The adsorption effect of three minerals on chemical oxygen demand, total nitrogen, total phosphorus and heavy metals in biogas slurry

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Abstract. Contraposing the intractable problem of high content of nitrogen, phosphorus and heavy metals in biogas slurry from livestock and poultry farm, the adsorption effect of three minerals (montmorillonite, kaolin and acticarbon) on chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP) and heavy metals (Zn, Cu, Cr and As) have been studied. In addition, the mineral material with good adsorption effect has been screened. Based on the screened mineral material, the adsorption effects of screened mineral material dosage and the initial pH value of biogas slurry on COD, TN, TP and heavy metals have been analysed. The results show that the adsorption effect of montmorillonite (MMT) is obvious, followed by kaolin and acticarbon. Concretely, the removal rates of TP, Zn, Cu, Cr are up to 63.0%, 72.1%, 67.4%, 58.5% respectively adsorbed by MMT; What is more, the removal rate increased by the increase of MMT dosage. Nevertheless, the adsorption of COD and TN gradually reaches equilibrium when the dosage of MMT is 3%. Likewise, the removal rate of TP, Zn, Cu and Cr increase slowly. In comparison, As has a highest removal rate, up to 58.5%. The adsorption of COD, TN, TP and heavy metals has little effect with the increase of pH adsorbed by MMT, while the removal rate of TP sharply increases with the increase of pH, from 29.1% to 77.8%. Specially, the removal rates of TP range from 71.6% to 77.8% when pH is between 8.0 and 9.5. All of the results indicate that MMT is the optimal adsorption material, and the optimum MMT dosage is 3%, the appropriately initial pH of biogas slurry is alkaline.

1. Introduction
With the continuous expansion of the scale of livestock breeding, the environmental problems caused by the massive discharge of livestock and poultry manure have become increasingly serious and have caused widespread concern [1]. Biogas slurry is a by-product of animal manure after anaerobic fermentation, which contains abundant N, P and K and organic matter [2]. Hence, biogas slurry is considered to be a superior liquid fertilizer [3,4]. However, biogas slurry should not be directly applied to farmland due to high concentrations of COD, N, and P contained in the biogas slurry. High concentrations of COD, N and P will cause seedling burnt and crop yield reduction [5]. After
anaerobic fermentation of livestock and poultry manure, 90% of the nutrients retain in the biogas slurry and biogas residue. The heavy metals detected in the biogas slurry are mainly Cu, Zn, Pb, Cd, As and Cr [6-9]. “Raising pigs -biogas - growing vegetables” is an eco-cycle agriculture model, which has been used to apply biogas slurry to fields through irrigation by the large-scale and medium-scale pig farms [10]. The heavy metals in biogas slurry contain high levels of Cu, Zn, As and Cr [11,12], which are much higher than the requirements of the water quality standards for farmland irrigation, and these are seriously excessive. Marcato studied the bioavailability of Zn and Cu in pig manure slurry [13]. Pig manure slurry will lead to the risk of Zn and Cu pollution and harm the healthy [14] of human beings by long-term agricultural irrigation of ineffectively treated biogas slurry. The amount of biogas slurry produced by biogas projects is far greater than that of surrounding farmland [3,15,16]. High-strength biogas slurry with difficult management is directly irrigated around the farmland, and there is a high risk of heavy metal pollution.

Therefore, in order to reduce the potential pollution risk of biogas slurry for agricultural irrigation and to use the huge organic fertilizer resources of livestock farms more safely and rationally [17], it is necessary to choose a mineral material for adsorption treatment of biogas slurry, reducing the concentrations of N, P and heavy metals, and decreasing the load for farmland soil. In this paper, the adsorption effects of different mineral adsorbent materials, dosage and initial pH of biogas slurry on COD, TN, TP, Zn, Cu, etc. in biogas slurry were studied, which will help to provide a new way for biogas slurry agricultural irrigation.

2. Materials and methods

2.1. Sample Collection

The biogas slurry sample was taken from a large-scale biogas project in a pig-breeding farm from Mianyang. The farm now has a total of 3,200 sows and slaughters 45,000 pig annually. The biogas slurry was taken from marsh gas tank and collected the supernatant fluid. After sealing, it was brought back to the laboratory for subsequent analysis. The basic properties of the biogas slurry are shown in Table 1.

| Factor | Measured value | Standard value* | Exceeding standard times | Factor | Measured value | Standard value* | Exceeding standard times |
|--------|----------------|----------------|--------------------------|--------|----------------|----------------|--------------------------|
| COD    | 7615.00        | 200            | 37.1                     | Cu     | 5.68           | 1              | 4.7                      |
| TN     | 1765.20        | 100            | 16.7                     | Cr     | 0.41           | 0.1            | 3.1                      |
| TP     | 55.81          | 8              | 6.0                      | Cd     | ND             | 0.01           | --                       |
| Zn     | 18.68          | 2              | 8.3                      | As     | 0.37           | 0.1            | 2.7                      |
| Pb     | ND             | 0.2            | --                       | pH     | 8.14           | 6.5-8.5        | --                       |

* Requirements for water quality standard for farmland irrigation (GB5084-2005).

2.2. Experimental methods

Study the adsorption of COD, TN, TP, Zn, Cu, As, and Cr in biogas slurry by different mineral materials (MMT, kaolin, and activated carbon) at 25°C. When the dosage of MMT is 3%, a mineral material with better adsorption effect was selected for determining the optimal dosage and pH; the dosage of adsorbent was changed to 0%, 1%, 1.5%, 2%, 2.5%, 3%, 5 %, respectively; the pH of the biogas slurry was adjusted with NaOH or HCl to be 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, respectively, and the original pH of the biogas slurry was 8.14 which was used as a control.

Biogas slurry was taken 500mL in a beaker, and then stirred 60min in a six-coupling agitator under moderate speed (150 r min⁻¹). After static for 60min, the supernatant about 2cm below the liquid
surface was taken to centrifuge for 10 min, through the centrifuge at the speed of 4000 r min⁻¹, and the supernatant was used for follow-up experiments.

2.3. Test methods
The content of heavy metals in biogas slurry was analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer, Optima 8300, America) after digested by the method of "Water quality -Total metal -Nitric acid digestion" (HJ677-2013). pH was determined with pHS-320 Acidmeter. Chemical oxygen demand in biogas slurry was determined by Rapid Digestion Method (HJ/T399-2007). Total nitrogen was determined by Alkaline Potassium Persulfate UV Spectrophotometry (HJ636-2012). Total phosphorus was determined by Ammonium Molybdate Spectrophotometric Method (GB11893-1989).

3. Results and discussion

3.1. Effect of mineral materials on various components in biogas slurry
As was shown in Figure 1, the removal effect of COD in biogas slurry absorbed by mineral materials is MMT>acticarbon>kaolin, and the COD removal rate of the three minerals are 32.2%, 14.0% and 11.6% respectively. As for TN, the removal effect is MMT>kaolin>acticarbon, and the removal rate of the three minerals is 32.6%, 31.6% and 8.6% respectively. And the adsorption effect of TP is MMT>kaolin>acticarbon, and the corresponding removal rate is 63%, 50.9%, 9.3%. The results show that the adsorption effect of COD, TN and TP by MMT is more obvious compared with kaolin and acticarbon. The MMT has the similar removal effect with kaolin on TN, while MMT has an obvious removal effect on TP compared with kaolin. This is because the addition of kaolin could increase the dissoluble phosphorus in biogas slurry.

There is certain removal effect on heavy metals through adding MMT, kaolin and acticarbon (Figure 1). Comparing with initial biogas slurry (the concentration of Zn, Cu, As and Cr is 18.68 mg L⁻¹, 5.68 mg L⁻¹, 0.37 mg L⁻¹ and 0.41 mg L⁻¹, respectively), the adsorption effect of MMT on Zn, Cu, As is much higher than kaolin and acticarbon, and the removal rate is 72.1%, 67.4% and 58.5% respectively. Specially, acticarbon has the optimized adsorption effect on Cr in biogas slurry, up to 17.3%. Which is corresponding to the researched results [18], not only the acticarbon has a good adsorption effect on Cr under weak alkaline environment, but also the acticarbon can be reused.

3.2. Effect of the MMT dosage on various components in biogas slurry
The removal rate of COD and TN gradually increases with the increase of MMT dosage. The adsorption of COD and TN tend to equilibrium when MMT dosage is 3%, and the removal rate of COD and TN is 32.2%, 32.6% respectively. While TP slightly increases with the increase of MMT dosage, and the removal rate of TP ranges from 42.6% to 74.3% when MMT dosage increases from 1% to 5%. This is mainly because phosphate ions have a higher affinity for MMT adsorption sites. As a fact, the removal rate of TP slightly increases with the increase of MMT dosage and tends to equilibrium.

The adsorption amounts of Zn and Cu in biogas slurry gradually increase with the increase of MMT adding amount (Figure 2c). The removal rates of Zn and Cu are 72.1% and 67.4% respectively. And the adsorption of Zn and Cu tends to equilibrium when MMT dosage is more than 3%. Specially, the removal rate of As is the highest, up to 58.5%. And the removal rate of Cr obtains to the highest when MMT adding amount is 2.5%. The concentration of Cr ranges from 0.450 mg L⁻¹ to 0.293 mg L⁻¹ while MMT dosage increases from 0% to 2.5%. The removal rate of Cr is not as good as to As, maybe MMT has a stronger adsorption capacity for As.
3.3. Effect of pH on adsorption of various components in biogas slurry

The pH of solution will cause the change of electrostatic potential on the surface of MMT, which is one of the important factors affecting the adsorption effect. In fact, it is not obvious for the removal effect of COD through changing the initial pH when adding MMT (Figure 3a). In this study, the removal rate of COD ranges from 10.1% to 21.2%, and the highest removal rate is obtained at a pH of 7.5. While pH has an obvious effect for the adsorption of TN and TP (Figure 3b). Specially, the removal rate of TN and TP increases with the increase of pH, which increases from 14.0% to 33.5% and 29.1% to 77.8% respectively. The reasonable explanation for this phenomenon is that phosphate ions absorbs Ca$^{2+}$ and forms precipitate under weak alkaline condition, which leads to decrease the concentration of TP in the biogas slurry. The adsorption tends to equilibrium with a removal rate of 71.6%, when the pH is 8.0.

The result of the effect of pH on MMT adsorbing biogas slurry shows that pH has little influence for removing Zn, Cu, Cr and As (Figure 3c). And the removal rate of Zn and Cu ranges from 60% to
80%. The concentration of Zn and Cu is between 6 and 8 mg L\(^{-1}\) after adsorbed by MMT. Likewise, the removal effects of Cr and As are 0.3-0.4 mg L\(^{-1}\) and 0.1-0.2 mg L\(^{-1}\), respectively. As well as, table 2 shows that pH has little differences for the adsorption effect of COD (CV, 6%), TN (CV, 11%), Zn (CV, 12%), Cu (CV, 13%), Cr (CV, 17%) and As (CV, 25%). While, MMT has a significant adsorption effect on TP (CV, 62%). Overall consideration of the removal rate, the alkaline pH is the optimum condition for MMT to adsorb various components in the biogas slurry.

| Biogas slurry properties | Mean (mg L\(^{-1}\)) | Minimum (mg L\(^{-1}\)) | Maximum (mg L\(^{-1}\)) | CV (%) |
|--------------------------|----------------------|-------------------------|-------------------------|--------|
| COD                      | 6598.86              | 6001.60                 | 7296.80                 | 6      |
| TN                       | 1343.91              | 11173.10                | 1682.10                 | 11     |
| TP                       | 24.71                | 12.40                   | 51.70                   | 62     |
| Zn                       | 6.74                 | 5.59                    | 8.03                    | 12     |
| Cu                       | 2.16                 | 1.72                    | 2.59                    | 13     |
| Cr                       | 0.35                 | 0.26                    | 0.40                    | 17     |
| As                       | 0.15                 | 0.11                    | 0.21                    | 25     |

4. Conclusion
Comparing with the initial biogas slurry, there are significant changes in COD, TN, TP, Zn, Cu, Cr and As when the biogas slurry treated by mineral materials (MMT, kaolin, acticarbon). According to the adsorption effect of COD, TN, TP, Zn, Cu, Cr and As, the removal rate ranks as: MMT > kaolin > acticarbon. And MMT can be chosen as an adsorbent to reduce the potential risks of the biogas slurry irrigation.

The removal rate of various components contained in biogas slurry increases with the increase of MMT dosage, and the adsorption effect of COD, TN, TP, Cu and Zn tends to equilibrium when MMT dosage is 3.0%. As has the highest removal rate, up to 58.5%. Comprehensive consideration, the optimum dosage of MMT is 3.0%.

There is little effect for pH to adsorb various components contained in biogas slurry when the biogas slurry is alkaline. But MMT adsorbed 71.6% to 77.8% TP when pH ranges between 8.0 and 9.5. Hence, the alkaline environment of biogas slurry is chosen for MMT to adsorb various components.

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