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Evaluating the biogas conversion potential of sewage sludge by surface site density of sludge particulate

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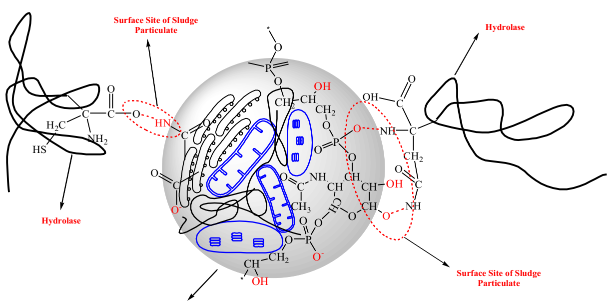
HIGHLIGHTS

- An evaluation index for biogas conversion potential of sewage sludge was proposed.
- Surface site of sludge particulate can be as the potential binding site for enzymes.
- A positive linear correlation between surface site density and efficiency was found.
- Surface site density of sludge particulate is considered to be the potential index.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a framework for conceiving an index that can quickly evaluate biogas conversion potential (BCP) of sewage sludge (SS) was proposed based on the surface site of sludge particulate (SP). As enzymes, the cornerstones of metabolism, are responsible for the efficiency of anaerobic digestion (AD) process, the adsorption of hydrolytic enzyme on the sludge with different surface site density (SSD) of SP was studied. The experimental results suggest that the surface site of SP can be considered as the binding site for hydrolytic enzyme, as confirmed by organic solubilisation tests of the sludge. To further explore the relationships between SSD and BCP of SS, the biochemical composition and long-term biochemical methane potential (BMP) tests of different sludge samples were conducted. The results show that both the methane production rate constant (k) and net cumulative methane production (NCMP) increased as the SSD values increased. Analyses of the statistical and fitting mathematical models for the SSD, biochemical composition, k, and NCMP revealed a significant positive linear correlation between k and NCMP versus SSD can be found ($R^2 = 0.910$, $P < 0.001$ and $R^2 = 0.939$, $P < 0.001$, respectively), indicating that the SSD of SP is a potential index to quickly evaluate the BCP of SS. These findings can enlighten environmental scientists on developing an evaluation index for the BCP of sludge without a long-term BMP test.

1. Introduction

The anaerobic sludge digestion is of great promise for the SS treatment as it removes odors and pathogens, stabilizes sludge and more importantly, produces renewable energy in the form of methane [1,2]. One of the main objectives for the current researches on AD of SS is to enhance the biogas productivity from

Abbreviations: AD, anaerobic digestion; SS, sewage sludge; NCMP, net cumulative methane production; BMP, biochemical methane potential; COD, chemical oxygen demand; TCOD, total chemical oxygen demand; BCP, biogas conversion potential; SP, sludge particulate; SSD, surface site density; DOM, dissolved organic matter; TS, total solid; VS, volatile solid; BSA, bovine serum albumin; STOC, soluble total organic carbon; TOC, total organic carbon; Q_e, equilibrium adsorption quantity; k, methane production rate constant.

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sludge. The evaluation index for the biogas productivity from SS is indispensable. According to the literature in the field of anaerobic sludge digestion, the k and NCMP (per unit organic matter) are currently the indexes most commonly used to evaluate the biogas productivity [3–7]. However, it usually takes a long time to obtain the two indexes due to the long solid retention time (more than 30 days). It is well known that the anaerobic biodegradability of organic matter in sludge depends on its quantity and composition [8,9], Mottet et al. [10] have found that the biodegradability can be expressed as a function of sludge's characteristics by using the partial least square regression technique. It enlightens us that the k and NCMP could be evaluated by the property of sludge rather than performing a long-term BMP test. From the standpoint of sludge's property, the BCP of SS can be proposed.

As is known to all, the AD process can be divided into four successive biochemical processes such as hydrolysis, acidogenesis, acetogenesis, and methanogenesis [11–15]. Because large amounts of complex organic matter are present in the form of particulates in SS, the hydrolysis process comprises the organic solubilisation from sludge particulates and hydrolysis of macromolecule organic matter, which is the biggest difference in the AD of SS and wastewater. This also suggests that the hydrolysis process is more complicated in the AD process of SS. In fact, hydrolysis of sludge particulates has been acknowledged to be the rate-limiting step in many studies [16–20]. That is to say, the BCP of SS is mainly restrained by the hydrolysis process of sludge organic matter, implying that the BCP can be evaluated by the hydrolysis degree. Liao et al. [21] found that the surface property of SP and the interparticle interaction by the surface are the key factors for the stability of sludge flocs. Sanders et al. [22] also found that the hydrolysis degree of SP was mainly determined by its surface hydrolysis degree. Moreover, enzymatic hydrolysis can enormously improve the AD efficiency [23–25] and that the surface hydrolysis of organic particulate depends on the amount of surface available for the hydrolytic enzymes has been recognized in many studies [26–28]. Logically, the evaluation of BCP could be determined by the amount of surface available for the hydrolytic enzyme. It is clear today that the formation of an enzyme-substrate binary complex is the first step in the enzymatic process, and a binding site of the substrate which can be used to evaluate the amount of surface available for the hydrolytic enzyme is the essential prerequisite for forming an enzyme-substrate binary complex [29]. This suggests that if there were more binding sites as it can increase the probability in forming the enzyme-substrate binary complex, the enzymatic process could be more efficient. The surface sites of SP, consisting of the metal-specific functional groups such as phosphoryl, carboxyl, sulphydryl, and hydroxyl, have typically been treated as the metal and proton binding sites [30,31]. According to recent studies [29,32] these functional groups are also the potential binding sites for hydrolytic enzymes. Therefore, we hypothesized that the SSD of SP can be used to evaluate the BCP without a long-term BMP test.

The aim of this paper is to provide a framework for conceiving an index that can evaluate the BCP of SS with the assistance of NCMP and k. The SSD values and biochemical parameters of the sludge samples from different wastewater treatment plants were firstly measured. Then the soluble hydrolase (i.e., trypsase) adsorption and organic solubilisation of the SP with different SSD values were studied. To explore the relationships between the SSD and the NCMP and k, 40-day BMP assays with different sludge samples and corresponding statistical analyses for the parameters were carried out. Finally, the hypothesis that the SSD of SS could be a potential index for quick evaluation of the sludge's BCP was preliminarily confirmed.

2. Materials and methods

2.1. Protocol for measuring the SSD of SP

The surface site of SP was determined by acid-base titration. Sludge samples (mixed liquor) typically contain not only SP but also DOM and carbonate species, which also consume bases or acids during titration [30]. Thus, the net base or acid consumed by the surface site of SP can be obtained by subtracting the amount of base or acid consumed by DOM and carbonate species from the overall base or acid added to the system, according to the following equation:

$$\Delta V_{SP} = \Delta V_{Overall} - \Delta V_{DOM} - \Delta V_{Carbonate} \tag{1}$$

Where

$\Delta V_{Overall}$ = total volume of base or acid added during titration, mL;
ΔV_{DIM} = volume of base or acid consumed by DOM, mL;
$\Delta V_{Carbonate}$ = volume of base or acid consumed by carbonate species, mL.

According to Wang et al. [30], ΔV_{SP}, ΔV_{DOM} and $\Delta V_{Carbonate}$ can be obtained by the following equations, respectively:

$$\Delta V_{SP} = \frac{V_0 S_T K_H}{C}\left\{\frac{1}{[H^+] + K_H} - \frac{1}{[H^+]_0 + K_H}\right\} \tag{2}$$

$$\Delta V_{DOM} = \frac{V_0 C_A K_{aA}}{C}\left\{\frac{1}{[H^+] + K_{aA}} - \frac{1}{[H^+]_0 + K_{aA}}\right\} \tag{3}$$

$$\Delta V_{Carbonate} = \frac{V_0 C_T K_{a1}}{C}\left\{\frac{1}{[H^+] + K_{a1}} - \frac{1}{[H^+]_0 + K_{a1}}\right\} \tag{4}$$

Where

S_T = total surface site concentration, M;
K_H = acidity constant;
$[H^+]$ = proton concentration in the bulk solution, M;
$[H^+]_0$ = proton concentration in the control unit to which no base or acid was added, M;
C_A = total concentration of type A site, which is equal to 10^{-5} mol/mg COD [33], M;
K_{aA} = acidity constants of the type A, $pK_{aA} = 5.3$;
C_T = total concentration of carbonate species, which can be calculated by inorganic carbon concentration, M;
K_{a1} = first acidity constants of the carbonate, $pK_{a1} = 6.32$.

The detailed protocol for measuring the SSD of SP is as follows:

a) Transfer 50 mL of sludge sample to centrifugation tubes and centrifuge at 12000*g* for 20 min to separate solids from the solution. Correct the supernatant and determine its inorganic carbon and COD concentrations.
b) Transfer 50 mL of sludge sample to a 100-mL beaker. Titrate the pH of the sample from initial pH to 8 or 4, step-by-step, using 1.0 M perchloric acid ($HClO_4$) or sodium hydroxide (NaOH) at 0.01 mL per step. Record the volume of acid or base added.
c) Calculate the ΔV_{DOM} and $\Delta V_{Carbonate}$ at each titration point using Eqs. (3) and (4), respectively (the initial pH ranging from 6 to 8).
d) Calculate the ΔV_{SP} net base or acid consumed by SP at each titration point using Eq. (1).