



Evaluation of thermally-modified calcium-rich attapulgite as a low-cost substrate for rapid phosphorus removal in constructed wetlands



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ARTICLE INFO

Article history:

Received 10 November 2016

Received in revised form

24 February 2017

Accepted 5 March 2017

Available online 6 March 2017

Keywords:

Constructed wetlands

Phosphorus removal

Column study

Thermally-treated Ca-rich attapulgite

ABSTRACT

The cost-effective and geographically available substrates are vital for the design of constructed wetlands (CWs), especially the saturated subsurface flow CWs, which are deemed as an efficient way to remove the inlet-lake phosphorus concentrations. In this study, phosphorus removal of thermally-treated calcium-rich attapulgite (TCAP) with varied particle sizes (0.2–0.5 mm, 0.5–1 mm and 1–2 mm) was assessed using batch and long-term column experiments to evaluate its feasibility as a CWs substrate. The phosphorus-bound mechanism in TCAP was identified in various initial phosphorus concentrations. Batch studies indicated that more than 95% of P can be rapidly (<1 h) removed by TCAP from solution with a concentration of 20 mg P/L, and P sorption can be well fitted by a pseudo-second-order equation. The maximum P sorption capacity of TCAP was in the range of 4.46–5.99 mg P/g, and the availability of Ca²⁺ concentration might limit the P removal capacity of TCAP at high phosphorus concentrations. Both the P removal rate and capacities decreased with the increase of TCAP particle sizes. Column P removal experiments indicated that hydraulic retention time (HRT) exerts great influence on P removal performance and longer HRTs favor the dissolution of CaO in TCAP, consequently increasing the P removal rate. In a 150-day P removal experiment, TCAP removed an average of 93.1%–95.4% of the influent P with a HRT of eight hours. Both the batch and chemical extraction of the P fraction of TCAP showed that the P removed by TCAP was mainly through formation of Ca phosphate precipitation. However, the species of Ca-P precipitation formed might be varied in different phosphorus concentrations. All results indicated that TCAP can be a suitable substrate when used in CWs, and field experiments should be carried out to test its real P removal performance in the future.

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1. Introduction

Excess of phosphorus in overlying water can cause lake eutrophication and consequently induce algal bloom (Kaasik et al., 2008). The reduction of inlet phosphorus from river to lake using constructed wetlands (CW) has been regarded as an effective method to restore lake eutrophication (Drizo et al., 1999; Vohla et al., 2011; Barca et al., 2012; Claveau-Mallet et al., 2012). The process of phosphorus removal mainly occurs through adsorption and chemical precipitation by the substrate in the CWs, which is especially evident in saturated subsurface flow CWs (Drizo et al., 1999; Kaasik et al., 2008; Bowden et al., 2009). Therefore,

selection of the proper substrate is very important in the construction of CWs because the substrate choice will largely determine the nutrient removal efficiency of CWs (Drizo et al., 1999; Vohla et al., 2011; Hua et al., 2016).

Traditionally, some inert materials such as sand, unpolluted soil and gravel were used as the substrate in CWs (Brix et al., 2001). However, the nutrient removal efficiency was not always acceptable (Garcia et al., 2010). Recently, materials containing Al, Ca or Fe, which have a high affinity for phosphorus were selected as substrate in CWs and this practice has gained lot of attention (Rentz et al., 2009; Sibrell et al., 2009; Vohla et al., 2011; Claveau-Mallet et al., 2012). These materials are also being called reactive material (Renman and Renman, 2010; Claveau-Mallet et al., 2012). However, the use of these reactive materials must meet the requirement of low economic cost and geographical availability (Claveau-Mallet et al., 2012). To date, a large number of reactive

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materials has been used and proposed as substrates in CWs or in other small-scale filter systems, including natural materials (minerals, rocks, soils and marine sediments), industrial byproducts (slags from steel, mining and power plants), and man-made products (lightweight aggregates, Polonite and Sorbulite) (Drizo et al., 2006; Gustafsson et al., 2008; Vohla et al., 2011; Claveau-Mallet et al., 2012; Nilsson et al., 2013b).

Among the slags including blast furnace (BF) iron slag, basic oxygen furnace (BOF) steel slag and electric arc furnace (EAF) steel slag have all been widely tested in the laboratory and in the field for their phosphorus removal capacity (Barca et al., 2012, 2013; Zuo et al., 2015). These results indicated that slags are suitable for substrates in CWs and phosphorus removal mainly through formation of calcium bound phosphorus such as tricalcium phosphate (TCP), octocalcium phosphate (OCP) and hydroxyapatite (HAP) (Claveau-Mallet et al., 2012; Barca et al., 2013). However, the high trace metal embedded in slags may still leach in the long-term and, thus, probably pose a threat to the environment. In addition, although slags are byproducts of industries, these materials can still be expensive in developing countries. This is mainly due to the fact that slags can be refined into iron or steel by some small factories for profit-making. Therefore, cost-effective and environmentally friendly reactive materials still need to be developed and used as substrates for CWs.

In recent years, the thermally-treated calcium-rich attapulgite (powder form) was found to have a high P binding capacity (42.0 mg P/g), which is non-toxic and inexpensive (about 250–300 USD/ton) (Gan et al., 2009). This material showed a very promising use in the aspect of wastewater treatment and P inactivation agents in the sediment of eutrophic lakes (Yin and Kong, 2015; Yin et al., 2016). A detailed description of attapulgite can be found in previous research (Gan et al., 2009). In brief, attapulgite is plentiful in China. The main mineral deposit is in Xuyi country, Jiangsu Province. There are about of 67 million tons of attapulgite in Xuyi, and this tonnage accounts for more 60% of the national reserves based on a rough estimation. However, more than half of the attapulgite is considered a low grade product due to the high content of dolomite embedded in attapulgite (around 10–30% CaO), which is also called calcium-rich attapulgite (CAP). The thermally-treated CAP has good mechanical strength and can be present either in fine powder or in large particle form (0.2–4.0 mm), which has the potential to be used as substrate in CWs.

Substrate used in CWs are mostly presented in large particles and should have high hydraulic power (Blanco et al., 2016). Previous research has focused on the fine powder of thermally-treated CAP in the aspect of phosphorus removal performance (Gan et al., 2009), but these data are not suitable to serve as a guideline for the selection of substrates used in CWs. In addition, a combination of short-batch and long-term experiments should be conducted to get the parameters of substrate such as P retention capacity, longevity and different P removal efficiency with varied hydraulic retention time (HRT) used in CWs (Köiv et al., 2010; Blanco et al., 2016).

In this study, the thermally-treated calcium attapulgite (TCAP) with different particle sizes (0.2–0.5 mm, 0.5–1.0 mm and 1–2 mm) was selected and evaluated its feasibility as substrate in CWs. The P removal capacity and kinetics were studied through synthetic wastewater using batch modes. Long-term P removal performance of thermally-treated calcium-rich attapulgite was studied using column experiments to simulate the real condition of P removal by substrate in CWs. In addition, spectrum and chemical analysis of the P adsorbed adsorbent were used to elucidate the P retention mechanism by thermally-treated calcium-rich attapulgite.

2. Materials and method

2.1. Sorbent preparation and characterization

Raw calcium-rich attapulgite was collected from the town of Qiuji, Xuyi country, Jiangsu Province. The collected mineral was manually ground and sieved into particle sizes of 0.2–0.5 mm, 0.5–1.0 mm, and 1–2 mm. These materials were then calcined at 700 °C for two hours to enhance its P sorption capacity according to the method proposed by Gan et al. (2009).

The chemical composition of CAP and TCAP were measured by ICP-AES (Ca, Mg, Al and Fe). Element composition of CAP and TCAP were analyzed by XRF. Porosity was determined from the amount of water needed to saturate a known volume of components, and density was measured by the volume of water displayed by a known mass of medium. The specific surface area of CAP and thermally-treated CAP with different particle sizes was measured by the N₂ adsorption-desorption technique on an ASAP 2020 M + C (Micrometrics) at a liquid N₂ temperature (–197 °C). XRD and SEM-EDS were used to determine the characteristics of the mineralogical composition and microstructure of CAP, thermally-treated CAP and P adsorbed thermally-treated CAP, respectively. TEM was used to characterize the microstructure of CAP and thermally-treated CAP.

2.2. Batch sorption study

2.2.1. Kinetics of P removal

A standard phosphate solution (1000 mg/L) was prepared by dissolving KH₂PO₄ in de-ion water. The experimental P solution was prepared by diluting the standard solution to a known working concentration. The kinetics of phosphorus removal by thermally-treated CAP was investigated using synthetic wastewater. In brief, 0.5 g of thermally-treated CAP with different particle sizes (0.2–0.5 mm, 0.5–1 mm, and 1–2 mm) was added into a series of centrifuge tubes containing 25 ml of 10, 20, and 100 mg P/L synthetic solution. Duplicate centrifuge tubes were retrieved at 0.5, 1, 2, 4, 6, 8, 16, 24, 32 and 48 h for phosphorus and pH analysis.

2.2.2. Kinetics of Ca²⁺ release

The kinetics of Ca²⁺ release from thermally-treated calcium-rich attapulgite was investigated using the method proposed by Barca et al. (2012). The aim of this study was to elucidate the Ca²⁺ release mechanism for the modified calcium-rich attapulgite. To perform this, 0.5 g of thermally-treated CAP with different sizes were added into a series of 50 ml centrifuge tubes containing 25 ml deionized water. These tubes were put into a constant shaker with 160 rpm at 25 °C. Duplicate centrifuge tubes were retrieved at 0.5, 1, 2, 4, 6, 8, 16, 24, 32 and 48 h for Ca²⁺ analysis.

The potential of Ca²⁺ release capacity from thermally-treated CAP was calculated using the following equation:

$$Q_t = \frac{Ca^t V}{M} \quad (1)$$

where Q_t is the capacity of Ca²⁺ release at time t (mg/g). V is the volume of the solution (L), M is the mass of thermally-treated CAP (g), and Ca^t is the total Ca²⁺ concentration of the solution at time t (mg/L).

Then, the potential Ca²⁺ release capacity was plotted according the pseudo-first order kinetic equation of Lagergren (1998):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

where Q_e is the potential Ca²⁺ release capacity at equilibrium (mg/g), Q_t is the potential Ca²⁺ release capacity at time t (mg/g), t is the

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