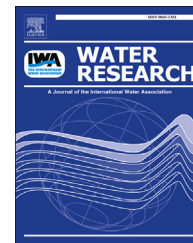




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Mechanism of red mud combined with Fenton's reagent in sewage sludge conditioning

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ABSTRACT

Red mud was evaluated as an alternative skeleton builder combined with Fenton's reagent in sewage sludge conditioning. The results show that red mud combined with Fenton's reagent showed good conditioning capability with the pH of the filtrate close to neutrality, indicating that red mud acted as a neutralizer as well as a skeleton builder when jointly used with Fenton's reagent. Through response surface methodology (RSM), the optimal dosages of Fe^{2+} , H_2O_2 and red mud were proposed as 31.9, 33.7 and 275.1 mg/g DS (dry solids), respectively. The mechanism of the composite conditioner could be illuminated as follows: (1) extracellular polymeric substances (EPS), including loosely bound EPS and tightly bound EPS, were degraded into dissolved organics, e.g., proteins and polysaccharides; (2) bound water was released and converted into free water due to the degradation of EPS; and (3) morphology of the conditioned sludge exhibited a porous structure in contrast with the compact structure of raw sludge, and the addition of red mud formed new mineral phases and a rigid lattice structure in sludge, allowing the outflow of free water. Thus, sludge dewatering performance was effectively improved. The economic assessment for a wastewater treatment plant of 370,000 equivalent inhabitants confirms that using red mud conditioning, combined with Fenton's reagent, leads to a saving of approximately 411,000 USD/y or 50.8 USD/t DS comparing with using lime and ordinary Portland cement combined with Fenton's reagent, and approximately 612,000 USD/y or 75.5 USD/t DS comparing with the traditional treatment.

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1. Introduction

Sewage sludge, a by-product of municipal wastewater treatment, is very difficult to be dewatered, which limits its

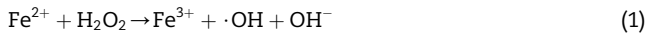
subsequent treatment and disposal. The key problems that prevent sewage sludge from dewatering are the highly hydrated nature of extracellular polymeric substances (EPS) that bind a large volume of water (i.e., bound water) within the sludge flocs and the high compressibility of sludge owing to its

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high organic content (Houghton et al., 2001; Liu et al., 2010; Sheng et al., 2010; Qi et al., 2011).

Fenton's reagent, i.e., Fe^{2+} and H_2O_2 , has been widely investigated and proven to be an efficient chemical conditioner for different sludges (Lu et al., 2003; Neyens et al., 2003; Buyukkamaci, 2004; Tony et al., 2008). The effect of Fenton's reagent lies in the degradation of EPS by the hydroxyl radicals, with powerful oxidizing ability, generated through the following reaction:



Drawbacks associated with the use of Fenton's reagent are the safety hazards associated with using H_2O_2 and the need to firstly reduce the pH, followed by a subsequent neutralization with alkaline additives (Neyens and Baeyens, 2003). Therefore, the reduction in the dosage of Fenton's reagent can alleviate the safety hazards of using H_2O_2 , and a suitable neutralizer needs to be proposed after the Fenton reaction.

Meanwhile, there are considerable researches employing physical conditioners, e.g., lime (Zall et al., 1987), gypsum (Zhao, 2002), lignite (Thapa et al., 2009) and fly ash (Chen et al., 2010), often referred to as skeleton builders for their function in building a rigid and permeable structure in sludge flocs, to decrease sludge compressibility.

Our previous studies have found that quick lime and ordinary Portland cement (OPC) as skeleton builders can significantly reduce the dosage of Fenton's reagent and enhance the dewaterability of sludge (Liu et al., 2012, 2013). However, both quick lime and OPC are non-renewable resources. The production of them consumes a massive quantity of limestone ores and emits a large amount of CO_2 in the high temperature calcination process using coal or coke as the source of energy. Moreover, the pH of the filtrate from the dewatering process of the sludge conditioned by quick lime and OPC tends to be high, usually above 12, which handicaps the subsequent recycle or disposal of the filtrate. The above-mentioned disadvantages have largely limited the application of quick lime and OPC in sludge conditioning. Thus, it is urgent to seek alternative skeleton builders capable of overcoming these weaknesses and yielding acceptable conditioning effectiveness when jointly used with Fenton's reagent.

Red mud is the solid residue from caustic soda leaching of bauxite ores to produce alumina (Yang et al., 2008). The huge global excess of red mud poses serious threats to the environment mainly due to its caustic nature (Yang and Xiao, 2008). Therefore, developing effective utilization methods for red mud is of great importance. Red mud has attracted many interests as cheap adsorbent, coagulant and catalyst in environmental protection fields (Wang et al., 2008), including wastewater treatment (Huang et al., 2008), waste gases purification (Sahu et al., 2011), soil amendment (Liu et al., 2011) and metal recovery (Wang and Liu, 2012). But the application of red mud in sludge conditioning has not been reported in literature. Red mud is superfine in particle size with a large surface area and a long-term persistence of alkalinity, which makes it a potential skeleton builder instead of lime and OPC and a potential neutralizer when jointly used with Fenton's reagent.

In this study, red mud was utilized as a novel skeleton builder in combination with Fenton's reagent to enhance sludge dewatering performance. As depicted in Fig. 1, the

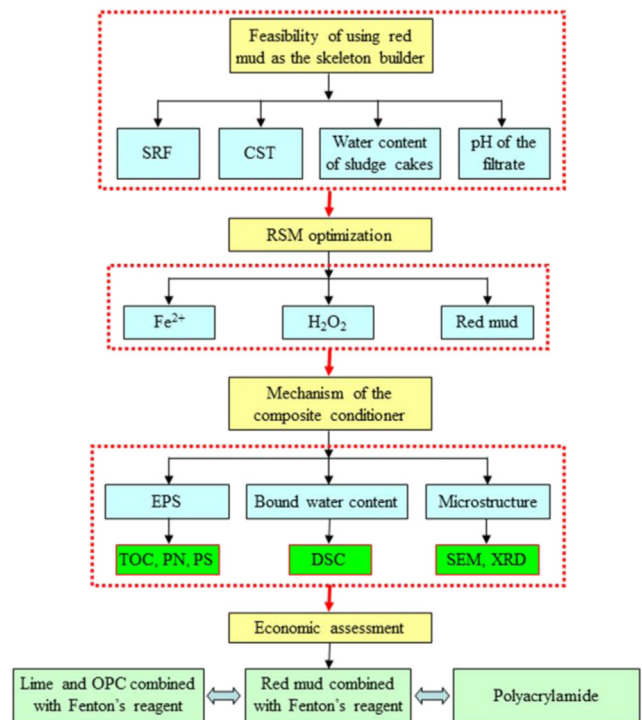


Fig. 1 – Schematic of the study.

objectives of this study were: (1) to demonstrate the feasibility of using red mud as an alternative skeleton builder by evaluating the dewaterability of the conditioned sludge and the pH of the filtrate, (2) to minimize the dosage of the composite conditioner through response surface methodology (RSM) when the water content of sludge cakes does not exceed 60%, (3) to clarify the mechanism of the composite conditioner in terms of EPS, bound water content and microstructure of sludge, and (4) to confirm the economic benefits of using red mud conditioning combined with Fenton's reagent for a wastewater treatment plant (WWTP) of 370,000 equivalent inhabitants (IE).

2. Materials and methods

2.1. Materials

The raw sludge (RS) used in this study was a mixture of sludge from the primary and secondary sedimentation tanks of Longwangzui municipal WWTP, Wuhan, China. Samples were transported to the laboratory in polypropylene containers and stored at 4 °C before use. The main characteristics of RS are listed in Table 1.

H_2SO_4 (analytical grade, Xinyang Chemical Company, China) was used to adjust the initial pH of sludge to 5 (Liu et al., 2012) before adding Fenton's reagent. Fe^{2+} in Fenton's reagent was prepared by making a solution of FeSO_4 (40 wt%). $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Fe^{2+} content of 18.6 wt%) and H_2O_2 (27.5 wt%) of industrial grade were obtained from Sinopharm Chemical Reagent Company, China. Quick lime, OPC and red mud were used as skeleton builders, which were milled and sieved to

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