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Stabilization of Pb(II) accumulated in biomass through phosphate-pretreated pyrolysis at low temperatures

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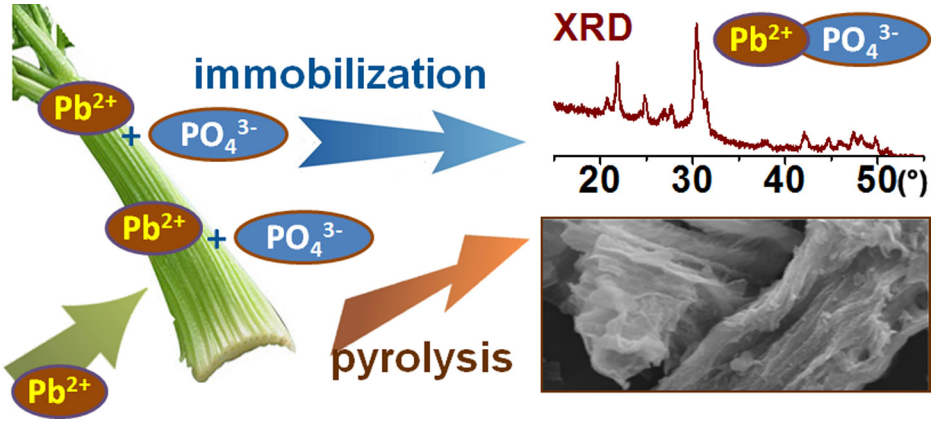
HIGHLIGHTS

- Phosphate-pretreated pyrolysis can stabilize Pb(II) accumulated in biomass.
- More than 95% of Pb(II) in celery and wood biomass was stabilized.
- Pb from biomass was almost totally retained in char.
- Most Pb was transformed into phosphates according to XRD and SEM/EDX analyses.

GRAPHICAL ABSTRACT



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ABSTRACT

The remediation of heavy metal-contaminated soil and water using plant biomass is considered to be a green technological approach, although the harmless disposal of biomass accumulated with heavy metals remains a challenge. A potential solution to this problem explored in this work involves combining phosphate pretreatment with pyrolysis. Pb(II) was accumulated in celery biomass with superior sorption capacity and also in ordinary wood biomass through biosorption. The Pb(II)-impregnated biomass was then pretreated with phosphoric acid or calcium dihydrogen phosphate (CaP) and pyrolyzed at 350 or 450 °C. Pb(II) from biomass was in turn almost totally retained in chars, and the percentage of DTPA-extractable Pb(II) was reduced to less than 5% of total Pb(II) in chars through CaP pretreatment. Pb(II) stabilization was further confirmed through a sequential extraction test, which showed that more than 95% of Pb(II) was converted into stable species composed mainly of lead phosphates according to X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) analyses. Overall, phosphate-pretreated pyrolysis can stabilize both Pb(II) and degradable biomass, so as to control efficiently the hazards of heavy metal-contaminated biomass.

1. Introduction

The contamination of water and soil by heavy metals (e.g., lead (Pb) and cadmium (Cd)) is a global environmental problem, and approaches for removal of heavy metals using plant biomass have

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Table 1
Availability of Pb(II) accumulated in the biomass and chars, and Pb(II) retentions in chars.

Sample	DTPA-extractable Pb(II) (%)	Pb(II) retention (%)	$Yield_{char}$ (%)	Q_{mass} or Q_{char} (mg/g)
Pb@CeMass	68.1 ± 3.2	/	/	22.6 ± 0.8
Pb@CeChar350	36.5 ± 1.5	97.5 ± 0.7	33.5 ± 1.1	65.8 ± 0.9
Pb@CeChar450	29.3 ± 0.9	94.9 ± 2.3	29.9 ± 0.6	71.7 ± 0.4
PA2/Pb@CeChar350	2.78 ± 0.31	100.3 ± 2.3	36.2 ± 1.3	62.6 ± 1.5
PA4/Pb@CeChar350	10.7 ± 1.1	101.6 ± 1.6	43.8 ± 0.9	52.4 ± 1.2
CaP2/Pb@CeChar350	2.34 ± 0.60	98.9 ± 2.6	34.8 ± 1.2	64.3 ± 2.2
CaP4/Pb@CeChar350	1.88 ± 0.55	102.5 ± 1.2	42.1 ± 0.8	55.0 ± 1.0
CaP4/Pb@CeChar450	1.18 ± 0.16	97.4 ± 2.8	33.3 ± 1.1	66.1 ± 1.5
Pb@PiMass	83.4 ± 1.5	/	/	6.53 ± 0.18
Pb@PiChar450	31.6 ± 1.9	88.9 ± 2.2	28.6 ± 0.8	20.3 ± 0.5
CaP4/Pb@PiChar450	4.25 ± 0.43	95.9 ± 1.0	35.0 ± 0.6	17.9 ± 0.5

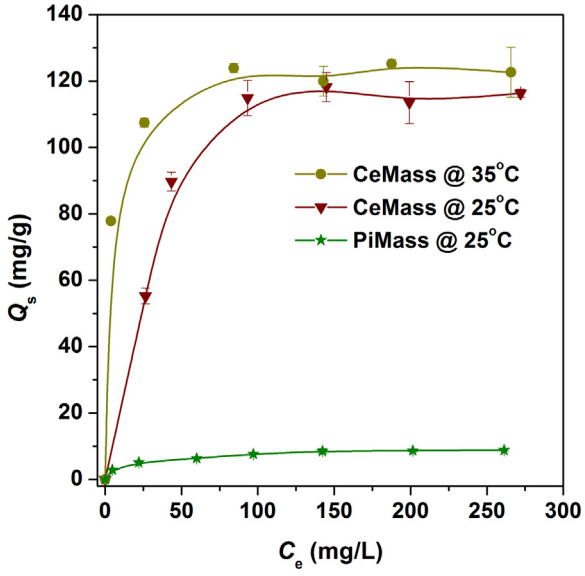

Fig. 1. Pb(II) Sorption to the celery and pinewood biomass.

attracted continuous attention from researchers due to the availability and renewability of biomass resources. Generally speaking, the applications of plant biomass for remediation of heavy metals can be categorized in the following three ways: the first involves the phytoremediation of heavy metals in soil and, in particular, the phytoextraction of heavy metals from soil using plants of high accumulating capacity [1,2], the second approach involves the absorption of heavy metals in water using aquatic vegetation, such as artificially constructed wetlands [3,4], and the third approach is often referred to as biosorption, which mainly involves the sorption of heavy metals from wastewater using biomass, such as wood sawdust, straw, algae and other agricultural residuals [5–7]. Despite the different efficiency of these approaches on removing heavy metals, the remediation using biomass is preferable to other methods as it is convenient to apply for *in-situ* operations and has negligible adverse effects on the environment. However, one vital issue in the post-treatment of hazardous biomass contaminated with heavy metals delays the promotion of such technologies. Rather, heavy metals accumulated in biomass would be released into the environment once again as biomass is readily degradable when not properly disposed of [8,9].

Currently, a number of studies have focused on the disposal of heavy metal-contaminated biomass, and proposed solutions include landfill [9], anaerobic digestion [9,10], incineration [11] and pyrolysis [12,13]. Landfill and digestion approaches would involve transferring heavy metal pollutants to new sites, although anaerobic digestion will facilitate the partial utilization of biomass through methane generation. Incineration is also likely to facilitate biomass energy recovery, but some toxic metals, such as Pb and Cd, may escape as volatile forms or may be retained in fly ash [14], which requires further processing. The pyrolysis of biomass has occurred at relatively lower temperatures and in an inert atmosphere, thus retaining heavy metals in solid char, while volatiles produced during pyrolysis can also be used as energy products [15–18]. For example, Koppolu et al. [12] found that over 98.5% of heavy metals (Ni, Zn and Cu) are concentrated in char following the fluidized-bed pyrolysis (at 600 °C) of synthetic hyperaccumulator biomass. Lievens et al. [15] reported that heavy metals Cu, Zn and Pb are almost fully retained in chars after the rapid pyrolysis of heavy metal contaminated biomass at 400–600 °C, while Cd is retained by only 52% at a pyrolysis temperature of 500 °C. Stals et al. [19] used lower temperatures of 350–550 °C for the flash pyrolysis of heavy metal contaminated biomass and found that Cd recovery in oil is increased with increasing pyrolysis temperatures. Recently, Chami et al. [20] made an interesting comparison between the flash and slow pyrolysis of Ni and Zn contaminated biomass and proposed that slow pyrolysis is more efficient than flash pyrolysis in terms of the retention of heavy metals in char, as a significant fraction of heavy metals (38% for Zn and 45% for Ni) is bound to sand as a heat transfer medium during flash pyrolysis. In spite of these research findings on the distribution of heavy metals in pyrolysis products (oil, gas and char), few previous reports have focused on the stability of heavy metals in char, which is essential to the suitable disposal of heavy metal-enriched chars. Furthermore, if heavy metals in chars were stable or could be converted into stable species, chars could be safely sequestered in soil like ordinary biochars that can serve as good soil amendments [21]. In this context, research focused on enhancing heavy metal stability in chars would facilitate the hazard control of heavy metal-contaminated biomass.

For this reason, we propose a novel solution to stabilize Pb(II) accumulated in biomass that involves combining phosphate pretreatment with the pyrolysis of biomass at low temperatures (350 or 450 °C). The hypothesis for this solution rests on the assumptions that low pyrolysis temperatures retain most Pb(II) species in solid residue and that phosphate facilitates the conversion of Pb(II) into stable species. In this work, a celery stalk was chosen as a model biomass because celery's capacity to accumulate heavy metals from soil has been highlighted in a study on heavy metal contamination in China [22], and we found celery biomass to be superior to ordinary plant biomass (like wood sawdust) in terms of Pb(II) sorption from water. Pb(II)-impregnated biomass was obtained through a biosorption process [17] that generally showed higher capacity of accumulating heavy metals than phytoextraction did [23,24], then the impregnated biomass was treated with phosphate and pyrolyzed in a nitrogen atmosphere. Pb(II) availability in chars was evaluated based on a DTPA-extractable concentration, the Pb(II) speciation was analyzed in reference to the sequential extraction procedure proposed by Tessier et al. [25], and chemical forms of