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# Waste activated sludge hydrolysis and acidification: A comparison between sodium hydroxide and steel slag addition

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## ABSTRACT

Alkaline treatment with steel slag and NaOH addition were investigated under different pH conditions for the fermentation of waste activated sludge. Better performance was achieved in steel slag addition scenarios for both sludge hydrolysis and acidification. More solubilization of organic matters and much production of higher VFA (volatile fatty acid) in a shorter time can be achieved at pH 10 when adjusted by steel slag. Higher enzyme activities were also observed in steel slag addition scenarios under the same pH conditions. Phosphorus concentration in the supernatant increased with fermentation time and pH in NaOH addition scenarios, while in contrast most phosphorus was released and captured by steel slag simultaneously in steel slag addition scenarios. These results suggest that steel slag can be used as a substitute for NaOH in sludge alkaline treatment.

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## Introduction

The number of wastewater treatment plants (WWTPs) worldwide has increased dramatically in recent decades due to rapid urbanization and population growth, resulting in a significant increase of waste activated sludge (WAS) production. Typically, WAS contains a large amount of organics, heavy metals and pathogens, which pose great threats to the environment, and its disposal cost can account for 20%–60% of the capital and operating cost of a WWTP (Fang et al., 2014; Su et al., 2013). Therefore, environmentally friendly and cost-effective means for sludge disposal are greatly needed.

Anaerobic digestion is one of the most widely used methods for activated sludge stabilization. Worldwide attention has been drawn to this technique due to its capability of simultaneously

achieving sludge mass reduction and generating valuable products, including methane, which is regarded as an important energy source, and volatile fatty acid (VFA), which could be used as carbon sources to enhance biological nutrient removal in WWTPs (Chen et al., 2007; Su et al., 2013). However, the application of anaerobic digestion has often been featured by long retention times (20–50 days), large digester volumes and low overall degradation efficiency (20%–50%) (Kim et al., 2010). Among the three well-known steps involved in anaerobic digestion, the hydrolysis step has been identified as the rate-limiting step (Higgins and Novak, 1997). Also, the major reasons for low digestibility are microbial cell walls containing glycan strands cross-linked by peptide chains and the existence of a large amount of extracellular polymeric substances (EPS) (Devlin et al., 2011). In order to improve the hydrolysis efficiency

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and digestibility of sludge, various pretreatment methods, also referred to as sludge disintegration techniques, have been investigated, including chemical treatment using alkali, acid or ozone (Devlin et al., 2011; Li et al., 2012; Zhang et al., 2009), mechanical treatment with ultrasound, high pressure homogenization or ball milling (Apul and Sanin, 2010; Wett et al., 2010; Zhang et al., 2012), thermal treatment (Xue et al., 2015), treatment with additional enzymes (Yang et al., 2010) and some of their combinations (Kim et al., 2010; Shehu et al., 2012). These pretreatment methods can normally destroy sludge flocs and cell walls, release intracellular and extracellular organic matters, and consequently accelerate sludge hydrolysis.

Alkaline treatment is a widely examined sludge disintegration method which is believed to be very effective in terms of solubilizing cellular substances and EPS (Fang et al., 2014; Li et al., 2008). Compared to other methods, alkaline treatment holds the advantages of simpler equipment, easy operation and lower energy demand. In addition, alkaline conditions are particularly favorable to the production of short-chain fatty acids or VFA, which are suitable carbon sources for biological nutrient removal processes and phosphorus recovery with MAP (magnesium ammonium phosphate hexahydrate) or HAP (calcium phosphates) (Tong and Chen, 2007). NaOH is the most commonly used chemical for alkaline treatment and has been found to be more effective in terms of sludge disintegration than lime ( $\text{Ca}(\text{OH})_2$ ) (Li et al., 2008). However, the consumption of NaOH involves higher chemical cost and thus will increase sludge treatment expense. New alternative chemicals with low cost must be further explored.

Steel slag is a porous non-metallic by-product produced in the steelmaking industry, the amount of which can be equivalent to 10%–20% of crude steel output. Every year there is around 100 million tons of steel slag generated in China, while only 50%–60% of it can be reutilized in proper ways, leaving a large amount of slag piled at the steel plants, which poses a great threat to groundwater quality. Although the chemical composition of steel slag varies with different slag production processes, normally it consists of CaO,  $\text{SiO}_2$ , FeO, MgO,  $\text{Al}_2\text{O}_3$ , MnO,  $\text{P}_2\text{O}_5$ , etc. (Shi, 2004). Steel slag has been used for treating acid mine drainage, since its alkaline compounds such as lime and magnesia can leach out, creating high levels of alkalinity (Simmons et al., 2002). Meanwhile, steel slag was found to be a very effective material for phosphorus removal in wastewater as a result of phosphorus adsorption onto metal oxides/oxyhydroxides throughout the porous slag matrix and on the slag surface, and precipitation in forms of metal phosphates such as Fe-phosphates and Ca-phosphates (Pratt et al., 2007). In the literature, however, the enhancement of sludge hydrolysis and acidification by steel slag has never been studied, although the capability of creating alkalinity and phosphorus capture make it a potentially useful chemical for sludge alkaline treatment.

Therefore, the purpose of this study was to investigate the feasibility of steel slag addition as a substitute of NaOH for the purpose of sludge hydrolysis and acidification enhancement and phosphorus recovery. As pH is a key parameter in alkaline or acid treatment, the effect of steel slag addition on WAS hydrolysis and acidification for different pH conditions was studied in comparison with NaOH addition scenarios.

## 1. Materials and methods

### 1.1. Sludge and steel slag

The waste activated sludge used in this study was collected from the secondary sedimentation tank of a municipal wastewater treatment plant in Shanghai, China. The plant is operated with an enhanced biological phosphorus removal process. The sludge was concentrated by settling at 4°C for 12 hr and was measured afterward (Table 1).

The steel slag used in this work was obtained from Baoshan Iron & Steel Co. Ltd. in Shanghai, China. The steel slag was crushed and sifted through a 50-mesh sieve before being added into the WAS. Elemental composition analysis with EDS (energy dispersive spectroscopy) showed the elemental composition (expressed as atomic percentage) of the steel slag to be O 33.7%, Fe 22.4%, C 15.6%, Ca 10.9%, Mg 6.5%, Mn 3.2%, Au 2.4%, Si 2.3%, etc.

### 1.2. Experimental procedure

Nine 1-L glass vessels with working volume of 0.9 L were utilized as the anaerobic fermentation reactors. A volume of 0.9 L of WAS were fed into each reactor. The pH in reactors 1–4 was controlled at 8.0, 9.0, 10.0 and 11.0 respectively, with steel slag and the same pH was established in reactors 5–8 with sodium hydroxide. Reactor 9, in which the pH was not adjusted, was set as the blank test. After 5 min nitrogen blowing, all reactors were placed in a shaking incubator maintained at the temperature of  $25 \pm 1^\circ\text{C}$  with a shaking speed of 100 r/min. Samples of the mixed liquor were taken at intervals. Supernatant samples were obtained after 3 min settling of the mixed liquor.

### 1.3. Analytical methods

Water content, TS (total solids), VS (volatile solids), and COD (chemical oxygen demand) were determined according to the standard methods (APHA et al., 2012). Sludge pH was measured with a pH meter (EUTECH Cyberscan510, Singapore).  $\text{PO}_4^{3-}\text{-P}$  and total phosphorus (TP) of the supernatant were also analyzed according to the standard methods (APHA et al., 2012). TP in steel slag was determined by the Capacity Method of Ammonium Phosphomolybdate (Song, 2007), while TP in the sludge was measured by the Vanadium Molybdate Yellow Colorimetric Method after Microwave Digestion (Wen et al., 2003). Soluble carbohydrate was determined using the phenol-sulfuric acid method (Miller, 1959). Soluble protein was determined by the Lowry-Folin method with BSA (Bovine Serum Albumin) as standard (Lowry et al., 1951).

**Table 1 – Characteristics of sludge.**

Parameter	Value
pH	6.8–7.0
Water content (%)	97–98
Total solids (TS, g/L)	13–21
Volatile solids (VS, g/L)	6–14
Total chemical oxygen demand (TCOD, mg/L)	14,000–20,000
Soluble chemical oxygen demand (SCOD, mg/L)	40–100

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