

Adsorptive Removal of Manganese from Manganese Slag Aqueous Solutions Using Biochars Loaded with Organic Acid-Fe

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Abstract. Manganese adsorptive removal is an important treatment process in constructed wetlands to deal with considerable amounts of tailing wastewater, many materials have been proposed for its removal. This work is aimed to examining the potential of biochars sorbent materials for removing Mn ions from manganese slag aqueous solutions by modified biochars. The biochars with different organic acid-Fe ratios were prepared; factors on Mn adsorption including mixing ratio, Fe adsorption rate, and the BET surface of the modified biochars were discussed and the sorption efficiency of Mn was investigated through column adsorption experiments. According to our study, it's clearly that loaded organic acid biochar with greater Fe content removed higher percent of Mn from the aqueous solution. Contents of Fe₂O₃(30-103%), Fe₃O₄ (65-106%)and CaCO₃ (4-80%)increased after loaded with organic acid-Fe in the biochars. With the increasing Fe content (2.58-5.07%) in biochar, the BET surface area of the Citric Acid-Fe biochar composites decreased from 81 m²/g to 35 m²/g, while the EDTA-Fe biochar composites decreased from 96 m²/g to 22 m²/g. The fixed loaded Fe biochars mixtures had a reduction of 4.02% to 32.01% in Mn sorption contrasting with raw biochar. The modified biochars could be used to remove the Mn ions in the tailing wastewater.

Introduction

The world rapidly growing demand for manganese has made it increasingly important to develop processes for economic recovery of manganese from low grade manganese ores and other secondary sources [1]. In recent years, the world manganese demand has been driven by soaring steel production, particularly in China. These manganese-containing industrial waste effluents could be potentially important manganese sources [2]. Several acid leaching processes have been developed to recover manganese from these kinds of manganese minerals. Das et al. [3] investigated the recovery of manganese from ferro-manganese slag by acid leaching. The slag from ferro-manganese manufacture contained 12-30% Mn (II) with the main impurities being CaO, SiO₂, and Al₂O₃.

The use of biochar is on the draft agenda for the international climate change negotiations in Copenhagen in December 2015. Biochar is exceptionally stable and can be stored underground for hundreds of years without releasing its carbon into the atmosphere and it improves the fertility of the soil [4]. These effects are the result of biochar's structure, which is full of microscopic pores that can harbor useful bacteria and fungi [5]. Turning vast amounts of biomass crop wastes and other biomass into charcoal and spreading it on soils can sequester carbon and boost crop productivity [6]. Recently, biochar has been used frequently as a suitable biosorbent to remove toxic metals from wastewater [7, 8]. This improvement of suitable biochars has been studied in numerous, very recent studies Trakal et al. [8], Mohan et al. [9], Wang et al. [10], Inyang et al. [11], where enhancement of metal sorption has been experimentally confirmed. Despite these novel studies, there is still missing information about the metal sorption mechanisms after the magnetization process. Considering this lack of knowledge, the biochar samples presented in the previous paper [6] were magnetically modified and subjected to identical geochemical and spectroscopic investigations.

The primary aim of this investigation was to develop a Fe-contained and organic acid magnetic biochar for the recovery of manganese from aqueous solution. For this purpose, locally available harvest trash biomass of agricultural crop was pyrolyzed at 600 °C after being impregnated with ferrous chloride and organic acid solution. The performance and adsorption mechanism for ferrous recovery from water solution, and subsequently the efficiency of organic acid - sorbed biochar as a fertilizer were examined. Leaching behavior of ferro-manganese slag was also investigated in simulating experiments. In order to realize the effect of biochar on manganese slag water contamination, and provides the theory basis of metal mobility of manganese slag for pollution control.

Materials and Methods

Materials Collection and Preparation

Exactly the same waste agro-materials as in previous study [6] were used for the biochar preparation in this study. The source of raw materials of biochar was straw of agricultural crop, and it was pyrolyzed at 600 °C in a muffle furnace at atmospheric pressure with a retention time of 30 min. The pyrolyzed products were cooled, and the resulting biochars were ground, homogenized, sieved (1 mm), washed with ultra-clean water (Merck Millipore D 24 UV, USA), and dried at 60 °C for 24 h until constant weight, and finally stored in polystyrene valve bag for later use. The electrolytic manganese slag were collected in Zhenyuan county of Guizhou province in China, all the collect samples of electrolytic manganese slag were compound samples of topsoil. The samples were grinded and sifted through 1 mm nylon sieve after natural air drying, and then loaded into polystyrene valve bag for later use.

The citric acid and the ethylene diamine tetraacetic acid (EDTA) were used as typical organic acid to load with Fe in this study. During this process, biochars (preparation above) were putted into the two organic acids respectively in the setting density 0.2-0.6mol/L, and there were the same amounts of Fe(III) molarity in the aqueous solution contrast with organic acids. Then, the suspensions of all organic acids experiments were shaken at 250 rpm using an end-over-end agitator for 24h, filtered through 1 mm nylon filter, washed with ultra-clean water and dried at 60 °C for 12 h until constant weight, and finally stored in polystyrene valve bag for further use.

Column Adsorption Experiments

Equipment: All column leaching tests have been conducted under laboratory conditions (20 °C) using PVC columns with an internal diameter of 7.5 cm and a length of 50 cm. The electrolytic manganese slags (preparation in section 2.1) were homogenized with the joined biochars (loaded with organic acid-Fe) in a series of fixed ratio (0%, 5%, 10%, and 15%). Packing of homogenized manganese slags took place in 15–20 increments, and each increment was packed slightly before the next one was placed on top until the column was completely filled with 4 kg manganese slags. After manganese slags were filled uniformly, a filter paper must be laid on the top of the slags. Make sure the filter paper was level, so the liquid drip onto the filter paper was uniformly distributed on the surface of manganese slags. Leaching solution was horizontally placed in a high position as far as possible; to make hydraulic change minimize during a leaching time.

Procedure: The leaching solution was ultra-clean water. The experiments were performed twice for all treatments. Continuously leaching manganese slags for 24 h with the leaching solution were taken up to simulate the light rain (13 mm•24 h⁻¹) leaching on the manganese slags. Prior to detection, samples were filtrated to a 50 ml plastic centrifuge tube with a 0.45 μm filter membrane. The remaining collected liquid solution in the collector must be poured away out entirely. The next leaching was carried every three days, and the whole leaching experiment last for 15 days.

Each collected water sample was acidified with pure HNO₃ to adjust its pH value to below 2 to avoid Mn hydroxide precipitation within 24 h after sample was taken. All the samples were stored at 4 °C in the refrigerator before determination.

Analytical Methods

To test the Fe(III) loading on iron oxide/activated carbon composite adsorbent, about 0.5g of

composite adsorbent was ashed at 600 °C and then digested with 25mL of concentrated hydrochloric acid. The fraction of dissolved heavy metals was attained by analyzing the content of filtered samples. The major elements (Fe and Mn) in dissolved solutions and digestion solutions were determined with Atomic Absorption Spectrophotometer (AAS ZEEnit-700P, Germany) unit with flame atomization, specific surface area determined using the BET multilayer adsorption isotherm (Micromeritics ASAP 2000, USA), and the precipitated phases detected using X-ray diffraction analyses (LabX XRD-6000, Japan). Blanks and appropriate certified standard reference materials were analyzed as unknowns with every batch of samples. All the related glassware were soaked in 20% HNO₃ for 24 hours and then thoroughly rinsed with the deionized water before being used.

The analysis of statistical data was conducted by using the Statistical Product and Service Solutions (SPSS 22). The entire graphs were drawn by MDI Jade 6.5 or Origin Pro 9.1.

Results and Discussion

Characteristics of Studied Biochars

XRD analysis was carried out for the composite adsorbent and the pure iron oxide, the analysis results are shown in Fig.1. The XRD analysis revealed that raw biochar without organic acid-Fe addition is dominated with abroad diffraction peak at two theta around 26 °. Compared with that of raw biochar, the prepared

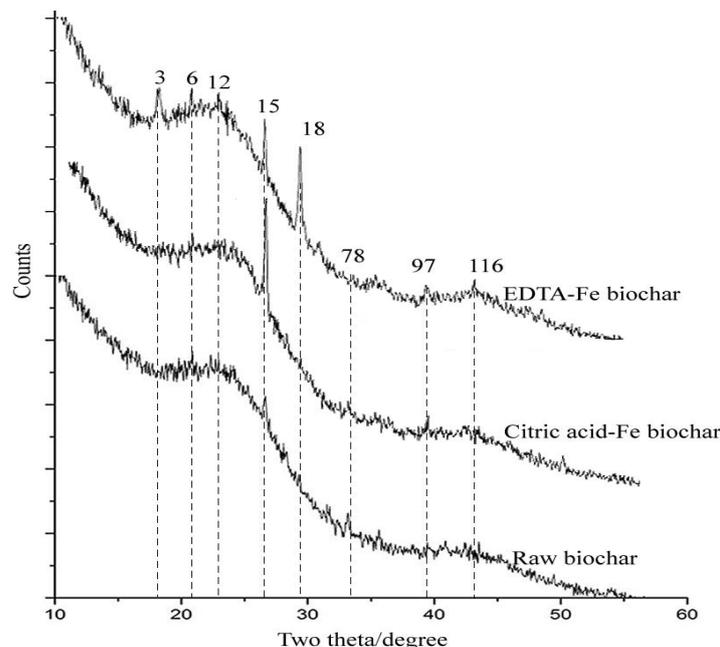


Fig.1 XRD patterns of studied biochar samples before and after modification.

Organic acid-Fe biochars composites showed typical hydrotalcite compound structure with sharp reflection peaks including “12”, “15”, “97”, as well as “6”, “116”. It was evident from Figure 1 that the contents of Fe₂O₃, Fe₃O₄ and CaCO₃ increased before and after loaded with organic acid-Fe in the range of 26-30 °. The three of them increased by 30%, 106% and 4%, respectively, after loaded with Citric Acid-Fe, while increased by 103%, 65% and 80%, respectively, after loaded with EDTA-Fe. Loaded with EDTA-Fe was a more effective than loaded with Citric Acid-Fe in modifying biochars characteristics. XRD analyses of the pure iron oxide suggest the presence of a cubic iron oxide phase, which may be related to the presence of maghemite (γ - Fe₂O₃), goethite (α - FeO(OH)) , hematite (α -Fe₂O₃) and magnetite (Fe₃O₄), so the prepared iron oxides are magnetic. For the composite, these peaks appear broader, suggesting a smaller crystallite size. In summary, the improvement of metal sorption by magnetic modification was related to the origin of the material, with the well-structured biochars more available for modification [6, 8].

Ferric Iron Loading Efficiency

The Fe content and textural properties of the prepared samples are showed in Fig.2. With concentration of Fe increasing from 0.2 to 0.6mol/L(Fig.2a), the loaded iron Fe content increased from 2.58% to 4.73% in citric acid solution, when the loaded iron Fe content increased from 3.45% to 5.07% in EDTA solution. As previously described, after the Fe introduction there were lots of Fe_2O_3 in biochar samples after loaded with organic acid-Fe. The specific formation of Fe_2O_3 was likely through the reaction sequence of $\text{FeCl}_3 \rightarrow \text{Fe}(\text{OH})_3 \rightarrow \text{FeO}(\text{OH}) \rightarrow 2\text{Fe}_3\text{O}_4$ with gases HCl, H_2O , and CO_2 released from the respective reactions [12]. Similar results were also observed during carbonizing the ferric chloride soaked sawdust [13], ferric and ferrous chloride impregnated orange peel powder [14]. The adsorption will be enhanced by the goethite-organic acid compound colloid which from the organic acid and goethite interaction. For this reason, 0.6mol/L samples were selected for subsequent evaluation.

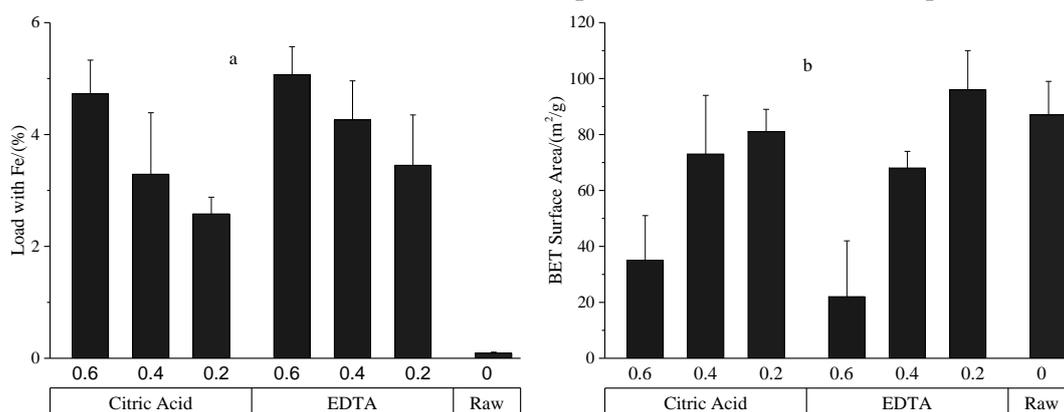


Fig.2 Properties of the studied biochars before and after loaded Fe modification

Compared with raw biochar (Fig.2b), after the Fe introduction the BET surface area in the two biochar samples decreased after loaded with organic acid-Fe introduction. With the increasing Fe content (0.2→0.6mol/L), the BET surface area of the Citric Acid-Fe biochar composites decreased from 81 m²/g to 35 m²/g, while the BET surface area of the EDTA-Fe biochar composites decreased from 96 m²/g to 22 m²/g also proved these results. The BET surface area decreased after modification of the two pristine biochars with high specific surface area, whereas it increased for those biochars with low surface area. This could be explained by the fact that with the metal salt content continuously increasing, some larger pore was probably produced or the surface of the biochar was possibly covered by the metal oxides formation during the salts dehydration process, resulted the BET surface area decrease[12, 15]. There were some previously studies described that with the increasing iron content(e.g. Fe, Mg), the total pore volume(TPV) and the average pore radius(APR) of the biochar samples increased proved these reasons.

Mn Sorption Efficiency

Compared with controlled experiment (CK), which were pure manganese slags presented in this study, the fixed biochars mixtures had significantly lower solute of Mn in all cases (decrease of 3.21 to 46.29%), and the higher sorption of Mn was in EDTA-Fe biochar (Fig.3). This improvement of the metal sorption efficiency can be explained by the presence of Fe oxides in the structure of the biochars, in agreement with the studies of Trakal et al. [8], Mohan et al. [9], Han et al. [16]. The sorption efficiency of raw biochars was changed minimally, and in the case of EDTA-Fe biochar, the efficiency was actually increased after the loaded Fe modification (46.29%). But the non-loaded Fe biochar had a non-significant effect on Mn sorption by raw biochars. On the other hand, loaded Fe modification had a significant effect on Mn sorption in all the modified biochars. Compared with the non-loaded Fe biochar (raw biochar), the fixed loaded Fe biochars mixtures had a reduction of 4.02% to 32.01% contrasting with raw biochar. But in addition there were no significant effect on Mn sorption in the same biochar with different fix ratio (5-15%). Nonetheless, our study clearly indicated that loaded organic acid biochar with greater Fe content removed higher percent of Mn from the solution.

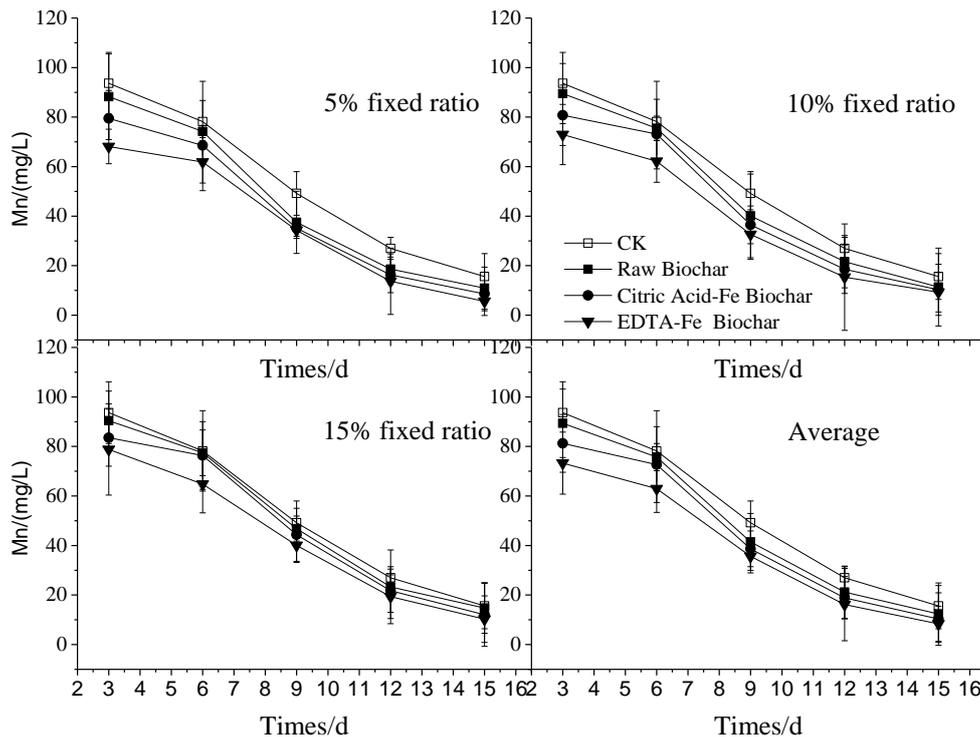


Fig.3 Time-dependent patterns of concentration curves of Mn in elution leachates from manganese slags.

Conclusions

The study clearly indicated that loaded organic acid biochar with greater Fe content removed higher percent of Mn from the aqueous solution. Impregnation with magnetite/maghemite greatly improved the sorption of Mn, cation release was improved significantly after Fe oxide impregnation into the biochar structure. Contents of Fe_2O_3 (30-103%), Fe_3O_4 (65-106%) and CaCO_3 (4-80%) increased after loaded with organic acid-Fe in the biochars. With the increasing Fe content (2.58-5.07%) in biochar, the BET surface area of the Citric Acid-Fe biochar composites decreased from $81 \text{ m}^2/\text{g}$ to $35 \text{ m}^2/\text{g}$, while the EDTA-Fe biochar composites decreased from $96 \text{ m}^2/\text{g}$ to $22 \text{ m}^2/\text{g}$. The fixed loaded Fe biochars mixtures had a reduction of 4.02% to 32.01% in Mn sorption contrasting with raw biochar.

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