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Lead removal by a magnetic biochar derived from persulfate-ZVI treated sludge together with one-pot pyrolysis

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ABSTRACT

In this study, a novel method to treat the persulfate-ZVI dewatered WAS by producing a magnetic biochar as an environmentally friendly biosorbent (nZVI-WSBC) to remove heavy metals (HMs) from wastewaters was proposed. The nZVI-WSBC exhibited good adsorption property of Pb^{2+} and the adsorption isotherm data were fitted well to Langmuir isotherm. Corresponding reaction kinetics fitted well with the pseudo second-order adsorption model. Notably, nZVI-WSBC was successfully used for efficient removal of HMs from real. This study comprehensively demonstrates the mechanisms between Pb^{2+} and nZVI-WSBC surfaces, providing a breakthrough in making a sustainable biosorbent from the dewatered iron-containing WAS.

1. Introduction

Waste activated sludge (WAS) dewatering is essential to reduce the sludge volume and subsequent transport/disposal costs in municipal wastewater treatment plants (Rincón et al., 2013). Conventional methods to improve sludge dewaterability include acid/alkaline treatment, flocculent addition, heating, freezing, and advanced oxidation (Zhen et al., 2012; Zhou et al., 2015). Among these, advanced oxidation is one of the most promising methods of WAS dewatering due to its low environmental impact and high efficiency (Xiao et al., 2017). For example, zero-valent iron (ZVI) combined with persulfate has been shown to effectively enhance the dewaterability of WAS (Kang et al., 2016). In the ZVI-persulfate system, persulfate anion ($S_2O_8^{2-}$) could oxidize Fe^0 to Fe^{2+}. Afterward, the sulfate radical ($SO_4^{\bullet-}$) could be produced via the reduction of persulfate anion by Fe^{2+} (Zhou et al., 2015). The resulting sulfate radicals anion ($SO_4^{\bullet-}$), which has a strong oxidation capacity, can efficiently destroy the structure of the sludge and convert bound water into free water (Lu et al., 2001), thus improving the dewatering of WAS. However, the introduced ZVI within the dewatered WAS might threat ecosystem and human health after the dewatering process. As a result, it is highly desirable to develop a post-treatment process to remove iron species from WAS that is dewatered by persulfate-ZVI.

Pyrolysis has recently been recognized as one of the most effective methods to post-treat WAS, and can also produce the biochar (an organic porous material) with a satisfactory surface area, stable structure, great ion exchange capacity and some value-added surface functional groups (e.g., −OH, −COOH, C−O/C═O) (Inyang et al., 2010). For the persulfate-ZVI system, pyrolysis of the iron-containing WAS for biochar offers several potential advantages.

The unique features of WAS-biochar (WSBC) are superior with regard to removing both organic and inorganic environmental contaminants. nZVI embedded on WSBC is capable of removing extra contaminants (Fajardo et al., 2012), due to its strong reducing power ($E_0 = -0.44$ V) and large specific surface area (Zhao et al., 2016). WSBC could be an ideal supporter material for nZVI, because biochar can not only reduce the aggregation of nZVI in solution, but also facilitate the performance of nZVI in various aspects (Zhou et al., 2014). Taken together, the composite of WSBC and nZVI is now being recognized as an efficient environment functional material. For instance, Su et al. (2016) reported that Cr(VI) was effectively reduced by biochar-supported nZVI in soil. Moreover, the embedded magnetite which was formed during pyrolysis in WSBC, together with intrinsic magnetic nZVI residuals, allows recycling of the biosorbent with an external magnetic field. However, most of the current studies merely focused on the characterization and performance of the biochar-supported nZVI composites (Zhou et al., 2014), while few of them discussed the mechanisms of contaminant removal in a biochar-supported nZVI system. In particular, a thorough understanding of the lead adsorption on WSBC as the

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nZVI supporter is still lacking.

To address these issues, ZVI-containing dewatered WAS was treated by one-pot pyrolysis, which gave a novel magnetic nZVI-WSBC. The WAS from a wastewater treatment plant and dewatered with the persulfate-ZVI system was initially collected. After the dewatering process, nZVI-WSBC biosorbent was then synthesized through direct one-pot pyrolysis from the dewatered iron-containing WAS. The physicochemical properties of nZVI-WSBC were systematically characterized by analyzing its surface chemical behavior using Fourier transform infrared spectroscopy (FTIR) and an X-ray diffractometer (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscope (XPS), and elemental analyzer (EA). Meanwhile, the removal efficiencies of various HMs (i.e., Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) by WSBC and nZVI-WSBC under mono- or multi-metal solutions were compared. Hereafter, Pb^{2+} was selected as the main removal target by nZVI-WSBC and the adsorption kinetics, sorption isotherms and corresponding mechanisms of Pb^{2+} was then comprehensively investigated. Notably, to investigate the practical feasibility of nZVI-WSBC, the removal of lead from real lead-battery wastewater was studied. The results of this study provide useful information to understand the lead adsorption mechanisms of nZVI-BC and maximize its lead removal capacity from the real wastewater.

2. Materials and methods

2.1. Sludge sources and batch dewatering tests

The WAS sample was collected from the second settling tank of Taiping Municipal Wastewater Treatment Plant (Harbin City, China), where an anaerobic-oxic activated sludge process (A/O) is used to treat 345,000 m^3 wastewater per day (Xie et al., 2016). The WAS sample was concentrated by settling for 24 h at 4 °C.

To test the sludge dewaterability by persulfate-ZVI pretreatment, concentrated WAS (20 mL), persulfate (0–0.25 g/g TS) and ZVI (0–4 g/g TS) were added into a 40 mL reactor and mixed at 100 rpm for 30 min at room temperature. Capillary Suction Time (CST), which indicates the dewaterability of sludge, was measured with a capillary suction timer (Type 304 M, Triton, London). The variation of sludge dewaterability was measured by the reduction percentage R (%) of CST:

$$R(\%) = \frac{CST_0 - CST_e}{CST_0} \times 100\%$$

where CST_0 is the initial CST value of untreated sludge, and CST_e is the value of the sludge after the treatment.

2.2. Preparation and characterization of biochar

WSBC and nZVI-WSBC were prepared by pyrolysis of WAS and persulfate-ZVI treated WAS, respectively. These two kinds of sludge were annealed at 600 °C for 90 min while the pyrolysis heating rate was 15 °C/min. N_2 was flown through the tubular furnace during the process (Tripathi, 2016). The ash of the biochar was annealed at 600 °C for 120 min. The contents of C, H, N and O in the synthesized biochar were measured with an elemental analyzer (EA, Vario Micro cube, Elementar, Germany). The other elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 8300, PerkinElmer, USA) after nitric acid digesting. The samples were characterized by X-ray powder diffraction (XRD, X'PERT Rro MPD, Panalytical, Holland) equipped with Cu Kα radiation (40 kV, 20 mA) over a 2θ collection range of 10–90° to examine possible sample crystallinity. The surface functional groups from samples were identified using Fourier transform infrared spectroscopy (FTIR, SPECTRUM one, PerkinElmer, USA) ranging from 400 to 4000 cm^{-1} wavenumber. X-ray photoelectron spectroscopy (XPS, ESCA Lab 250Xi, Thermo Fisher, USA) was used to analyze the surface composition of samples within a depth of < 10 nm. The micro-morphological images of biochar were obtained with a scanning electron microscope (SEM, TM3030 and S4800, Hitachi, Japan) and energy dispersive spectrometer (EDS). The magnetic properties of WSBC were obtained using a precision magnetic measurement system (Lakeshore 7404, USA). The pH of the biochar was determined at a quality ratio of 1:10 for solid to DI water (Xu et al., 2013).

2.3. Determination of heavy metals (HMs) removal

Solutions (20 mL) of mono- and multi-HMs (i.e., Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) were prepared in a 40 mL glass reactor with a concentration of 100 mg/L, followed by the addition of 0.04 g WSBC or nZVI-WSBC. The biochar and metal solutions were mixed in a shaker at 200 rpm for 8 h at room temperature. For the regeneration, the particles were immersed in 10 mL of a 0.1 M HCl solution for 2 h and washed with DI water for three times, then employed for next adsorption. After reaction and drying with 105 °C, the nZVI-WSBC was removed by magnet for XRD, FTIR and SEM-EDX analysis. The supernatant was filtered for the measurements of the residual HMs by ICP-AES.

For investigating the effect of adsorbent dosages, the adsorbent mass placed into an equilibrium system was 10, 40, 100, 160 and 200 mg, with the S:L (the solid mass/the liquid volume) value of 0.05%, 0.20%, 0.50%, 0.80% and 1.00%, respectively. In addition, the effect of pH on the removal efficiency of Pb^{2+} was also investigated. For studying the application potential of nZVI-WSBC in HMs removal from real polluted wastewater, the wastewater were obtained from the local lead-battery factory (Harbin, China), which was mainly composed of lead (8–10 mg/L) and Zinc (3–4 mg/L).

3. Results and discussion

3.1. Performance of persulfate-ZVI assisted WAS dewaterability

The effects of the amount of ZVI and the concentration of persulfate on CST was firstly investigated, which indicates the dewaterability of WAS. The percentage of CST reduction increased from 8.51% to 56.97% when the amount of ZVI increased from 0 to 2 g/g TS, whereas the concentration of persulfate was kept at 0.5 g/g TS. This suggests that persulfate oxidized ZVI to form Fe^{2+}ions that activated persulfate to sulfate radicals. The oxidizing radicals thus formed to destroy the structure of the sludge floc and microbial cells, resulting in the release of bond water (Zhang et al., 2016b). However, the CST reduction of sludge only changed slightly upon further dosing with ZVI (from 2 to 4 g/g TS), which may be ascribed to the scavenging of sulfate radicals by excess ZVI. This is consistent with a previous study which reported that an overdose of ZVI can only result in an increased amount of sulfate ions, which are not able to facilitate the WAS dewaterability (Song et al., 2016).

Similarly, when the ZVI concentration was maintained at 2 g/g TS, the percentage reduction in CST increased from 20.11% to 59.60% as a result of increasing persulfate concentrations from 0 to 0.25 g/g TS. However, further increases in persulfate concentration to 1.0 g/g TS produced a similar CST value, suggesting that an overdose of persulfate could inhibit the production of sulfate radicals ($S_2O_8^{2-} + SO_4^{\cdot-} \rightarrow S_2O_8^{\cdot-} + SO_4^{2-}$), which is in a good agreement with previous reports (Liu, 2014; Mo et al., 2015). Therefore, the optimal dosing amounts of persulfate and ZVI are 0.25 g/TS and 2 g/TS, respectively.

3.2. Synthesis and characterization of nZVI-WSBC

3.2.1. Elemental composition and surface morphology of nZVI-WSBC

After dewatering, the persulfate-ZVI dewatered WAS was converted to nZVI-WSBC through a one-pot pyrolysis process. As shown in Table 1, compared with the blank sample (i.e., the WSBC group), the contents of C, H, O and N in nZVI-WSBC decreased dramatically along