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Removal of arsenic from water by porous charred granulated attapulgite-supported hydrated iron oxide in bath and column modes

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ABSTRACT

Clays are increasingly used as hosting materials to develop cost-effective adsorbents for pollutant removal from water. This is especially urgent for arsenic purification in rural and undeveloped areas. However, the fine powder form of modified clay cannot be used directly in water treatment due to the separation difficulty. Herein, a simple and easy method was used to prepare a low-cost arsenic adsorbent through loading hydrated iron oxide into porous charred granulated attapulgite. The results show that iron impregnation can increase the Brunauer-Emmett-Teller surface area and micropore volume of charred granulated attapulgite, which was possibly caused by the nano-sized iron formed in the channel of charred granulated attapulgite. Batch studies indicate that As(III) (arsenite) and As(V) (arsenate) sorption on the prepared adsorbent fit well with the Langmuir equation as the maximum sorption capacities were 3.25 and 5.09 mg/g, respectively, which were higher than the reported low-cost arsenic adsorbent. The arsenic sorption rate on the iron impregnated sorbents varied with initial arsenic concentrations, but all can be described by a pseudo-second-order model. The iron modified charred granulated attapulgite performed well with a wider pH value (5–9). However, inhibition effects of arsenic sorption by coexisting ions SO_4^{2-}, HCO_3^- and PO_4^{3-} increased with the increase of their concentrations. Of these, PO_4^{3-} exerted the largest effect. The arsenic adsorbed sorbent can be regenerated by 0.5 mol/L NaOH four times with an approximate 11.3% and 25.6% sorption capacity lost for As (V) and As (III), respectively. A fixed bed column experiment showed that iron-modified charred granulated attapulgite can treat 397 BV for As (V) and 175 BV for As (III) of arsenic contaminated water below 10 μg/L. These results indicated that the first reported low-cost iron modified charred granulated attapulgite is very promising for arsenic contaminated water purification in rural and developing area.

1. Introduction

Great efforts have been taken by scientists around the world to lower the arsenic (As) concentration in groundwater, drinking water, and wastewater (Brammer and Ravenscroft, 2009). This is due to the huge harmful effect posed by elevated arsenic concentrations to human health including skin alteration, damage to major body organs and many types of cancer (Jomova et al., 2011). The occurrence of health problems associated high arsenic concentration has been frequently reported in developing countries such as China, India and west Africa (Brammer and Ravenscroft, 2009; Guo et al., 2014). To mitigate these problems, the World Health Organization (WHO) set a very strict limit of 10 μg/L as the maximum permissible arsenic level in drinking water. However, it is hard to lower the high arsenic level in contaminated waters to this strict 10 μg/L limit due to the difficulty of trace arsenic removal.

It is widely accepted that adsorption is the most effective arsenic removal method because it takes advantage of other activities such as precipitation, membrane separation and ion exchange to easily remove arsenic from water and wastewater at a relatively low cost (Mohan and Pittman, 2007; Aredes et al., 2013; Awual et al., 2013; Zhang et al., 2013). In the past few decades, various kinds of adsorbents have been developed and tested in water and wastewater treatment (Mohan and Pittman, 2007). In summary, these sorbents

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can be classified into iron, zirconium oxide or binary oxide-based nanomaterials (Zhang et al., 2013; Saldaña-Robles et al., 2017), resin-supported nanosized materials (Pan et al., 2009), industry byproducts (Namasivayam and Senthilkumar, 1998; Bibi et al., 2015; Shih et al., 2015; Ociński et al., 2016), engineered biochar (Hu et al., 2015; Wang et al., 2015) and modified clays (Aredes et al., 2013; Uddin, 2017). Although the manmade nanomaterials have excellent arsenic sorption and performance, their high cost is prohibitive in rural and underdeveloped areas with high arsenic groundwater or wastewater. Hence, additional investigations are still needed to develop low-cost and easy operation sorbents for the removal of arsenic from aqueous solutions.

Recently, scientists have paid great attention to clay-based low cost adsorbents (Babel and Kurniawan, 2003; Uddin, 2017). This is mainly due to the fact that clay is inexpensive, nontoxic, plentiful, and easily modified (Choi et al., 2017). However, raw clay normally has a low-pollutant sorption capacity and must be impregnated with reactive elements in order to enhance their sorption capacity (Uddin, 2017). Iron (Fe) salt, zero-valent iron or iron oxyhydroxide has been regarded as favorable as they support reactive substances, which can greatly enhance the arsenic sorption capacities of pristine clays (Li et al., 2011; Bhowmick et al., 2014; Bentahar et al., 2016; Saldaña-Robles et al., 2017). However, natural clay has poor mechanic strength and the powder form of modified clay cannot be used directly in column or fluidized systems due to the excessive pressure drop and separation difficulty resulting from modified clays' ultrafine particles (Pan et al., 2014). Hence, a pre-solidified treatment is essential before incorporating any reactive elements into the porous clay-based sorbents. Normally, high-temperature calcination of granulated clay was thought to be a better way to solidify these clays, which could then can be used as supporting materials for further modification. Although high temperature of heating can cause a reduction in the Brunauer-Emmett-Teller (BET) surface area of raw clay, the heating process can sometimes increase the average pore diameter and channel of modified clays, which is favorable when loading reactive elements (Gan et al., 2009).

Attapulgite (AP) is made up of magnesium aluminum phyllosilicate ($(Mg,Al)_2Si_4O_{10}.4H_2O$) and can be found in the form of natural hydrated magnesium silicate minerals. The AP structure is made up of parallel ribbons in 2:1 layers and is characterized by a high viscosity, a high surface area, a moderate layer charge, and many silanol groups on its surface. These physico-chemical characters make it a potentially attractive adsorbent. Attapulgite is abundant in China with more than 60% of the national deposits located in Xuyi County, Jiangsu Province (Wang and Wang, 2016; Yin et al., 2017). Raw AP is quite cheap (about 15–20 USD/ton) and is also a nontoxic clay used mostly as a clarifying agent for edible (cooking) oils and as filter aids as well as a fertilizer component (Wang and Wang, 2016). In contrast, the usage of AP in environmental research and especially in practical applications is quite scare. Furthermore, most of the environmental research is based on the modification of AP in its fine powder form (Chen et al., 2011; Cui et al., 2013; He et al., 2013; Quan et al., 2014). However, the powder form of modified AP products might not be useful in wastewater treatment due to the separation difficulty. Consequently, a solidified granular AP is a promising option. In this study, the charred granulated attapulgite (GAP) was used as a supporting material and subsequently impregnated the charred GAP with hydrous iron oxide to prepare low-cost arsenic adsorbents. Further, the arsenic sorption performance on the iron (Fe)-modified charred GAP was systematically assessed in batch and column modes and to investigate its arsenic sorption mechanism using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) analysis.

2. Material and method

2.1. Chemical reagents

All the chemical reagents used were of analytical grade. As (V) (arsenate) stock solution was prepared with deionized water using $Na_2HAsO_4.7H_2O$. The As (III) (arsenite) stock solution was prepared with NaOH solution using As_2O_3. The As (V) and As (III) working solutions were freshly prepared by diluting arsenic stock solution with deionized water.

2.2. Preparation of the hydrated iron oxide impregnated charred GAP

Attapulgite (AP) was collected from Xuyi County of Jiangsu Province. Granulated attapulgite (GAP) was prepared by the drum granulator method making it easy to produce these materials at large-scale. The particle size of GAP was in the range of 1.0–2.0 mm. To enhance the mechanical strength of GAP, the prepared GAP was calcined in a muffle furnace for two hours at 700 °C. The temperature of calcination was based on weight loss of charred GAP in water and was also used to evaluate the mechanic strength of the charred GAP. Test results are accessible in the supplemental material (Table S1).

Fe-impregnated charred GAP was prepared by adding 10.0 g charred GAP into 40 ml of iron salt solution ($FeCl_3.6H_2O$) with 0 to 2 mol/L under continuous strong agitation using a magnetic stirrer for 24 h, and then dried at 90 °C for another 24 h. The dried Fe-impregnated charred GAP was washed with deionized water several times until there was no Cl^- detection; then, it was once again oven dried at 60 °C. The resulting product was the Fe-modified charred GAP.

2.3. Batch arsenic adsorption experiments

To evaluate the arsenic sorption capacity of charred GAP and Fe-impregnated charred GAP, 0.5 g charred GAP and Fe modified products were added into 100 mg/L arsenic (III and V) solutions. The mixtures were then placed in a shaker (25 °C) for 24 h at 160 rpm to ensure complete mixing. The solutions were then centrifuged and the supernatants filtered through a 0.45-μm membrane. The arsenic concentration in the resulting solution was then measured and the arsenic sorption capacity of various Fe modified charred GAP samples were compared before the optimum material was selected.

Arsenic (III and V) sorption isotherms and the kinetics of the Fe-modified charred GAP were evaluated by batch experiments. Analysis of the arsenic sorption kinetics was carried out at 25 °C with an initial arsenic (III and V) concentration of 5, 20 and 100 mg/L at a pH of 7.0. In brief, 10.0 g of optimum Fe modified charred GAP was added to 500 ml of arsenic solution in three 1-L Erlenmeyer flasks, which were subsequently placed in a rotary shaker set at 160 rpm. Periodically, 1 ml of each of the well-mixed aliquots in the flasks was sampled, centrifuged and filtered through a 0.45-μm membrane. The resulting solutions were kept at 4 °C until further analysis. For the sorption isotherms, 0.50 g of Fe-modified charred GAP were added to 50-ml polyethylene centrifuge tubes with 25 ml of various As (III and V) solutions (0.05–200 mg/L) at a pH of 7.0. The tubes were then placed on a temperature shaker (25 °C) for 24 h at 160 rpm, to ensure complete mixing. The solutions were then centrifuged and the supernatants filtered through a 0.45-μm membrane. The resulting solutions were kept at 4 °C until further analysis.

To examine the effect of pH and co-existing anions (sulfate (SO_4^{2-}), phosphate (PO_4^{3-}) and bicarbonate (HCO_3^-)), temperature