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Recovery of phosphate and dissolved organic matter from aqueous solution using a novel CaO-MgO hybrid carbon composite and its feasibility in phosphorus recycling

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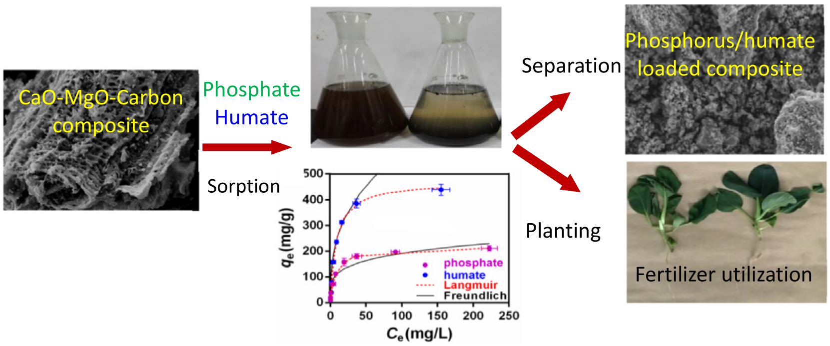
HIGHLIGHTS

- A MgO-CaO-Carbon composite was produced by co-pyrolysis of sawdust and dolomite.
- The composite showed maximum adsorption of 207 mg/g phosphorus and 469 mg/g humate.
- Phosphate-loaded composite as fertilizer significantly improved plant growth.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal oxide-Carbon composites have been developed tailoring towards specific functionalities for removing pollutants from contaminated environmental systems. In this study, we synthesized a novel CaO-MgO hybrid carbon composite for removal of phosphate and humate by co-pyrolysis of dolomite and sawdust at various temperatures. Increasing of pyrolysis temperature to 900 °C generated a composite rich in carbon, CaO and MgO particles. Phosphate and humate can be removed efficiently by the synthesized composite with the initial solution in the range of pH 3.0–11.0. The phosphate adsorption was best fitted by pseudo-second-order kinetic model, while the humate adsorption followed the pseudo-second-order and the intra-particle diffusion kinetic models. The maximum adsorption capabilities quantified by the Langmuir isotherm model were up to 207 mg phosphorus (or 621 mg phosphate) and 469 mg humate per one-gram composite used, respectively. Characterization of composites after adsorption revealed the contributions of phosphate crystal deposition and electrostatic attraction on the phosphate uptake and involvement of $\pi - \pi$ interaction in the humate adsorption. The prepared composite has great potential for recovering phosphorus from wastewater, and the phosphate sorbed composite can be employed as a promising phosphorus slow-releasing fertilizer for improving plant growth.

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1. Introduction

The limited mineral reserve of phosphorus in nature is predicted to run out quickly within the next century due to the excessive utilization of phosphate-fertilizer during the agricultural production process (Gilbert, 2009). Accordingly, phosphorus levels in surface waterbodies had increased with the result of widespread runoff loss of phosphate from agricultural land (Maavara et al., 2015). Nearly all the lakes in the United State and China are suffering from eutrophication with phosphorus as the inducement of the problem (Conley et al., 2009; Liu et al., 2016). Therefore, reclaiming of phosphorus from the phosphate-rich aqueous system will be a win–win sustainable strategy for preventing surface water from eutrophication and alleviating phosphorus shortage crisis (Desmidt et al., 2015).

Numerous technologies, such as chemical precipitation, biological uptake, membrane filtration, and adsorptive recovery, have been developed for phosphate removal (Geng et al., 2018; Hermassi et al., 2018; Furuya et al., 2017; Zhang et al., 2018). Comparatively, attributing to the low consumption and easy operation, adsorption has attracted attention and has been employed to treat the phosphorus-containing wastewaters, especially as an alternative method for phosphate recovery (Li et al., 2016a, 2016b; Veni et al., 2017). Although traditional adsorbents (i.e. activated carbon and artificial organic resin polymer) and new type nano-adsorbents (i.e. carbon nanotube and graphene) are effective on phosphate adsorptive recovery (Kumar et al., 2017; Luo et al., 2016; You et al., 2018; Zong, 2013), they generally pose the high cost and difficulty in disposal after use, which have hindered their wide application in practice (Nguyen et al., 2014). Consequently, the application of low-cost carbon material as an environment-friendly adsorbent for phosphate recovery has attracted great attention recently (Veni et al., 2017).

To date, various studies had shown the potential of low-cost carbon adsorbents on resources recovery from effluents, but the challenges still remained due to the limited phosphate adsorption capacity and the requirement for a large number of pure carbon adsorbents to use in practice (Li et al., 2017, 2018a). For this reason, researchers have recently shifted the sight into the exploration of functionalized metal/metal oxide-carbon composite adsorbents through impregnation of exogenous metal elements into organic feedstocks including waste biomass followed by pyrolysis under oxygen-limited condition (Li et al., 2018a, 2018b; Vikrant et al., 2018). It is believed that the thermal pyrolysis of waste biomass materials into a metal/metal oxide–carbon composite not only benefits organic solid waste disposal (Huang et al., 2018) but also facilitates the functional carbon material development (Tan et al., 2015; Park et al., 2017). This approach of carbonation process favors the porous carbon structure formation (Li et al., 2017) and in turn improves phosphate recovery ability (Vikrant et al., 2018). Till now, several low-cost adsorbents like Ca, La, Mg, Mn, Fe, and Al oxides hybrid carbon composites had been produced (Chen et al., 2011; Dai et al., 2017; Fang et al., 2015; Jung et al., 2015; Li et al., 2017; Marshall et al., 2017; Song et al., 2014; Wang et al., 2015; Yang et al., 2018; Yao et al., 2013a, 2013b; Zhang and Gao, 2013). For instance, a magnetic orange peel carbon composite synthesized by Fe^{3+}/Fe^{2+} co-precipitation-pyrolysis procedure showed promising phosphate adsorptive recovery potential (Chen et al., 2011). A layered double Mg/Al hydroxides carbon composite prepared by using a post-precipitation method yielded reasonably high phosphate affinity (Li et al., 2016a). Grafting macroalgae carbon composite with AlOOH nanoparticles in a specific electric-field-assisted pyrolysis approach increased phosphate adsorption capacity up to 96 mg/g (Jung et al., 2015). A Ca-Mg-Carbon composite is made by an adsorption-pyrolysis combined procedure recycled phosphate from biogas fermentation liquid with phosphate adsorption capacities as high as 294–327 mg/g (Fang et al., 2015). Furthermore, the presence of solid metal oxide (e.g. MgO or $Mg(OH)_2$, etc.) on the carbon structure matrix was found to present many benefits like acting as kinds of metals source for phosphate attraction (Vikrant et al., 2018), neutralizing acidity with their alkalinity nature, and providing suitable pH ranges for phosphate recovery (Li et al., 2017). Nevertheless, in view of engineering production of the metal oxide–carbon hybrid composite, these reported procedures are effective but somewhat complicated, and often involve several steps in feedstock pretreatment and carbon composite production. For example, in an integrated adsorption-pyrolysis procedure to produce the MnOx-biochar composite, corn straw powder was firstly heated at 600 °C under N_2 to obtain raw biochar, followed by immersing the raw biochar in $KMnO_4$ solution and ultrasonically irradiating for 2 h, oven-dried at 80°C, and then the dried product was further pyrolyzed at 600 °C under N_2 to finally produce the composite (Song et al., 2014). Clearly, such complicated synthesis requirements may limit the potential of these carbon composites for the widespread application (Li et al., 2018a, 2018b). Therefore, it is important to develop an alternative method for metal-carbon composite production with direct one-step pyrolysis procedure so that it does not require restrictive operating conditions and complicated synthesis (Li et al., 2018a, 2018b; Park et al., 2017; Vikrant et al., 2018).

In addition, it is known that carbon material adsorbent often has excellent performance for removing dissolved organic contaminant (DOC). Recently, Oh et al. (2016) successfully fabricated a Fe–carbon composite with exceptional 2,4-dinitrotoluene and 2,4-dichlorophenol removal performances by thoroughly mixing Fe^0 particle with rice straw before pyrolysis. Such a co-pyrolysis method is clearly simpler than the abovementioned metal–carbon composite synthesis processes. Therefore, it is assumed that the co-pyrolysis method could be used in the synthesis of the metal-carbon composite with superior phosphate and DOC removal capacities from solutions. However, till now, this hypothesis still needs to be proved in practice, and there is no investigation of synthesis of the CaO and MgO particles hybrid carbon composite through co-pyrolysis of dolomite and biowaste. Such an approach on metal/metal oxide–carbon composite fabrication has not been thoroughly explored due to the knowledge gaps (Li et al., 2018a, 2018b; Takaya et al., 2016), and the possibility of CaO and MgO particles hybrid carbon composite served as adsorbents for both phosphate and DOC removal from aqueous solutions is still unknown.

Herein, in this manuscript, we present a novel CaO and MgO particle hybrid carbon composite synthesized through thermal treatment of dolomite and sawdust with aiming to enhance phosphate recycling capacity and DOC removing ability from aqueous solution. Its characterization, performance, and mechanism on phosphate and DOC adsorptive removal were evaluated. In addition, the feasibility of the CaO and MgO particle hybrid carbon composite on phosphate recovery from actual wastewater and the potential as phosphate fertilizer were investigated as well.

2. Material and methods

2.1. Materials

Poplar tree wood sawdust obtained from a local drum factory near campus was used as the feedstock biomass. The sawdust was washed with tap and deionized water (DI, 18.2 MΩ) three times before drying at 55 °C for overnight. Then, dry sawdust was milled in a ball grinder; the powder with a size smaller than 0.15 mm was collected for use. Natural dolomite powder (<0.15 mm) of high purity (CO_2 balance, SiO_2 0.37%, Al_2O_3 0.08%, Fe_2O_3 0.1%, MgO 20.96%, CaO 29.27%, and pH 8.78) was purchased from Xin Jing Ling Shou mineral processing plant (Hebei province, China). Dolomite was utilized without further purification. Real wastewater samples were collected from a local wastewater tank of swine slaughterhouse near the campus. The wastewater of slaughtering and the leachate of the slaughterhouse landfill site were all stored in this tank. Suspended solids in the collected wastewater were removed by filtrating with the assistance of a 0.45 μm membrane filter. Physicochemical characteristics of wastewater were pH 8.87, COD