Enhanced arsenate removal by lanthanum and nano–magnetite composite incorporated palm shell waste–based activated carbon

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ABSTRACT

Palm shell waste–based activated carbon (PSAC) was magnetized via hydrothermal impregnation of nano–magnetite, and further coated by various amounts of lanthanum (La) followed by calcination. Numerous batch tests were carried out to observe arsenate removal by La–impregnated, magnetized PSAC (MPSAC–La) in aqueous phase. Isotherm data showed that MPSAC–La(0.36) (weight ratio of La to Fe = 0.36) gave the highest adsorption capacity (227.6 mg g^{-1}), which was approximately 16.5 and 1.6 times higher than PSAC and magnetized PSAC (MPSAC), respectively. As an indication of sorption affinity, MPSAC–La(0.36) had the highest Langmuir constant (K_L), which was approximately 230 times greater than that of MPSAC. Based on the pH effect and speciation modeling, arsenate was predominantly removed by precipitation at pH < 8, while it complexed on the surface of La(OH)$_3$ at pH > 8. Lesser La dissolution resulted, owing to a strong binding effect of nano–magnetite with La. XRD, FTIR, SEM–EDS, and N$_2$ gas isotherms showed that the coating of nano–magnetite introduced substantial clogging in the micropores of PSAC, but increased meso– and macropores. However, lanthanum oxide/hydroxide (LO/LH) glued the spaces of nano–magnetite to eliminate most pore structures, and effectively removed arsenate as LaAsO$_4$ at pH 6. Overall, MPSAC–La(0.36) is considered a competitive granular material due to its extremely high sorption capabilities, easy magnetic separation and high regeneration rate.

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1. Introduction

As a group 1 human carcinogen [1,2], arsenate has been found to originate from natural geochemical or anthropogenic activities such as underground geochemical mobilization, pesticide and herbicide application, and mining activities [3–5]. Arsenate contamination causes serious environmental and human health problems. For example, prolonged uptake of arsenic contaminated water may lead to serious health problems including skin lesions [6,7], liver cancer [8], and gastrointestinal injuries [9].

Techniques such as oxidation, coagulation–flocculation, adsorption, ion exchange, and membrane transfer have been developed to remove arsenic from contaminated water. Adsorption is a promising method as it is uncomplicated, economical and comprehensive [4,10,11]. Activated carbon (AC) is a prevalent sorption material that is widely applicable, owing to its high surface area and pore volume [12–14]. However, commercial AC is expensive,

so efforts have been made to yield AC from renewable and cheaper precursors such as rice husk ash [15], bamboo [16], date pits [17], silk cotton hull [18], jute fiber [19], groundnut shell [20], corncob [21], and rattan sawdust [22].

In this study, for the first time, we used palm shell waste–based activated carbon (PSAC), a cost–effective material that is available in bulk, for the preparation of sorption materials that can be used for purifying water contaminated with arsenate. PSAC has not only a high surface area and pore volume, but also structural rigidity and size selectivity. However, its hydrophobic characteristics are not compatible with the removal of anionic hydrophilic arsenate [23]. Therefore, it is essential to modify the PSAC surface to achieve high speed and capacity for arsenate removal. Since arsenate can be effectively removed by metal (hydr)oxides through the formation of mono– and bidentate inner–sphere complexes [24,25], a properly incorporated metal oxide may lead to high sorption capacity and affinity [26–28]. Nano–magnetite, a reactive metal oxide, has attracted interest in many fields as it is cost–effective, magnetically separable, and has a large surface area [4,29–31]. Magnetite is attractive for its high adsorption capacities [32] and affinity toward arsenic species [33], resulting in a low desorption characteristic for retained arsenic. Bimetallic (hydr)oxide

particles have been introduced as a promising adsorbent to increase adsorption capacities by integrating their own unique properties [32,34]. Zhang et al. [4] proposed a novel Fe–La composite hydroxide by removing arsenate, and presented sorption capacities between 116 mg g^{-1} and 368 mg g^{-1} for a range of Fe–La composite proportions. Lanthanum hydroxide has been classified as non–toxic [35] and has good arsenate removal capabilities over a wide pH range [4,36]. However, the composites are nano–sized, not magnetically separable, and very effective at leaching La in acidic conditions, such that practical implementation for water treatment is difficult. Therefore, we aimed to develop an economic PSAC–based granular material with a relatively high sorption speed and capacity, which was magnetically separable and did not leach La across a wide pH range. Specifically, we attempted to prepare magnetically separable granular bimetallic composite materials through sequential impregnation of Fe and La into PSAC. First, magnetite was impregnated into PSAC to form magnetized PSAC (MPSAC). Then, La was immobilized on the MPSAC to form MPBAC–La. Through these processes, MPSAC–La was expected to be a firm, durable, and recoverable bimetallic adsorbent material for arsenate removal.

The main objectives of this study were (i) to prepare MPSAC–La with different La proportions, (ii) to characterize the prepared MPSAC–La by several techniques, (iii) to evaluate the arsenate sorption kinetics and capacities, as well as the effects of pH, temperature, and co–existing anions on a sample's sorption behavior, and (iv) to investigate regeneration mechanisms for arsenate removal.

2. Materials and methods

2.1. Materials

PSAC (75–150 μm) was purchased from Bravo Green Sdn Bhd, Kuching, Malaysia. The PSAC was used as a host material for nano–magnetite and La (hydr)oxide. Sodium arsenate heptahydrate (Na$_2$HAsO$_4$·7H$_2$O), La (III) chloride heptahydrate (LaCl$_3$·7H$_2$O), Fe (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O), and sodium hydroxide (NaOH) were purchased from R&M Chemical.

2.2. Preparation of magnetized palm shell waste–based activated carbon

MPSAC was prepared using a hydrothermal wetness impregnation method. Fe$_2$SO$_4$·7H$_2$O (2.78 g) was dissolved in 100 mL deionized (DI) water. PSAC (0.5 g) was added to the solution and continuously stirred. Ten milliliters of 10% (w/w) NaOH was added to this solution over five min to precipitate the iron into a hydroxide form. The solution was heated in a sonicator for 1 h at 80 °C and allowed to cool to room temperature before repeated washing in DI water. The MPSAC was oven–dried at 100 °C for 1 h and stored in a clean, sealed container.

2.3. Preparation of lanthanum impregnated MPSAC

MPSAC–La was prepared using an incipient wetness impregnation method. The predetermined masses (0.801 g, 1.335 g, and 2.136 g) of LaCl$_3$·7H$_2$O were dissolved into 0.9 mL DI water, after which 1 g of MPSAC was added to the solution, stirred for 24 h and calcinated at 500 °C for 5 h. The impregnated products were washed until the solution produced was clear, and then oven–dried at 100 °C for 2 h. Oven–dried products were kept at room temperature in a sealed container to prevent contamination. Aqua–regia extraction was added to determine the volume of Fe and La in the MPSAC–La. The weight ratios of La to Fe were 0.084, 0.23, 0.28, and 0.36, which were designated as MPSAC–La

(0.084), MPSAC–La(0.23), MPSAC–La(0.28), and MPSAC–La(0.36), respectively.

2.4. Batch tests

2.4.1. Adsorption isotherms

Arsenate stock solution (1000 mg L^{-1}) was prepared by dissolving 4.165 g of Na$_2$HAsO$_4$·7H$_2$O into 1 L DI water. Prepared media (0.025 g) was added to 25 mL arsenate solution (with a concentration between 10 mg L^{-1} and 350 mg L^{-1}) in a 50 mL centrifuge tube. The initial pH of the solution was adjusted to pH 6 ± 0.1 and final pH was measured. The conical flasks were agitated on an orbital shaker for 24 h at 150 rpm and room temperature (26 ± 1 °C). After 24 h, the final pH was measured and 10 mL of the suspension was filtered out using a 0.45–μm–pore filter, and the arsenate concentration of the filtrate was analyzed by inductively coupled plasma optical emission spectrometry (ICP–OES, Optima 5300V, Perkin Elmer).

The equilibrated adsorption capacity was calculated using the following equation:

$$Q_{eq} = (C_0 - C_{eq}) \times \frac{V}{M}, \tag{1}$$

where Q_{eq}, C_o, and C_{eq} are the adsorption capacity (mg g^{-1}), initial concentration (mg L^{-1}), and final concentration (mg L^{-1}), respectively, and V and M are the volume of solution (L) and mass of adsorbent (g), respectively. The isotherm data were well–fitted using Langmuir and Freundlich isotherm models that are explained further in the supporting information (SI).

2.4.2. Adsorption kinetics

Kinetic studies were performed in a 1 L conical flask with 500 mL arsenate solution (350 mg L^{-1} initial concentration). The pH and solution temperature were maintained at pH 6 ± 0.1 and 26 ± 1 °C, and the conical flask was shaken at a rate of 150 rpm for 5 h. At predetermined intervals, 5 mL samples were removed for analysis. All kinetic data were fitted using pseudo–second order kinetic and intraparticle diffusion models. All models are described in the SI.

2.4.3. pH effects

pH effect studies were carried out using the same method as the isotherm studies. The fixed initial arsenate concentration was 350 mg L^{-1}, and the initial pH ranged from 2 to 10. After 24 h, the final solution pHs were recorded, and the remaining arsenate concentrations were measured.

2.4.4. Temperature effect

The effect of temperature was investigated using the same method as the kinetic study. Solution temperatures of 288 K, 298 K, and 308 K were selected.

2.4.5. Competition effects

Adsorbent (0.03 g) and arsenate solution (30 mL), with initial concentration of 50 mg L^{-1} or 350 mg L^{-1} were combined in a 50 mL centrifuge tube. Sodium salts (2.5 mmol L^{-1} of NO$_3^-$, Cl$^-$, HCO$_3^-$, or SO$_4^{2-}$) were also added to the solution. As a reference, a set of arsenate solutions without competing anions was also prepared to compare sorption capacities. The pH and solution temperatures were maintained at pH 6 ± 0.1 and 26 ± 1 °C, respectively. The suspensions were then agitated at 150 rpm for 24 h.

2.5. Regeneration

Three cycles of adsorption and desorption were carried out to investigate the reusability of MPBAC–La(0.36) that exhibited the