Phosphorus recovery from biogas slurry by ultrasound/H_2O_2 digestion coupled with HFO/biochar adsorption process

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A B S T R A C T

Phosphorus (P) recovery from biogas slurry has recently attracted considerable interest. In this work, ultrasound/H_2O_2 digestion coupled with ferric oxide hydrate/biochar (HFO/biochar) adsorption process was performed to promote P dissolution, release, and recovery from biogas slurry. The results showed that the optimal total phosphorus release efficiency was achieved at an inorganic phosphorus/total phosphorus ratio of 95.0% at pH 4, 1 mL of added H_2O_2, and ultrasonication for 30 min. The P adsorption by the HFO/biochar followed pseudo second-order kinetics and was mainly controlled by chemical processes. The Langmuir-Freundlich model matched the experimental data best for P adsorption by HFO/biochar at 298 and 308 K, whereas the Freundlich model matched best at 318 K. The maximum amount of P adsorbed was 220 mg/g. The process was endothermic, spontaneous, and showed an increase in disorder at the solid-liquid interface. The saturated adsorbed HFO/biochar continually releases P and is most suitable for use in an alkaline environment. The amount of P released reached 29.1 mg/g after five extractions. P mass balance calculation revealed that 11.3% of the total P can be made available.

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1. Introduction

The loss of phosphorus (P) not only results in water eutrophication, but also relates to non-renewable P resource waste (Elser and Bennett, 2011). With the notable increase in intensive farming in China, biogas projects have become biomass energy systems that provide clean energy and reduce environmental pollution (Noike and Mizuno, 2000). However, many problems still exist in the processing of fermentation residues, such as biogas slurry and residue. Biogas slurry is the liquor from anaerobic digestion process, in which biodegradable organic waste (such as human and animal feces or various agricultural and forestry wastes) at a certain moisture content, temperature, and in the presence of methanogenic bacteria yields fermentation products after the production of methane and carbon dioxide under airtight anaerobic conditions. Little research has focused on nutrient management in large amounts of biogas slurry. This not only restricts reasonable resource recycling and causes P pollution of the environment, but also hinders the development and application of biogas projects.

Meanwhile, P, as one of the three most important elements involved in plant growth, is indispensable to agriculture and important for food security. Gilbert (2009) stated that the total global reserves of P should be adequate for nearly a hundred years, but, depending on exploitation technologies and economics, in fact may only last for approximately 50 more years.

Therefore, the recovery of P contained in biogas slurry is important for P pollution relief and nutrient recycling. There are two main problems inhibiting the practical recovery of P from biogas slurry. Firstly, organic phosphorus (OP) (mainly referring to phospholipids, DNA, simple phosphate monoesters and phytic acid P (Dai et al., 2015; Ekpo et al., 2015, 2016) and sparingly soluble P contained in the feces) that cannot be directly recovered, so it is necessary to perform P-solubilization processes to release phosphate into the supernatant (Gong et al., 2015a). Secondly, owing to the many kinds of substances contained in biogas slurry, recovery methods with high selectivity towards P are required.

Advanced oxidation technologies to digest organic feces have recently become a hot topic, including ultrasonic degradation (Gong et al., 2015a), H_2O_2 oxidation (Gifford et al., 2015), ozone oxidation (Matusiewicz, 2001), and photocatalytic degradation (Tong et al., 2015). Ozone oxidation performs strongly in terms of oxidation effectiveness, but poorly in terms of ozone utilization efficiency (Ikehata et al., 2006). Photocatalytic degradation performs well in terms of low energy consumption and rapid response, but poorly in terms of light utilization (Pehkonen and

Zhang, 2002). H_2O_2 oxidation has the advantage of strong reactivity and does not produce secondary pollution (Dargahi et al., 2015). Ultrasonic degradation does not require exogenous substances and uses only its own ultrasonic field effect (Naddeo et al., 2015). Recently, an ultrasound/H_2O_2 degradation process has been used to treat organic pollutants because it does not cause waste accumulation or secondary pollution (Zhang et al., 2011). The treatment of biogas slurry by such an ultrasound/H_2O_2 process can digest organic substances through both the ultrasonic field effect that can overcome the rate-limiting step and reduce the digestion time (Khanal et al., 2007) and the catalytic decomposition of H_2O_2 into effective oxyradicals, such as ·OH and ·OOH. Coupling the two processes can improve the digestibility of phosphorus (Appels et al., 2008). H_2O_2 is both a source of ·OH and an agent for its elimination, so the amount of H_2O_2 is an important factor for the successful application of the ultrasound/H_2O_2 process (Zhang et al., 2011).

Common methods for the highly selective recovery of P include chemical precipitation, adsorption/desorption, crystallization, and membrane technologies. Chemical precipitation can recover a high concentration of P rapidly but has problems such as high cost, incomplete precipitation, and the generation of large amounts of chemical sludge. Crystallization can reduce the amount of chemicals required for the precipitation reaction, but fine crystals will be lost by entrainment in the effluent, resulting in downstream scaling and plugging (Zhang et al., 2014). Membrane processes commonly suffer from membrane pollution and high processing cost. The adsorption/desorption method involves a simple process, convenient control, low resource consumption, and easy recycling, but suffers from problems such as low adsorbent capacity and selectivity (Fang et al., 2014). Consequently, research has focused on modified adsorbents loaded with metal oxide. Fang et al. (2015) developed a Ca-Mg/biochar adsorbent with an improved ability to adsorb P from biogas slurry, but dissolved organic matter in the biogas slurry occupied the adsorption sites. Research into ferric oxide hydrate (HFO) modified adsorbents has recently attracted significant interest. HFO has been found to be strongly selective towards P adsorption (Dixit and Hering, 2003; Lee et al., 2007), while possessing the advantages of easy production method, low material cost, and low ecotoxicity (Pan et al., 2009a).

In the current work, an ultrasound/H_2O_2 process was adopted to improve the solubilization of biogas slurry and optimize the conditions to promote the performance of OP and other sparingly soluble P species to convert into soluble IP. An HFO/biochar absorbent for P recovery was also synthesized. The surface morphology and chemistry, adsorption kinetics, adsorption isotherms, and thermodynamic calculations of the HFO/biochar were investigated. Finally, the P availability of the saturated adsorbed HFO/biochar was identified and the P mass balance calculation was evaluated.

2. Materials and methods

2.1. Materials

Raw biogas slurry was obtained from an anaerobic digestion tank at a pig farm near Beijing, China. The sample was stored in an icebox prior to experiments. Table 1 shows the parameters of the biogas slurry sample.

To synthesize the HFO/biochar adsorbent, ground cornstraw was charred at 500 °C for 3 h in a muffle furnace and then dipped in 0.8 mol/L $FeCl_3$ solution at a mass to volume ratio of 1:10. Next, 5 mol/L NaOH solution was added to the mixture to adjust its pH to 7 and the mixture was reacted for 24 h. Finally, the synthesized HFO/biochar sample was cleaned with deionized water (DI) to

Table 1
Characteristics of biogas slurry samples.

Items	Value
pH	8.30 ± 0.1
Electrical conductivity (mS/cm)	8.20 ± 0.15
COD (mg/L)	3492 ± 68
NH_4^+-N (mg/L)	649 ± 54
Total P (mg/L)	72.45 ± 3.45
PO_4^{3-}-P (mg/L)	9.48 ± 0.26
Available K (mg/L)	22.41 ± 2.79
Dissolved Fe (mg/L)	2.01 ± 0.88
Dissolved Zn (mg/L)	3.54 ± 1.95
Dissolved Mn (mg/L)	0.22 ± 0.1
Dissolved Mg (mg/L)	8.54 ± 1.31
Dissolved Ca (mg/L)	17.84 ± 3.51

remove residual surface ash, dried at 60 °C, and sealed in an airtight container until use.

2.2. Methods

Ultrasound/H_2O_2 digestion: 1–7 mL H_2O_2 was added to 50 mL of the biogas slurry at pH 4–10 and 30 °C, and then the mixture was reacted for 30 min. The supernatant was collected with a common filter after the reaction.

For kinetics adsorption experiments, 0.2 g samples of HFO/biochar were mixed with 20 mL of biogas slurry and shaken at 200 r/min at 298 ± 0.5, 308 ± 0.5, or 318 ± 0.5 K (pH is about 5). The supernatant was collected at specific time intervals using a 0.45-μm Millipore filter. Finally, the P adsorption kinetics of the biochar and HFO/biochar samples were fitted by three models (Huang et al., 2014; Rouquerol et al., 2013):

The linear expression of the pseudo first order kinetics equation as follows.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{1}$$

The linear expression of the pseudo second order kinetics equation as follows.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{2}$$

The particle diffusion equation as follows.

$$Q_t = k_{id} t^{\frac{1}{2}} + C \tag{3}$$

where Q_e (mg/g) represents the amount of adsorbed P at adsorption equilibrium, Q_t (mg/g) represents the amount of adsorbed P at adsorption time t; k_1 (h^{-1}), k_2 (g/(mg h)), and k_{id} (g/(mg h)) represent the reaction rate constants, and C is a constant related to boundary layer thickness.

To obtain the adsorption isotherms, 0.2 g samples of HFO/biochar were mixed with 20 mL of P solution (diluted biogas slurry or biogas slurry mixed with NaH_2PO_4 to obtain initial P concentrations in the range of 30–4000 mg/L) and shaken at 200 r/min at 298 ± 0.5, 308 ± 0.5, or 318 ± 0.5 K for 24 h until adsorption equilibrium was achieved (pH is about 5). Finally, the P adsorption isotherm was fitted by three isotherm equations as follows (Rouquerol et al., 2013; Yao et al., 2013a).

The Freundlich adsorption isotherm describes non-ideal adsorption on a non-uniform surface, and can be expressed as follows:

$$Q_e = K_F C_e^{1/n} \tag{4}$$

The Langmuir adsorption isotherm describes the monolayer adsorption on uniform surface, which can be expressed as follows:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{5}$$