Chemical Engineering Journal 292 (2016) 224–232

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Enhanced removal of Pb(II) by supported nanoscale Ni/Fe on hydrochar derived from biogas residues

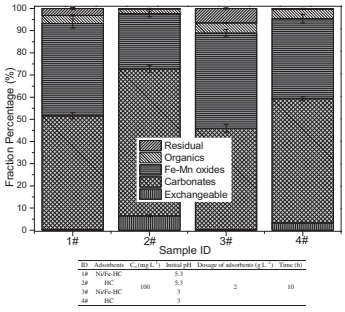
Zhi Tang [a,c], Yuanfang Deng [b], Tao Luo [a,c], Yan-sheng Xu [a,c], Neng-min Zhu [a,c,*]

[a] Biogas Institute of Ministry of Agriculture, Chengdu 610041, Sichuan Province, China
[b] Jiangsu Key Laboratory for Biomass-based Energy and Enzyme Technology, Huaiyin Normal University, Huaian 223300, Jiangsu Province, China
[c] Key Laboratory of Development and Application of Rural Renewable Energy, Ministry of Agriculture, Chengdu 610041, Sichuan Province, China

HIGHLIGHTS

- Biogas residues was used as precursor to prepare a hydrochar (HC) via HTC.
- Ni/Fe was anchored tightly to HC particles to form supported Ni/Fe-HC.
- 99.5% of Pb(II) was removed by Ni/Fe-HC in 1.5 h regardless of initial solution pH.
- Ni/Fe-HC acted as a *pseudo*- black hole for sweeping Pb(II) from bulk solution.
- Adsorptive precipitation and specific adsorption dominated Pb(II) removal by Ni/Fe-HC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 November 2015
Received in revised form 27 January 2016
Accepted 28 January 2016
Available online 22 February 2016

Keywords:
Biogas residues
Hydrothermal carbonization
Ni/Fe nanoparticles
Pb(II)
Adsorptive precipitation

ABSTRACT

A functionalized carbonaceous material was prepared via hydrothermal carbonization (HTC) of biogas residues and denoted as hydrochar (HC). The obtained HC was used to synthesize a hybrid (Ni/Fe-HC) to conduct Pb(II) removal from aqueous solution. SEM images show that Ni^0/Fe^0 was anchored tightly to HC particles due to a cellular structure of HC formed during HTC. Complete Pb(II) removal (>99.5%) was achieved within 1.5 h using Ni/Fe-HC whereas more than 85% of Pb(II) remained in bulk solution after 10 h with bare HC. SEP results indicate that Pb(II) was mainly associated with the fraction bound to carbonates and Fe–Mn oxides in the spent Ni/Fe-HC particles. Consequently, the adsorptive precipitation and specific adsorption dominated Pb(II) removal by Ni/Fe-HC despite minor reduction of Pb(II) to Pb^0. However, the reduction of Pb(II) to Pb^0 was conducted by the catalytically generated atomic hydrogen rather than Ni/Fe nanoparticles as electron donor. Ni/Fe-HC not only acted as an effective adsorbent for Pb(II) but also played a role of catalyst to generate atomic hydrogen. HC prepared with biogas residues can be used as an excellent supporting material to prepare a hybrid of Ni/Fe-HC for Pb(II) removal.

1. Introduction

Supported nanoscale zero-valent iron particles (s-n-ZVI) have been developed as a promising substitute for bare n-ZVI to restore contaminated soil and water by heavy metals [1] due to some arising drawbacks of bare n-ZVI, such as agglomeration and formation of oxidation layer [2,3]. An excellent supporting material is vital for preparing s-n-ZVI particles to achieve good remediation performance [4–6]. Some types of solid waste biomass, such as crop straws and nut peak, have been employed as cost-effective precursors to prepare carbon-based supporting materials from the standpoint of reuse of organic waste [7,8]. Among various preparation methods, hydrothermal carbonization (HTC) conducted in the

* Corresponding author at: Biogas Institute of Ministry of Agriculture, Chengdu 610041, Sichuan Province, China. Tel./fax: +86 28 85215106.
E-mail address: zhunengmin2004@163.com (N.-m. Zhu).

http://dx.doi.org/10.1016/j.cej.2016.01.113
1385-8947/

presence of activating agent, such as phosphoric acid, is proven to be a novel and cost-effective process due to its mild operation temperature (<300 °C) comparing with that for conventional pyrolysis carbonization (>500 °C) [9], and therefore attracts increasing public attentions. During HTC process, the thermal unstable components of biomass dissolved into the activating agent following the formation of main cellular structure [10–12].

As one type of secondary biomass, biogas residues has emerged as an urgent environmental issue in some agricultural regions of China in recent years because its production as organic fertilizer has exceeded the accepted capacity of local farmland [13,14]. More and more public attentions are paid to the benign utilization of these redundant undesirable biogas residues. Comparing with the fresh crop straws, its biogas residues after anaerobic digestion retained main fibrous texture which is essential for preparing supporting materials via HTC [12]. However, the biogas residues from anaerobic digestion of livestock and poultry manure mainly consisted of dissolved organic matters and inorganic solids [15]. In view of its main fibrous structure, the biogas residues of crop straws could be re-utilized as precursors to prepare carbon-based supporting materials via HTC from the standpoint of carbon cycle, which was rarely documented until now.

It was commonly supposed that the supporting material in s-n-ZVI, such as activated carbon, could enhance the adsorption capacity of n-ZVI significantly comparing with a bare n-ZVI [2,4]. However, the adsorbed metal ions was easy to re-dissolve in bulk solution in the case of bare carbon-based adsorbent used [16,17], whereas a strong immobilization of metal ions on the s-n-ZVI was observed after introduction of n-ZVI into carbon-based supporting material [1,4]. It means the bonding between metal ions and adsorbent particles might be affected by the composition of adsorbent considerably. Sequential extraction procedure (SEP) was usually used to determine the metal species in solid matrix in terms of the bonding force between metals and solid particulates [18]. As a consequence, SEP also could be applied to determine the metal species formed during the adsorption process conducted by s-n-ZVI.

In this study, one type of biogas residues was used to prepare hydrochar (HC) by HTC process. Supported Ni/Fe nanoparticles (NPs) were synthesized using the obtained HC and applied to remove Pb(II) from aqueous solution. SEP was performed to investigate the absorption characteristics of Pb(II) and the corresponding removal mechanism was also proposed.

2. Materials and methods

2.1. Chemicals and biogas residues

Analytical or higher grade chemical reagents were all purchased from the Sinopharm Group Chemical Reagent, China and used without any pretreatment. Milli-Q ultrapure water (18.2 MΩ cm^{-1}) was adequately purged with N_2 before use to create an anoxic aqueous environment. Biogas residues was sampled from a medium-scale biogas plant which used rice straws as main substrates. The sample was oven-dried at 105 °C and then gently ground and homogenized to pass through a 60 μm sieve. The obtained dry biogas residues particles were storied in a refrigerator at 4 °C for subsequent experiments. A Pb(II) stock solution was prepared by dissolving $Pb(NO_3)_2$ in 1000 mL of ultrapure water, which was diluted and used as working solution.

2.2. Preparation of hydrochar and supported Ni/Fe-HC

The hydrothermal carbonization of biogas residues by HTC was carried out according to previous reports with slight modification [10–12]. 10 g of dried biogas residues particles was fully soaked in H_3PO_4 solution (75 wt.%) at a ratio of 60/10 (mL H_3PO_4 solution/g dry particles) overnight and then transferred to a 150-mL stainless steel autoclave, which was then sealed and heated up to 250 °C for 10 h. After natural cooling, the solid product was recovered by centrifugation, washed with denized water following rinsing with acetone and final flush with distilled water. The obtained black solid product was dried at 150 °C and referred as hydrochar (HC). The chemical characteristics of the raw biogas residues and the obtained hydrochar are presented in Table 1.

Ni/Fe-HC particles were prepared in an ethanol/water (3:7 v/v) solution by $NaBH_4$ reduction under a N_2 atmosphere to avoid the oxidation of Ni/Fe [19]. $FeSO_4{\cdot}7H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in 200 mL ethanol/water solution to form 0.1 M Fe(II) and 0.01 M Ni(II) mixed solution. 3 g of HC were immersed into the mixed solution with continuous magnetic stirring for 5 h. Then, 250 mL of 0.2 M $NaBH_4$ solution was added drop-wise into the mixed solution at 2 mL min^{-1} with constant magnetic stirring for 30 min after addition. The resultant black suspension was centrifuged and the black solid product (Ni/Fe-HC) was flushed with distilled water following rinse with acetone and then stored in a sealed glass container filled with acetone. Before experiment, the particles were subjected to vacuum drying to eliminate the acetone for use.

2.3. Batch experiments for Pb(II) removal

Removal of Pb^{2+} was conducted in a 80 mL anaerobic jar with rubber stopper and aluminium cap by mixing 0.1 g of particles in 50 mL of Pb(II) solution. The mixture in anaerobic jar was purged with a gentle nitrogen gas using a syringe and then agitated (180 rpm) in a shaker at room temperature after sealing with rubber stopper and aluminium cap. At regular intervals, the samples were withdrawn and filtered through a 0.22 μm mixed cellulose ester membranes. The obtained filtrate was recorded pH using pH meter (Mettler Toledo) and then used for Pb determination by ICP-OES. At the end of experiment, the remaining mixture in anaerobic jar was centrifuged and the obtained solid phase was subjected to vacuum freeze drying for SEP analysis according to Tessier et al. [20]. The aqueous extract from SEP was digested using HNO_3 for ICP-OES analysis. The final solid phase from SEP was subjected to microwave assisted acid digestion for ICP-OES analysis [21]. All experiments were performed in triplicates and the results were averaged.

2.4. Analytical methods

SEM was obtained using a Phenom Pro microscope (Netherlands). X-ray diffraction (XRD) analysis of particles was carried out using PANalytical X'Pert Powder X-ray diffractometer (Netherlands). Fourier transform infrared spectroscopy (FTIR) was performed by Bruker vertex 70 (Germany). Inductively coupled plasma-optical emission spectrometry (ICP-OES) was conducted using Perkin Elmer OPTIMA 2000 spectrometer (USA).

Table 1
Characteristics of the biogas residues and obtained hydrochar.

Characteristics	Biogas residues	Hydrochar
Total solids (%)	85.78	97.95
Volatile solids (% TS)	85.46	45.61
Ash (% TS)	14.54	54.39
Total organic carbon (% TS)	24.35	11.63
Cellulose (% TS)	28.68	9.98
Hemicellulose (% TS)	19.37	6.37
Lignin (% TS)	17.16	12.84