and the centrifugal solution among ammonia nitrogen (NH_3-N) , potassium (K), total phosphorus (TP)

Pearson coefficient	Original fluid			Centrifugal solution		
	NH_3-N	K	TP	NH_3-N	K	TP
NH_3-N	1	0.712**	0.349	1	0.787**	0.448
K	0.712**	1	0.037	0.787**	1	0.636*
TP	0.349	0.037	1	0.448	0.636*	1
Cd	0.456*	0.036	0.528*	0.046	0.081	0.349
Cu	0.501*	-0.069	0.810**	0.802**	0.763*	0.730*
Pb	0.483*	-0.088	0.469*	.[a]	.	.
Zn	0.335	-0.027	0.859**	0.693*	0.778**	0.846**
As	0.408	-0.02	0.653**	0.214	0.011	0.177
Se	0.186	0.226	0.675**	-0.182	-0.126	0.201
Cr	0.25	-0.302	0.254	-0.022	0.379	0.838**
Ni	0.31	-0.08	0.861**	-0.185	0.18	0.696*
Mn	0.323	-0.107	0.841**	-0.208	0.266	0.663*

Note: ** Means correlation at the 0.01 level (bilateral); * Means correlation at the 0.05 level (bilateral).

[a] Means it cannot be calculated because at least one variable is constant.

3.2.2 Correlation analysis of concentrations of heavy metals and total suspended solids (TS)

The Pearson coefficients among the nine metals and TS are 0.693, 0.875, 0.920, 0.636, 0733, 0.331, 0.709, 0.789, 0.785 for Cd, Cu, Pb, Zn, As, Se, Cr, Ni, Mn, respectively. The correlation analysis among the nine metals and TS showed that there was a significant correlation among Cu, Pb and TS at the 0.01 level (bilateral), stronger correlation among Cd, Zn, As, Cr, Ni, Mn and TS at the 0.01 level (bilateral) was found. This provided a strong theoretical basis for the TS-removal-oriented method for removing heavy metals.

For further removal of the heavy metals in centrifugal solution may remove the major nutritive elements together, so further study about a well-rounded approach is needed.

3.3 Conversion of the elements in accordance with the results and analysis

Major nutritive elements were calculated by the Equation (1).

$$C = N + K_2O + P_2O_5 \quad (1)$$

Where, C is the number of elements, mg/L; N, K_2O and P_2O_5 represents the molecular weight corresponding to each element.

Below is the conversion Equation (2):

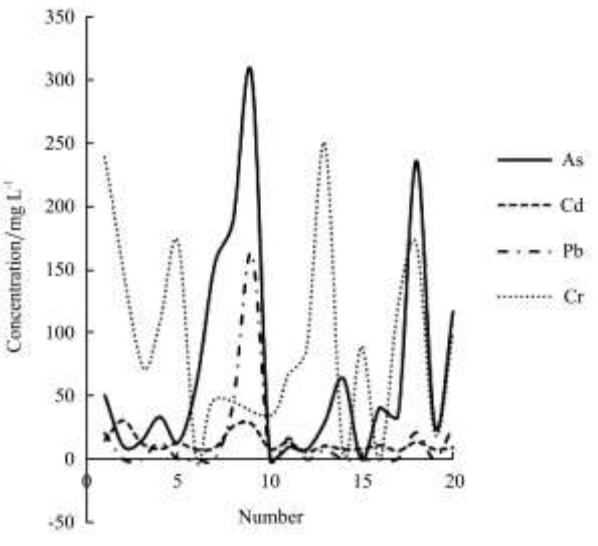
$$A = c \times (200/C) \quad (2)$$

where, A is the heavy metal content after conversion, mg/L; c is the actual value of heavy metals, mg/L; C is the number of elements, mg/L; 200 is a constant which come from water soluble humic acid fertilizer liquid product technical indicators is the minimum requirements (a large number of elements ≥ 200 g/L).

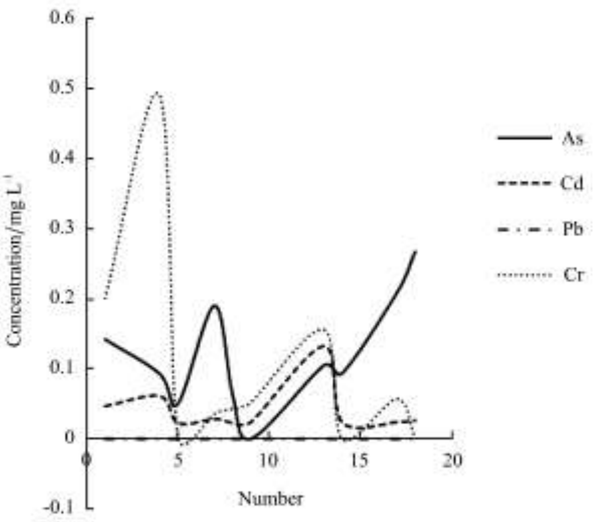
The conversion results were showed in Figure 3. The absolute contents of heavy metals after centrifugation declined significantly compared with that before centrifugation. Those ratios are 63.6%, 32.4%, 79.3% 100% for As, Cd, Cr, Pb, respectively. Conversion results showed (Table 7) that Cd, Pb and Cr did not exceed the standard after centrifugation except for As.

Table 7 Comparison between standard values and heavy metals in original fluid and the centrifugal solution after conversion

Exceed ratio	As	Cd	Pb	Cr
Original fluid/%	80	50	5	70
Centrifugal solution/%	70	20	0	10
Original fluid average	exceeded	exceeded	Not exceeded	exceeded
Centrifugal solution average	exceeded	Not exceeded	Not exceeded	Not exceeded



a. Original fluid



b. Centrifugal solution

Figure 3 The contents of As, Cd, Pb, and Cr after conversion

4 Discussion

4.1 Biogas slurry residue sources of heavy metals

The properties of biogas residues from different biogas project are very different; there are a lot of factors and the differences among the fodder matter. Feed additive is the core of feed. At present, there are 18 categories, hundreds of varieties of feed additives in the China's domestic market, including amino acids, vitamins, minerals, other non-nutritional additives, and pharmaceutical additives[17].

Contaminant levels are intimately linked with raw material of anaerobic fermentation. With the development of rural economy in China, more and more farmers use compound feed on pigs. Some heavy metals were retained in swine waste during pig's metabolism, which led to significant changes of biogas liquid fertilizer after the anaerobic fermentation[18,19].

Non-green feed additives used in swine industry include compounds of copper, iron and selenium, compound amino acids, phosphate rock, cobalt chloride, potassium iodide, hormones and other chemical ingredients which are all chemical constituents of western medicine and can bring toxic and side effects on animals and humans and serious environmental pollution[20]. Heavy metal in biogas residues mainly come from non-feed additives and mineral additives.

Because of the uneven development of feed industry, feed companies lack the knowledge on quality and safety; business practitioners lack knowledge of regulations; and market excessively pursues of nutritive index. All of these results in elements adding were above normal level[21].

4.2 Feasibility analysis of fertilizer residue slurry

Biogas slurry contains N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Mo, Cl and the other 16 kinds of essential elements, which belong to fertilizer ingredients. Biogas slurry can reduce the input of chemical fertilizer and improve soil fertility after returning to the field[22]. By comparison of the results with the standard, part of sampling points after centrifugation exceeded standard, while the soil itself has carrying capacity.

In addition, heavy metal contents of the fertilizer in the market also exceeded standard in varying degrees. Chen et al.[23] investigated the heavy metal contents of fertilizer from Hangzhou, Ningbo and other places, and the results showed that the amount ranges of Cd, Pb, Cu, Zn were 0. 02-6.56, 0.07-35.93, 0.11-164.95, 0.75-459.87 mg/kg, respectively. Organic fertilizer has the highest amount of Cd, Cu, Zn, calcium superphosphate has the highest amount of Pb, urea and potassium have a low level of heavy metal content. According to relevant standards, the over-limit ratios of Cd, Cu, and Zn were 24.1%, 13.8% and 17.2%, respectively. There is a pollution tendency of higher concentration and larger region of heavy metal with the development of economy.

Scholars have done some researches on fertilizer characteristics and the effect on soil microenvironment using biogas residues fertilizer. Abubaker[24,25] studied that fertilization with biogas residues gave similar biomass yields but increased nitrogen mineralization capacity and potential ammonium oxidation rate in soil compared with mineral fertilizer and the effects of biogas residues on microbial activities were comparable in magnitude to those of cattle slurry and the bacterial community structure was less affected. There was no reason for not recommending using biogas residues as fertilizers.

Based on above analysis, biogas residues are effective agricultural resources and rational use is needed. After treatment biogas residues can be used as fertilizer, especially after removal of TS, which can be applied as water-solubility fertilizer.

4.3 Method and countermeasures for processing biogas residue slurry

During treatment process, with the precipitation and anaerobic treatment, heavy metals enrich in the middle solid and finally in biogas residues[26].

The amount of biogas residues from biogas projects in China is more than 200 million tons every year. For the biogas users, processing methods cannot be too complicated and the economic costs are not too much. Further and more research is needed for exploring simple and effective treatment methods[27].

The nutrient and heavy metal content of biogas residues have significant difference in different seasons as well as different raw material of anaerobic fermentation, unified processing is needed in order to achieve a unified standard[26].

The method for removal of suspended matter applied in this study is centrifugation, which is simple and easy to operate. We have to be aware that further processing is usually necessary since heavy metals still exceed standard after TS-removal. Therefore, the TS-removal can be used as a pretreatment method.

4.4 Safety assessment of biogas fertilizer

There are many reports about the issues of arsenic. The study by Zhao et al.[28] showed that Cd, Cr, Hg in the soil where biogas residues were used as fertilizer increased slightly compared with the control which used pure water as fertilizer, Pb and As showed little change, but all meet the national soil environmental quality standard (GB15618-1995). But the level of Cd, Cr, Pb in the maize grain increased slightly with the increase of biogas fertilizer, while As still has little change and all meet the food limited Standard (GB2762-2005).

It indicated that using the right amount of biogas residues can make a greater contribution to the resource utilization and will not bring risk of heavy metal contamination of soil and plants. Zhang et al.[29] reported that using biogas slurry as basal fertilizer or topdressing fertilizer can significantly promote tillering and growth of rice, the level of Cu, Cd of rice did not change significantly, but it specially fortified Zn, Fe and significantly reduced the Pb content, the nutritional quality of rice was significantly improved. The test also showed that it was unfavorable for rice growth and yield that biogas completely replaces chemical fertilizer.

Studies have shown that As level in plant and soil did not change significantly when fertilizing biogas residues mixed with chemical fertilizer[28], the rich collection effect of As on the soil surface layer was not obvious.

Contents of four heavy metal elements (As, Hg, Cd, Pb) in soil (in 1989, 1995, 1998, and 2001) in a long-term fertilization experiment were investigated by Chen et al[30]. The results showed that the contents of four heavy metal elements were increased along with cultivation time as a whole and the increase varied in the order of Hg > Cd > Pb > As. All the four elements investigated, however, did not exceed the first grade criteria of the national standard for environmental quality by 2001.

Lu et al.[31] reported that the level of heavy metal of groundwater quality, test soil and rice were not affected by the biogas residues fertilizer. To ensure food safety, environmental carrying capacity and rice production, 867-1734 m^3/ha was given as the appropriate amount of biogas residues fertilizer.

It indicated that there is a certain risk for biogas liquid as fertilizer without any treatment and heavy metals in soil enrichment can be caused by long-term fertilization. There are certain risks in the process of biogas completely replacing chemical fertilizers. For safely returning to field biogas, slurry residue still need to be processed.

5 Conclusions

1) Biogas slurry contains a lot of heavy metals, exceeding the national wastewater discharge standards and irrigation water quality standards, which cannot be directly used for farm irrigation;

2) TS-removal by centrifugation can significantly reduce the heavy metal content, but it cannot remove all of heavy metals, with still some exceeding standards. After excluding heavily polluted spot the application of TS-removal slurry as water-solubility fertilizer is feasible.

3) The majority of heavy metals have significant correlation with TS, TS-removal has a good effect on removal of heavy metals and can be used as treatment or pretreatment process for biogas slurry.

Acknowledgements

This work was supported by Tongji Eco-park and biogas project in Chongming County, shanghai. Authors also would like to express gratitude to Shen Wenyan, Fan Biying,Wang Yaohua, Chen Tinghua and all the personnel working in the field for their supports and suggestions.

[References]

[1] Jin H M, Chang Z Z, Ye X M, Ma Y, Zhu J. Physical and chemical characteristics of anaerobically digested slurry from large-scale biogas project in Jiangsu province. Transactions of the Chinese Society of Agricultural Engineering, 2011; 27(1): 291-296. (in Chinese with English abstract)

[2] Li Y Q, Yang L J, Zhang N H. Safety and content analysis of biogas residues heavy metal from pig farm. Agro-Environment and Development, 2012; (3): 106-108. (in Chinese with English abstract)

[3] Fuentes A, Lloréns M, Sáez J, Soler A, Aguilar M I, Ortuño J F, et al. Simple and sequential extractions of heavy metals from different sewage sludges. Chemosphere, 2004; 54(8): 1039-1047.

[4] Fuentes A, Lloréns M, Sáez J, Isabel Aguilar M, Ortuño J F, Meseguer V F. Comparative study of six different sludges by sequential speciation of heavy metals. Bioresource Technology, 2008; 99(3): 517-525.

[5] He Q, Mhamadi T A, Ji F Y, Yu D N, Zhou G M, Li S. Simultaneous determination of heavy metals in waste and biogas slurry of scale farm by microwave digestion/ inductively coupled plasma-mass spectrometry. Spectroscopy and Spectral Analysis, 2012; 32(12): 3399-3401. (in Chinese with English abstract)

[6] Dąbrowska L, Rosińska A. Change of PCBs and forms of heavy metals in sewage sludge during thermophilic anaerobic digestion. Chemosphere, 2012; 88(2): 168-173.

[7] Zhang X W. Effect of biogas slurry irrigation on plants, water and soil water environment. Southwest University, 2012. (in Chinese with English abstract

[8] Liu Y P, Zhang J F, Zou D X, Yuan H R, Li X J. Security risk analysis on the nutrients and heavy metals of biogas slurry in agricultural application. Agricultural Science & Technology, 2012; 13(5): 1067-1072.

[9] Ni L, Sun G H, Luo G E, Shi W Y, Lu H, Ye W Z. Effect of marsh gas sewage irrigation on soil quality. Soils, 2008; 40(4): 608-611.(in Chinese with English abstract)

[10] Li Y Z, Li G X, Diao J X, Zhu J B, Sun Y. The optimization of straw xanthates' synthesis condition and the application in elimination of heavy metal ions from biogas slurry. Journal of Agro-Environment Science, 2012; 31(9): 1848-1853. (in Chinese with English abstract)

[11] Xu Y Z, Ma C, Cheng Y X, Wang Q Q, Zhong Z Y. Removal of heavy metals from sludge by bio-leaching. Journal of Southwest Jiaotong University, 2012; 47(1): 169-174. (in Chinese with English abstract)

[12] Gao Z X, Wu Y H, Zhao J H, Mou Q S, Zhou G M, Luo Y W, et al. Determination of heavy metal elements in biogas slurry with inductively coupled plasma mass spectrometry (ICP-MS). Journal of Southwest University (Natural Science Edition), 2013; 35(1): 104-108. (in Chinese with English abstract)

[13] Ministry of agriculture, environmental protection institute. Irrigation water quality standards. (in Chinese with English abstract)

[14] Beijing environmental protection science research institute. Wastewater discharge standards. (in Chinese with English abstract)

[15] Beijing national quality supervision and inspection center of fertilizer containing humic acid soluble fertilizers. The industry standard -Agriculture. (in Chinese with English abstract)

[16] Beijing national fertilizer quality supervision and inspection center, Beijing new fertilizer quality supervision and inspection station, Chengdu, Ministry of agriculture fertilizer quality supervision and inspection center soluble fertilizers mercury, arsenic, cadmium, lead, chromium limit its determination. Industry standards-Agriculture. (in Chinese with English abstract)

[17] Fu T L. The market and current situation of Chinese feed additives analysis. Fine Chemicals, 1997; 1: 3-6. (in Chinese with English abstract)

[18] Li J, Zheng S X. Preliminary study on the heavy metal content in biogas manure. Renewable Energy Resources, 2009; 27(1): 62-64. (in Chinese with English abstract)

[19] Tulayakul P, Boonsoongnern A, Kasemsuwan S, Wiriyarampa S, Pankumnoed J, Tippayaluck S, et al. Comparative study of heavy metal and pathogenic bacterial contamination in sludge and manure in biogas and non-biogas swine farms. Journal of Environmental Sciences, 2011; 23(6): 991-997.

[20] Liu Y L, Ren Z A, Yan M J. Feed additive status and development trend. Journal of Animal Science and Veterinary Medicine, 2008; 27(5): 36-37. (in Chinese with English abstract)

[21] Zhao W N. The detecting results analysis of the heavy metals (lead, cadmium) in pig feed. Jiangxi Agricultural University, 2011. (in Chinese with English abstract)

[22] Xiong D W, Xie J, Wu Z L, Yang C F, Yu P. A Set of integrated fertilizer and water irrigation equipment on disposal of biogas slurry pollution-free and utilization. South China Agriculture, 2011, 5(3): 5-9. (in Chinese with English abstract)

[23] Chen L H, Ni W Z, Li X L, Sun J B. Investigation of heavy metal concentrations in commercial fertilizers commonly-used. Journal of Zhejiang Sci-Tech University, 2009; 26(2): 223-227. (in Chinese with English abstract)

[24] Abubaker J, Cederlund H, Arthurson V, Pell M. Bacterial community structure and microbial activity in different soils amended with biogas residues and cattle slurry. Applied Soil Ecology, 2013; 72: 171-180.

[25] Abubaker J, Risberg K, Pell M. Biogas residues as fertilisers – Effects on wheat growth and soil microbial activities. Applied Energy, 2012; 99: 126-134.

[26] Ye M F, Wu F L, Lin D Y. Large-scale pig manure dynamic flow analysis of heavy metals. Energy and Environment, 2010; (4): 15-16. (in Chinese with English abstract)

[27] Sun G H. Studies on the effects of vegetable yield and qualities and soil qualities after application of biogas slurry. Zhejiang University, 2006. (in Chinese with English abstract)

[28] Zhao Q L, Wu J, Chen B X, Lv W L. Effect of biogas slurry on heavy metal accumulation of soil and maize. Journal of Soil and Water Conservation, 2012; 26(2): 251-255. (in Chinese with English abstract)

[29] Zhang J, Zhang M X, Shan S D, Luo L P, Wang M Y. Grain yield and heavy metals content of rice (Oryza sativa L.) as affected by biogas slurry application. Journal of Agro-Environment Science, 2009; 28(10): 2005-2009. (in Chinese with English abstract)

[30] Chen F, Dong Y H, An Q, Qin S W. Variation of Soil heavy metal contents in long-term fertilization experiment. Soils, 2005; 37(3): 308-311. (in Chinese with English abstract)

[31] Lu J, Jiang L, Chen D, Toyota K, Strong P J, Wang H, et al. Decontamination of anaerobically digested slurry in a paddy field ecosystem in Jiaxing region of China. Agriculture, Ecosystems & Environment, 2012; 146(1): 13-22.