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Research article

Investigations on phosphorus recovery from aqueous solutions by biochars derived from magnesium-pretreated cypress sawdust

Khouloud Haddad [a, b], Salah Jellali [a, *], Mejdi Jeguirim [b], Aida Ben Hassen Trabelsi [c], Lionel Limousy [b]

[a] *Wastewaters and Environment Laboratory, Water Research and Technologies Center (CERTE), BP 273, Soliman, 8020, Tunisia*
[b] *Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, 15 rue Jean Starcky, 68057, Mulhouse, France*
[c] *Laboratory of Wind Power Control and Energy Valorization of Waste, Research and Technology Centre of Energy (CRTEn), B.P 95, 2050, Hammam Lif, Tunisia*

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ABSTRACT

The ability of biochars, derived from the pyrolysis at 400 °C; 500 °C and 600 °C of pretreated cypress sawdust with 20 wt% magnesium chloride ($MgCl_2$) solutions, in recovering phosphorus from aqueous solutions was investigated under various experimental conditions in batch mode. The experimental results indicated that cypress sawdust pretreatment with $MgCl_2$ induced important modifications of the physical and chemical biochars' properties favoring phosphorus recovery from the used synthetic solutions. Moreover, phosphorus recovery efficiency increased with the increase of the used pyrolysis temperature. Indeed, for an aqueous pH of 5.2 and a phosphorus concentration of 75 mg L^{-1}, the recovered amounts increased from 19.2 mg g^{-1} to 33.8 mg g^{-1} when the used pyrolysis temperature was raised from 400 °C to 600 °C. For all the tested biochars, the phosphorus recovery kinetics data were well fitted by the pseudo-second-order model, and the equilibrium state was obtained after 180 min of contact time. Furthermore, the phosphorus recovery data at equilibrium were well described by the Langmuir model with a maximal recovery capacity of 66.7 mg g^{-1} for the magnesium pretreated biochar at 600 °C. Phosphorus recovery by the used biochars occurred probably through adsorption onto biochars' active sites as well as precipitation with magnesium ions as magnesium phosphates components. All these results suggested that biochars derived from $MgCl_2$ pretreated cypress sawdust could be considered as promising materials for phosphorus recovery from wastewaters for a possible further subsequent use in agriculture as amendments.

1. Introduction

Wastewaters discharged from agriculture and urban activities are generally rich in phosphorus compounds (Li et al., 2016). Phosphorus (P), could be a potential pollutant of fresh water resources as it may contribute to the eutrophication of aquatic environments and be potentially toxic for aquatic organisms (Zhang et al., 2012). In the same time, phosphorus, which is an essential element for food production, is a finite resource on the earth and it may be depleted over the next 100 years. In this context, Schröder et al. (2011) have estimated that 2035 would be the date where phosphates demand exceed supply. Thus, P recovery from wastewaters has become a necessity in order to preserve the environment and to balance the intensively exhaustion of high-grade phosphates ores. Numerous P recovery methods such as chemical precipitation, enhanced chemical crystallization as struvite, biological uptake, and adsorption onto natural and modified materials have been developed and tested in the last decades. The chemical precipitation and crystallization processes have the drawback of the consumption of costly chemicals and the production of huge amounts of sludges (Nguyen et al., 2014). Likewise, biological P accumulation may be intensively reduced because of the difficulties of culturing adapted microorganisms and the lack of sufficient carbon contents which is necessary for their growth (Rittmann et al., 2011). Phosphorus recovery through adsorption onto natural/modified materials and wastes has been identified as a

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* Corresponding author.
E-mail addresses: khouloud.haddad@uha.fr (K. Haddad), salah.jallali@certe.rnrt.tn (S. Jellali), mejdi.jeguirim@uha.fr (M. Jeguirim), aida.benhassen@crten.rnrt.tn (A. Ben Hassen Trabelsi), lionel.limousy@uha.fr (L. Limousy).

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promising research topic since it has the advantages of low reagents and energy consumption and offers the possibility of the P-loaded products use in agriculture as fertilizers (Vohla et al., 2011). Several mineral and organic natural materials have been tested for phosphorus recovery from both synthetic solutions or real urban/industrials wastewaters such as powdered marble wastes (Jaouadi et al., 2014; Haddad et al., 2015), phosphates mine slimes (Jellali et al., 2010), Aleppo pine sawdust (Benyoucef and Amrani, 2011) and Posidonia Oceanica fibers (Jellali et al., 2011). These studies indicated that raw organic materials were not sufficient in recovering phosphorus compared to the mineral products. Indeed, the highest phosphorus recovery yields were obtained for alkaline pH and calcium-rich mineral products such as Sepiolite (Yin et al., 2013), crab shells (Jeon and Yeom, 2009) and calcinated powdered marble wastes (Haddad et al., 2015). Therefore, there was an urgent need for the development of novel, low cost and environmental-friendly organic materials which could be efficiently applied for phosphorus recovery from both low and highly concentrated phosphorus-containing effluents and then valorized in agriculture as fertilizers.

Biochars are carbon-rich solid products which are generated by the thermal stabilization of organic agricultural and animal biomasses (Kung et al., 2014). Thanks to their stability and attractive physicochemical properties, biochars have been effectively applied for carbon sequestration (Lehmann et al., 2011), greenhouse-gas emissions reduction (Wang et al., 2013), soil quality and crop yields improvement (Zheng et al., 2013) and environmental pollution control (Tan et al., 2017). Therefore, the use of biochars as efficient sorbents of dissolved pollutants could be a promising solution in order to ensure a sustainable waste management and the preservation of the environment (Cao and Harris, 2010; Jellali et al., 2016). In order to enhance the biochars' efficiencies in removing and/or recovering pollutants from effluents, huge scientific efforts have been made this last decade regarding the improvement of their properties through their physical and/or chemical modification (Inyang et al., 2014; Mohan et al., 2014). The tested methods included steam-activation (Inyang et al., 2014), and the biomasses pre-impregnation with mineral functional additives such as aluminum, iron, calcium and magnesium (Zhang et al., 2012; Zhang and Gao, 2013; Wang et al., 2015a,b). The assessment of the ability of certain biochars generated from the pyrolysis of raw and salts-pre-impregnated biomasses for P recovery from aqueous solutions has proved the role of such chemical modification in the enhancement of the P uptake under specific physicochemical conditions (Fang et al., 2014; Chen et al., 2011; Wang et al., 2015a,b). However, to the best of our knowledge, there were no studies reported in literature regarding the correlation of magnesium pretreated cypress sawdust biochars characteristics to their phosphorus recovery and release efficiencies for different pyrolysis temperatures.

In this paper, biochars prepared from the slow pyrolysis of magnesium pretreated cypress sawdust at temperatures varying between 400 and 600 °C were firstly well characterized using specific apparatus and then tested for phosphorus recovery and desorption under various experimental conditions. The main objectives of this work are: (1) to examine the effect of the pretreatment step with magnesium chloride on the main physicochemical characteristics of the produced biochars under different pyrolysis temperatures, (2) to assess the effects of contact time, initial phosphorus concentrations, pH solutions, biochars dosages and the presence of other anionic pollutants on the P recovery effectiveness, (3) to acquire further insights into the underlying recovery mechanisms and (4) to study the phosphorus release from the tested biochars and its implication for their reuse in agriculture.

2. Materials and methods

2.1. Biochars preparation

The raw cypress sawdust (RCS) used in this work was taken from a carpentry manufactory located in the city of Menzel Bouzelfa (North East of Tunisia). The RCS feedstock was firstly air-dried for 10 days until a constant weight and sieved for a particle size of 2 mm. Then, the RCS was chemically modified by immersing at once 40 g of RCS in 400 mL of 20 wt% magnesium chloride solution ($MgCl_2,6H_2O$). The resulting mixture was stirred at room temperature during 4 h. After filtering, the Mg-impregnated sample was dried in an oven at 60 °C for 24 h and the obtained solid sample was referred to "Magnesium pretreated cypress sawdust (CS-Mg)". Afterwards, the pretreated cypress sawdust was pyrolyzed in a fixed-bed stainless reactor with a length of 30 cm and a diameter of 15 cm. During the pyrolysis tests, 600 g of CS-Mg were placed in the reactor and heated by an electric furnace from room temperature until the desired temperature (400 °C; 500 °C and 600 °C) at a rate of 5 C°/min under 0.5 L min^{-1} nitrogen flow. More details regarding this reactor are given by Kraiem et al. (2015). At the end of the pyrolysis operation, the biochars were recuperated from the reactor when its temperature becomes equal to the ambient one. The generated biochars at pyrolysis temperatures of 400; 500 and 600 °C were labeled B-Mg400, B-Mg500, and B-Mg600, respectively and used for the study of phosphorus recovery from aqueous solutions and release.

2.2. Biochars characterization

At a given pyrolysis temperature, the biochars production yield ($Y_{biochar}$) was determined as the ratio between the weight of collected biochar ($M_{biochar}$ (g)) and the weight of magnesium pretreated cypress sawdust ($M_{biomass}$(g)) as follows:

$$Y_{biochar}(wt\%) = \frac{M_{biochar}}{M_{biomass}} * 100 \tag{1}$$

Proximate analysis, including volatile matter (VM), fixed carbon (FC) and ash in biochars, was performed on the basis of the standard methods in ASTM D 1762-84 (ASTM, 2013).

The pH of zero point charge (pH_{ZPC}) values of the studied biochars were determined according to the solid addition method using 0.01 M NaCl solutions, 1 g of solid matrix for initial pH values varying between 2 and 12 (Jellali et al., 2010).

The surface chemistry of biochars was provided through Fourier transform infrared spectroscopy (FTIR) analyses using the KBr method with an IFTR-BX, Perkin Elmer apparatus. All biochars samples were carefully dried before mixing with KBr to avoid any additional effect due to the presence of water. The related spectral resolution is 1 cm-1 measured between 400 and 4000 cm^{-1}.

The possible existence of any crystallographic structure in the tested biochars was assessed thanks to X-ray diffraction analysis (PW 1710). Furthermore, the mineral contents of the produced biochars were quantified by an X-ray fluorescence spectrophotometer (XRF: Philips PW2540) equipped with a rhodium target X-ray tube and a 4 kW generator. During this analysis, 100 mg of the used biochars were ground and mixed with 200 mg of boric acid then pressed into a pellet under a 10^9 Pa pressure for 15 min.

The morphologic and surface elemental composition of the biochars were characterized with a scanning electron microscopy (SEM) and energy dispersive EDX (X-ray spectrometry) (Philips XL 30 FEG).

Finally, biochars textural properties were measured by nitrogen adsorption at 77 K using a Micromeritics ASAP 2420 instrument.

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