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The transformation behaviors of heavy metals and dewaterability of sewage sludge during the dual conditioning with Fe^{2+}-sodium persulfate oxidation and rice husk

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HIGHLIGHTS

- RH is a novel skeleton builder by evaluating the sludge dewaterability.
- Fe^{2+}/SPS-RH is an effective composite conditioner for enhancing the sludge dewaterability.
- Fe^{2+}/SPS-RH has a synergistic effect on risk reduction and immobilization of HMs.

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ABSTRACT

This study focused on the behavior of heavy metals (HMs) in sewage sludge after conditioning based on total HMs concentration, fractionation and leaching tests. Fe^{2+}-sodium persulfate (SPS) oxidation was applied as chemical conditioner and rice husk (RH) was added as a physical conditioner to improve the dewaterability of sewage sludge. Combined the response surface methodology analysis and our previous research, the capillary suction time (CST) and the water content of sludge cake reduced by 93.8% and 25%, respectively, after conditioned by 125 mg g^{-1} dry solid (DS) SPS, 33 mg g^{-1} DS Fe^{2+}, 333 mg g^{-1} DS RH at original pH of sludge. The HMs analysis indicated that the concentrations of Cu, Pb, Cd, Zn and Cr were increased in liquid phase after conditioning process. And after conditioned by Fe^{2+}/SPS with RH, the leaching toxicity reduction are 79%, 100%, 93%, 80% and 68% for Cu, Pb, Cd, Zn and Cr, respectively. Results showed that RH combined with Fe^{2+}/SPS oxidation has a synergistic effect on risk reduction and immobilization of HMs. The chemical species of HMs were redistributed and the risk of Pb was reduced from medium risk to no risk after sludge conditioning process according to the risk assessment.

1. Introduction

Considerable amounts of sludge were generated with the increase of wastewater treatment activities (Liu et al., 2012a). In China, about more than 9.2 million tons of dry sewage sludge produced in 2017 (Hei et al., 2016). In both US and Europe, it was estimated that the annual production of dry sewage sludge will be more than 10 million tons in 2020 (Chanaka Udayanga et al., 2018; Kwon et al., 2018). Sludge dewatering is a key pretreat step in sludge volume reduction before further treatment and disposal because of its high moisture content (more than 75%) after mechanical process. It was reported that the distribution and content of extracellular polymeric substances (EPS) have a significant influence on sludge dewatering property (Mikkelsen and Keiding, 2002; Niu et al., 2013). EPS are highly hydrated and combine with a large volume of water (Liu and Fang, 2003). So how to change the property of EPS to remove the bound and intercellular water in sludge flocs is a significant point for sludge dewatering.

Chemical conditioning is commonly used to improve sludge dewaterability, many new advanced sludge conditioning technologies have been proposed in recent years. Persulfate oxidation, which based on sulfate radical ($SO_4{}^{\bullet -}$, $E^0 = 2.5–3.1$ V), is an alternative to Fenton or Fenton-like oxidation (Wu et al., 2017). Persulfate can generate $SO_4{}^{\bullet -}$ activated by heat (Waldemer et al., 2007; Nie et al., 2014), ultraviolet (Ye et al., 2016), ultrasound (Babu et al.,

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2017) and transit metal (Oh et al., 2009; Matzek and Carter, 2017). Fe^{2+} activation is of particular attention of various activation methods because of its high efficiency and no undesired side-products (Petri, 2010). But the Fe^{2+} concentration should keep in a suitable scale because excess Fe^{2+} will react with $SO_4^{\bullet -}$ (Khandarkhaeva et al., 2017). Fe^{2+} activate persulfate oxidation has proved to be an efficient and convenient method for improving the sludge dewaterability because it can degrade EPS and change the structure of the sludge floc and consequently, decrease the bound water in sludge (Zhen et al., 2012). In addition, physical conditioners or skeleton builders, such as red mud, gypsum, wood chips, fly ash, lime, lignite and polyelectrolytes have been used to further enhance the sludge dewaterability because they can decrease the sludge compressibility and provide the flow channel for the free water (Thapa et al., 2009; Liu et al., 2012b; Shi et al., 2015; Song et al., 2016; Li et al., 2017).

The sludge cake after conditioning often contains pollutants such as pathogens, organic matter dioxins and heavy metals (HMs) will present the potential risk to ecological system and human health (Vogel and Adam, 2011). Many countries have law to limit the content of heavy metals in sewage sludge before reused for land application. The allowable concentrations of Cu, Zn, Cd, Cr and Pb in USA are 4300, 7500, 85, 3000, 840 mg kg^{-1}, respectively, and in Europe Union, the allowable concentrations of Cu, Zn, Cd and Pb are 1000–1750, 2500–4000, 20–40, 750–1200 mg kg^{-1}, respectively (Chanaka Udayanga et al., 2018). Therefore, the environmental risk of the sludge cake should be evaluated and verified before its final disposal, especially HMs should be taken into consideration seriously. Li et al. (2015) reported that the distribution and speciation of HMs in sludge can be significantly altered after chemical conditioning.

The main objective of this study was to evaluate the toxicity and bioavailability of HMs in sludge cakes produced from conditioning process. In this study, the pretreatment pH and conditioning concentration of Fe^{2+}, SPS were optimized and the sludge dewaterability conditioned under different formulations were compared. In this study, Cu, Pb, Cd, Zn and Cr were selected for being existed widely in sludge.

2. Materials and methods

2.1. Materials

The raw sludge (RS) was collected after mechanical dewatering from a municipal wastewater treatment plant in Wuhan, China. RS samples were collected in polypropylene containers and stored at 4 °C before use. The characteristics of the RS were tested according to standard methods (US EPA1995). The RH was collected from Wuhan, Hubei. The rice husk (RH) was dried in an oven at 105 °C for 5 h to ensure complete dehydration and then ground using a ball mill (XQM-4L) for 10 m at 3500 rpm. Finally, the RH was sieved through a 0.25 mm sieve and washed with deionized water, and then dried at 105 °C for 5 h for future use in the following experiments. Table S1 lists the characteristic of the RS and RH.

Sodium persulfate (SPS) ($Na_2S_2O_8$, purity>99.9 wt%) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$, purity>99.9 wt%) were analytical reagent grade (Sinopharm Chemical Reagent, China) and were used without further purification. The SPS and Fe^{2+} solutions were freshly prepared immediately prior to the experiments. Deionized water was used for all the experiments.

2.2. Conditioning procedure

Firstly, the RS was transferred to 500 mL beakers and stirred for 30 m to ensure the sludge particles were evenly mixed with the water. Then the RS was conditioned using the following procedure: SPS addition → 150 rpm stirring for 5 m → addition of Fe^{2+} → 150 rpm stirring for 5 m → addition of RH → 150 rpm stirring for 10 m. And the speed and time of conditioning were determined by the research of Yu et al. (2016) and our exploration experiments.

After conditioning, the residue and liquid phase were separated by vacuum filtration through a 0.45 μm membrane, and the liquid samples were kept at 4 °C in a refrigerator. The sludge cakes were dried at 105 °C for 24 h and grounded before further HMs analysis. The experimental setup of the sludge conditioning system is shown in our previous work (Xiong et al., 2017b).

In order to compare the behavior of HMs in sludge before and after conditioning, a set of experiments with different formulations were conducted. The concentrations of the constituents were obtained from the RSM optimization in this study. And the concentration of RH was decided by our previous RSM optimization study (Xiong et al., 2017b). RS was used as the control. Table S2 shows that the sludges conditioned with RH (at 25 °C); SPS and Fe^{2+} (at 25 °C); SPS, Fe^{2+} and RH at 25 °C; SPS, Fe^{2+} and RH at 52 °C; and SPS, Fe^{2+} and RH at 80 °C are labelled RH25, SF25, SFR25, SFR52 and SFR80, respectively. And the collected liquid samples are labelled LRS, LRH, LSF, L25, L52, L80, respectively. The sludge cakes were labelled CRS, CRH, CSF, C25, C52, C80, respectively.

2.3. RSM design

A Box–Behnken design (Montgomery, 2009) was used to optimize the pH and the concentrations of SPS and Fe^{2+}. Table S3 shows the ranges and levels of these three constituents, which were defined using preliminary tests (Xiong et al., 2017a). The CST reduction efficiency was considered as the response. Seventeen runs were required for a complete set of the experimental design and the experimental results were analyzed using the Design Expert 8 software.

2.4. Total metal concentrations

The total HMs concentrations of the sludge cakes were measured using the microwave-assisted leach method which can be found elsewhere (Link et al., 1998; Wang et al., 2017).

2.5. Fractionation procedure of HMs

The chemical speciation of HMs (Cu, Pb, Cd, Zn and Cr) was conducted by using Community Bureau of Reference (BCR) sequential extraction procedure (Rauret et al., 1999; Xiao et al., 2015). Table S4 describes the chemical sequential extraction procedure. Four fractions of the metals speciation, including the soluble and exchangeable (F1), bound to iron and manganese oxides (F2), bound to organic and sulfide (F3) and residual (F4) were categorized following the methods mentioned in Table S4.

2.6. Treatment efficiency assessment

2.6.1. Sludge dewatering performance

The CST (capillary suction time) and the water content of the sludge cakes were used to evaluate the sludge dewatering performance. The CST was measured using a 304 M CST instrument (Triton, UK). The CST reduction efficiency (Y) was calculated as follows:

$$Y = (CST_b - CST_a)/CST_a \quad (1)$$

where: