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

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A B S T R A C T

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 (KL), 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 N₂ 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 LaAsO₄ 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 arsenate. 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 (Na₂HAsO₄·7H₂O), La (III) chloride heptahydrate (LaCl₃·7H₂O), Fe (II) sulfate heptahydrate (FeSO₄·7H₂O), 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. FeSO₄·7H₂O (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 LaCl₃·7H₂O 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

2.4. Batch tests

2.4.1. Adsorption isotherms

Arsenate stock solution (1000 mg L⁻¹) was prepared by dissolving 4.165 g of Na₂HAsO₄·7H₂O 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:

\[ Q_{eq} = (C_0 - C_{eq}) \times \frac{V}{M} \]  

where \( Q_{eq} \), \( C_0 \), 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 NO₃⁻, Cl⁻, HCO₃⁻, or SO₄²⁻) 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
highest sorption capacity in previous tests. The adsorption tests were carried using 0.2 g of adsorbent in a 350 mg L\(^{-1}\) arsenate solution. The suspensions were agitated for 24 h at 150 rpm. The adsorbents were separated from the solution using a magnet and dried at 105 °C for 1 h. The adsorption capacity was measured for each cycle. Desorption tests were conducted by stirring the dried adsorbent into a 100 mL NaOH solution (0.5 M) at 150 rpm for 6 h. Then, the adsorbents were washed with distilled water and dried in a vacuum oven under the same conditions as described above prior to re-adsorption tests.

2.6. Characterization

Morphological changes of adsorbent particles were examined using field emission scanning electron microscopy (FESEM, FEG Quanta 450, EDX–Oxford). X-ray powder diffraction (XRD, PANalytical, EMPYREAN) was used to verify the presence and type of composites with their corresponding diffraction peaks for PSAC, MPSAC, MPSAC–La(0.28), MPSAC–La(0.36), and arsenate–retained media [MPSAC–La(0.36)–As(V)] over a range of 20–80°. Texture characterization of the PSAC and MPSAC–La was performed on the N\(_2\) adsorption–desorption isotherm, which was obtained at 77 K by TriStar II 3020 (Micrometrics\textsuperscript{\textregistered}, USA). The specific surface area and pore specific volume were measured by the Brunauer–Emmett–Teller (BET) method, whereas the pore diameter and pore size distribution were determined by the Barret–Joyner–Halenda (BJH) method. Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, FTIR–spectrum 400) was carried out to analyze changes in the functional group on the oxide surfaces, as well as the structural stability of PSAC, MPSAC, MPSAC–La(0.36), and arsenate–retained MPSAC–La(0.36). The pH of the point of zero charge (pH\(_{PZC}\)) of PSAC, MPSAC, and MPSAC–La(0.36) were determined using a pH drift method \[37\] with a 0.1 M NaCl solution at pH 2–12 (±0.1). The pH\(_{PZC}\) of the adsorbent was determined by plotting graphs of the initial pH against the change in pH (pH\(_{\text{final}}\)–pH\(_{\text{initial}}\)).

3. Results

3.1. Arsenate isotherms

The arsenate adsorption isotherms for various samples at the initial arsenate concentrations (10–350 mg L\(^{-1}\)) are illustrated in Fig. 1(A). Measured final pHs for all samples show no significant differences with the initial pHs. As a result, the samples had different adsorption trends. At 90 mg L\(^{-1}\) of C\(_{eq}\) PSAC, MPSAC, and MPSAC–La(0.084) achieved approximately 20 mg g\(^{-1}\), 40 mg g\(^{-1}\), and 70 mg g\(^{-1}\) adsorption capacities (q\(_{eq}\)), respectively. At the same C\(_{eq}\), MPSAC–La(0.23), MPSAC–La(0.28), and MPSAC–La(0.36) had adsorption capacities of 170 mg g\(^{-1}\), 190 mg g\(^{-1}\), and 220 mg g\(^{-1}\), respectively.

Isotherm data were fitted using two isotherm models, Langmuir and Freundlich. Table S1 shows that Langmuir more accurately represented the isotherm data (except for PSAC), because its determination coefficients (R\(^2\) > 0.92) were higher than those R\(^2\) (>0.77) for MPSAC and MPSAC–La(0.084–0.36) fit by Freundlich. The lowest q\(_{\text{max}}\) value for PSAC was only 13.8 mg g\(^{-1}\), but MPSAC–La(0.36) had the highest q\(_{\text{max}}\) of 227.6 mg g\(^{-1}\). Thus, surface modification by dual impregnation of Fe and La [i.e. MPSAC–La(0.36)] increased the adsorption capacity by 16.5 times that of the unmodified PSAC. Although MPSAC–La(0.36) had a q\(_{\text{max}}\) 1.6 times greater than that of MPSAC (141.8 mg g\(^{-1}\)), its Langmuir constant (K\(_{L}\) = 2.25) was 230 times greater than that of MPSAC (0.01) (see Fig. 1(B)).

Limousin et al. specified four main types of Langmuir isotherm. La–impregnated media (La/Fe mass ratio >0.23) can be classified as an H–type Langmuir isotherm, indicating a high affinity. The other media are L–type Langmuir isotherms, as they have an adsorption capacity on arsenate concentration and active site on adsorbent surface \[38\]. Based on Table S1 at SI, it was observed that the K\(_{L}\) values significantly increased as the impregnated amount of La increased. The higher value of K\(_{L}\), the stronger sorption affinity between adsorbate and adsorbent can be obtained \[39\]. Fe–La composite hydroxide synthesized by Zhang et al. \[4\] also showed the larger K\(_{L}\) and q\(_{\text{max}}\) values were obtained with the higher ratio of La/Fe (in the range of 1/3–1/0). As an interesting aspect, MPSAC–La(0.36) had a much higher q\(_{\text{max}}\) than Fe–La composite [La/Fe (1/3), 116 mg g\(^{-1}\), which had a similar La/Fe ratio. This might be happened by the structural differences since MPSAC–La has a sequence of Fe and La at inner– and outer layers, respectively, while Fe–La composite has a mixed matrix.

The following experiments were conducted using MPSAC and MPSAC–La(0.36) because the MPSAC–La(0.36) had the highest K\(_{L}\) and q\(_{\text{max}}\) as well as MPSAC was chosen as a comparative media to find out the influence of La for the efficiency of arsenate removal.

3.2. Kinetics

Fig. 2(A) shows the kinetic data of MPSAC–La(0.36), as well as fit lines of pseudo–second order kinetic model. At first for ~30 min, MPSAC–La(0.36) had fast sorption speeds with 78% arsenate removal percentages over equilibrated capacity (q\(_{eq}\)).
240.6 mg g⁻¹. To investigate the adsorption rate and removal mechanism of arsenate by MPSAC–La(0.36), the pseudo first-order and pseudo second-order kinetic models were utilized. By comparing their R² values (Table 1), the pseudo first-order kinetic model had a higher value (0.994) than the pseudo second-order kinetic model (0.991). Thus, it can deduce that physical-sorption (i.e. precipitation) is an influenced removal mechanism. In addition, the intra particle diffusion model was also plotted to prove the diffusion mechanism. Fig. 2(B) shows MPSAC–La(0.36) kinetic data and fit lines using IPD model did not passed through the origin, proving that IPD is not the only affecting factor [40,41]. Lately, Liu et al. reported predominant formation of bidentate binuclear corner–sharing inner–sphere complexes between arsenate and nano–magnetite based on their spectroscopic analyses [42]. Through XPS analyses, Zhang et al. also conveyed nano–magnetite doped on the activated carbon fiber had a major role to eliminate arsenate with the mechanism of inner–sphere complexation [43]. Based on those evidences, further tests were conducted to prove the removal mechanism of arsenate by MPSAC–La(0.36).

Table 1 shows the kinetic parameters of MPSAC–La(0.36), as well as their comparison with other references (Table S2). It shows that MPSAC–La(0.36) had the highest v₀ (20.8 mg g⁻¹ h⁻¹). In fact, faster adsorption rate might occur when higher amount of positive charge of sorbent are available [44] due to an electrostatic interaction with arsenate oxyanion [45]. To prove the electrostatic characteristics of media, pHₚZC was measured and data were presented in the SI, Fig. S1. Consequently, MPSAC–La(0.36) had pHₚZC (7.4). At pH < pHₚZC, positive charges will dominate and increase attraction effect with arsenate oxyanion [46]. Thus, at pH 6, MPSAC–La(0.36) has high amount of positive charge and eventually gives higher arsenate removal speed.

3.3. pH effects

Fig. 3(A) shows arsenate speciation and equilibrated sorption capacity (qₑq) by MPSAC–La(0.36) at different pH. MPSAC–La (0.36) had high sorption capacities at most pH range. The highest sorption capacities for MPSAC–La(0.36) was 247.3 mg g⁻¹ at pH 5.4. As pH was <5, qₑq of MPSAC–La(0.36) was reduced significantly to a pH 2.3. Fig. 3(B) shows La³⁺/Fe³⁺ dissolution and La speciation according to pH. The dissolved concentration of La³⁺ ions exponentially increased as pH reduced. Zhang et al. [4] also measured the dissolution of La with various La–Fe composite by pH. As their results, La dissolution increased when the La/Fe increased. For example, La/Fe (1/3) started to dissolve La at pH < 7 while La/Fe (1/0) had La dissolution at pH < 9. In our case, however, MPSAC–La (0.36) (La/Fe, 0.36/1) had La dissolution occurred at pH < 4. Accordingly, as shown at Zhang et al., this demonstrates that heterogeneous metal oxide might have a particular stabilization effect on La dissolution, inferring that nano–magnetite might have a strong binding strength to stabilize La.

The highest La³⁺ ion dissolution, 340 mg g⁻¹ was obtained at pH 2.3 and this value was equivalent to 94% of La amounts incorporated to media. Thus, it deduces that most La coated on media was dissolved out into solution at acidic condition. This minimized sorption capacity might be due to dissolution of La³⁺, which does not participate in the arsenate removal as a precipitation agent [47]. Due to this fact, MPSAC–La (0.36) had the lowest sorption capacity at pH 2.3. For all range of pH, Fe³⁺ was not dissolved due to the La coating and low solubility of magnetite [48].

The sorption capacities of arsenate were gradually reduced from pH 5.4–8 and they were stable to be about ~190 mg g⁻¹ at pH > 8. In this study, the chemical equilibrium–modeling program, ‘Medusa/Hydra’, was applied to generate the soluble and solid complexes. Table S3 shows the soluble and solid species of individual metals, terms of reaction, and equilibrium constants (logK). The La speciation shows that La³⁺ exists dominantly as cationic species at pH < 8 and La(OH)₃ is prevalent at pH > 8. Based on this speciation, therefore, arsenate is dominantly removed by precipitation at pH < 8 while it complexes on the surface of La(OH)₃ at pH > 8. Soluble La³⁺ ions are expected to react with arsenate to form LaAsO₄ precipitate [4]. There are two available precipitation reactions as shown below.

\[
\text{La}^{3+} + \text{H}_2\text{AsO}_4^- + \text{La}^{3+} + 2\text{H}^+ \\
\text{La}^{3+} + \text{HASO}_4^- + \text{La}^{3+} + \text{H}^+ 
\]

The maximum sorption capacity was found when species H₂AsO₄⁻ is dominant [33]. This might be happened by the following circumstance. As shown at above precipitation reactions, (R1) releases double hydrogen ions (H⁺) of (R2) and soluble H⁺ ions help to further solubilize La(OH)₃ to release La³⁺ for precipitation. Along with the stability of La phase, dissolved La³⁺ was not detected because it was involved in precipitation reaction at 4 < pH < 8. When pH is <4, however, H₂AsO₄⁻ non–ionic prevalent species, does not react with La³⁺ ion to form precipitate. The dissolution trend of La³⁺ was reversed related to the speciation fraction of H₂AsO₄⁻. Meanwhile, arsenate (as HASO₄⁻ species) might be mainly removed by the inner–sphere complexation [4] onto the surface of La(OH)₃ under alkaline condition (pH > 8).

3.4. Mechanism of arsenate removal by MPSAC–La

In order to elucidate the arsenate removal mechanism, spectroscopic analyses such as XRD, SEM–EDS, N₂ gas isotherm and FT–IR
were performed for prepared media and arsenate retained media. Fig. 4 shows the XRD results of PSAC, MPSAC, MPSAC–La(0.28), MPSAC–La(0.36) and arsenate retained MPSAC–La(0.36) at pH 6. PSAC has significant graphite peaks of (0 0 2) and (1 0 0) at 28° and 43°, respectively. The magnetic materials coated on the surface of MPSAC were identified as magnetite and maghemite. Three broad peaks at 37°, 43° and 62° of 2 theta were corresponding to (3 1 1), (4 0 0) and (4 4 0) planes of magnetite [JCPDS : 19-0629] [49] while two broad peaks at 53° and 56° were identified as (4 2 2) and (5 1 1) planes of maghemite [JCPDS : 39-1346] [50]. Although the magnetization properties between magnetite and maghemite is similar [51], the oxidation of magnetite might lead to the formation of maghemite during the drying process of MPSAC. Once La was incorporated into MPSAC with a ratio of 0.28:1 (La:Fe), peaks of lanthanum oxide (LO) phase were shown on (1 1 0), (1 0 1), (1 1 1) and (2 0 2) planes while phase of lanthanum hydroxide (LH) was emerged at 28°, 33°, 37 and 49° on (1 1 0), (1 0 1), (2 0 0), (1 1 1) and (3 0 0) planes, respectively. However, it still has magnetite and maghemite peaks. As for MPSAC–La(0.36), the phase of LH increased more than LO, and magnetite/maghemite phases still existed but reduced significantly. The peaks of LO and LH were determined to refer to LaO3 [JCPDS : 05-0602] and La(OH)3 [JCPDS : 36-1481]. The XRD pattern for arsenate retained MPSAC–La(0.36) showed the formation of LaAsO4 phase [JCPDS : 15-756] at 28° and 30° which are the plane of (1 2 0) and (0 1 2), correspondingly. The results exhibited that the arsenate was dominantly removed by precipitation mechanism [4]. In addition, while LO peaks still existed, the disappearance of LH peaks revealed that LH was leached away and LaAsO4 layer was covered on the LO phase during the removal of arsenate from liquid phase.

The morphology of PSAC, MPSAC, MPSAC–La(0.36) and arsenate retained MPSAC–La(0.36) at pH 6 were analyzed by using FESEM–EDS. Fig. 5(A) and (B) shows morphological structures of PSAC, in which outer pores were highly developed. Fig. 5(C) shows the morphology of MPSAC and ball–like nanoparticles were seen on the surface although outer pores were still found. The EDS shows that MPSAC contained 72.3% Fe and 27.7% O. Through the molecular weight calculation, the iron oxide deposited on the PSAC shows that MPSAC contained 72.3% Fe and 27.7% O. Through the molecular weight calculation, the iron oxide deposited on the PSAC was identified as a dominant phase of magnetite (Fe3O4). Fig. 5(D) shows the morphological structure of MPSAC–La(0.36), in which the nano–particles of magnetite/maghemite were disappeared.

Table 1
Parameters of pseudo–first and pseudo–second order kinetic models for arsenate adsorption by MPSAC–La(0.36).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo first order kinetic model</th>
<th>Pseudo second order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qe (mg g−1)</td>
<td>Kads (min−1)</td>
</tr>
<tr>
<td>MPSAC–La(0.36)</td>
<td>265.2</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

Fig. 3. (A) arsenate speciation and sorption capacity by MPSAC–La(0.36) at different pH and (B) La3+ speciation and leaching concentrations of La3+ and Fe3+ ions.

Fig. 4. XRD results of PSAC, MPSAC, MPSAC–La(0.28), MPSAC–La(0.36) and arsenate retained MPSAC–La(0.36) after adsorption at pH 6, C0 = 150 mg L−1, 1 g L−1 of adsorbent.
weight ratio (2.62) of La to As is higher than the theoretical ratio (1.85) for LaAsO₄ which was seen at XRD. This result is well matched to the finding of XRD, in which LO and LaAsO₄ phases were co–existed.

In the SI, Fig. S2 shows N₂ gas isotherm and BJH pore size distribution of various media. According to the IUPAC standard classification, PSAC shows type 1 isotherm curve to represent the long horizontal knee feature of isotherm, predominantly consisting of micropore structures. Meanwhile, others have type 4 isotherm curves. Accordingly, with a small incorporation of La, micropores largely reduced, instead mesopore structures developed. However, as the incorporation amount of La increased, the microporous structure completely disappeared mesopores size significantly enlarged. Based on those results, it can infer that mesopores were created by inter–spaces of nano–magnetite/maghemite. However, incorporated LH/LO glued between nano–particles to eliminate most pore structures.

Based on Table 2, PSAC has the highest BET surface area (842.5 m² g⁻¹) and micropore area (777.8 m² g⁻¹) so that micropores were dominant. Whiles, PSAC–La(0.28) had the lowest BET surface area (23 m² g⁻¹) and micropore area (3.1 m² g⁻¹). About 99.6% of micropores were disappeared with La incorporation, indicating that most pores were clogged by LO/LH.

Table 3 shows the comparison of qₘₐₓ and sorption densities with other references. MPSAC–La(0.36) had a comparable qₘₐₓ (227.6 mg g⁻¹) to Fe–La (1:3) composite (hydr)oxides (235.4 mg g⁻¹) [4]. As a remarkable result, MPSAC–La(0.36) had a higher sorption density (6.9 mg m⁻²) than Fe–La (3:1) composite (hydr)oxides (4.3 mg m⁻²) [4], even though it has a smaller ratio of La to Fe (0.36:1). Thus, beside of high sorption density, MPSAC–La(0.36) has advantages in a high amount of sorption capacity (227.6 mg g⁻¹) than Fe–La (3:1) composite (hydr)oxides (47.1 mg g⁻¹).

The FT–IR spectra for PSAC, MPSAC, MPSAC–La(0.36) and arsenate retained MPSAC–La(0.36) were illustrated in Fig. 6. The peaks at 2915/2917, 2074/2100 and 1409/1499 cm⁻¹ in the IR spectra of PSAC/MPSAC, were indicated to C=H, aromatic and C=O aromatic stretching, respectively. The peak at 612 cm⁻¹ for MPSAC is assigned to Fe–O stretching. The difference between PSAC and MPSAC is the OH peak which can be seen at 3000–3500 cm⁻¹. This difference shows that MPSAC media was coated with magnetite/maghemite. When La is impregnated, new IR peaks at 3395 and 3556 cm⁻¹ were emerged to indicate O=H stretching group of LH [54]. The peak at 1629 cm⁻¹, H–O–H was observed to be deformation of water molecules by forming physi–sorbed water on the oxide. The IR peak at 1484 and 1423 cm⁻¹ is characteristic of LO [55]. When arsenate is retained at MPSAC–La(0.36), the peaks of O=H and LO/LH at 3556, ~1400, 500–700 cm⁻¹ were significantly reduced and new peaks at 808 and 839 cm⁻¹ were assigned to As–O–La precipitate as LaAsO₄ [4]. Thus, these facts can infer that LO/LH were utilized to form arsenate precipitate. Overall, Scheme 1 presents MPSAC–La(0.36) preparation and arsenate removal mechanism.
Comparison of maximum adsorption capacities and sorption densities of various media.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Molar ratio of La:Fe</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micropore area (m²/g)</th>
<th>Volume (cm³/g)</th>
<th>Primary mesopore area (m²/g)</th>
<th>Volume (cm³/g)</th>
<th>Size (W_{eq}, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSAC</td>
<td>N/A</td>
<td>842.5</td>
<td>0.428</td>
<td>777.8</td>
<td>0.428</td>
<td>153.1</td>
<td>0.116</td>
<td>18.4</td>
</tr>
<tr>
<td>MPSAC-La(0.084)</td>
<td>0.17:1</td>
<td>332.1</td>
<td>0.389</td>
<td>247.6</td>
<td>0.389</td>
<td>109.1</td>
<td>0.389</td>
<td>43.7</td>
</tr>
<tr>
<td>MPSAC-La(0.28)</td>
<td>0.56:1</td>
<td>23.0</td>
<td>0.098</td>
<td>3.1</td>
<td>0.001</td>
<td>20.0</td>
<td>0.095</td>
<td>169.7</td>
</tr>
<tr>
<td>MPSAC-La(0.36)</td>
<td>0.72:1</td>
<td>32.7</td>
<td>0.091</td>
<td>6.0</td>
<td>0.003</td>
<td>26.8</td>
<td>0.087</td>
<td>111.34</td>
</tr>
</tbody>
</table>

* Not available.

### 3.5. Thermodynamics

Temperature is one of the factors to affect adsorption capacity of arsenate by media at liquid–solid medium. In this study, the temperature effect was studied at 289, 299 and 309 K. In Supporting Information (SI), Fig. S3(A) shows that the arsenate adsorption capacity increased from 146 to 266 mg g⁻¹/C₀ as temperature increased from 289 to 309 K, indicating an endothermic nature and chemisorption process [56]. The kinetic data was fitted by pseudo–second order kinetic model as showed in Fig. S3(B). The increment in temperature caused not only an increment of driving force between arsenate and MPSAC–La(0.36), but also a decrement of energy barrier. Thermodynamics curve was constructed in Fig. S3(C) and analysis was conducted by evaluating the changes of enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°). Based on the following equations, ln(mq eq/Ceq) vs. 1/T was plotted.

\[
\ln \left( \frac{m_{\text{eq}}}{C_{\text{eq}}} \right) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} (2)
\]

\[
\Delta G^o = -RT \ln \left( \frac{m_{\text{eq}}}{C_{\text{eq}}} \right) (3)
\]

where m is the dosage of MPSAC–La (0.36) (g L⁻¹), A is the Arrhenius factor and R (8.314 J/mol/K) and T are the gas constant and temperature in K, respectively.

Thermodynamics constants were tabulated in Table 4. The positive values of ΔH° (55.46 kJ/mol) and ΔS° (190.12 J/mol K) indicate that the adsorption is endothermic reaction and there is some structural disturbances of MPSAC–La(0.36) during the adsorption process [32,57]. This structural disturbance was also proved by the results of SEM–EDS, XRD and FT–IR analyses. Since ΔG° values show an increase of negative value with the increase of temperature, arsenate adsorption by MPSAC–La(0.36) is efficient at higher temperature.

### 3.6. Competition effect and regeneration

The effect of co-existing anions (HCO₃⁻, NO₃⁻, Cl⁻ and SO₄²⁻) toward arsenate adsorption capacity was illustrated in the SI, Fig. S4. The concentration of coexisting anion in this study is much higher than that of phosphite (1 mM) to determine adsorbate selectivity [58]. While, in this experiment, 2.5 mM coexisting anions were used ~4 times higher than 50 mg L⁻¹ (0.67 mM) to show MPSAC–La (0.36) able to remove arsenate even in the presence of high concentration coexisting anion. In the study of Seliem et al., the concentration of various coexisting anions (5 mM) were used at 5 times higher than that of phosphite (1 mM) to determine adsorbate selectivity. As results, the adsorption capacities of arsenate by MPSAC were reduced >30% with the addition of Cl⁻ at Cᵢ = 350 mg L⁻¹ (Fig. S4(A)), while those of MPSAC–La(0.36) were
<30% for all co-existing anions (Fig. S4(B)). Accordingly, the adsorption of arsenate to both media were interfered by anion \((\text{HCO}_3^-/\text{CO}_3^2-, \text{SO}_4^{2-}/\text{CO}_3^2-, \text{NO}_3^-/\text{CO}_3^2-, \text{Cl}^-/\text{CO}_3^2-)\) [59], but MPSAC–La(0.36) has less sensitivity on anionic competition than MPSAC.

Three cycles of adsorption and desorption were carried out to examine the reusability of MPSAC–La(0.36) and illustrated in Fig. 7. Once arsenate adsorption was completed, spent MPSAC–La(0.36) was regenerated using 0.5 M NaOH solution. As a result, MPSAC–La(0.36) had approximately 75% of 1st arsenate adsorption capacity at the 3rd cycle. As per the analogous case, Zhang et al. reported that Fe–La composite hydroxide achieved 75% adsorption rate at the 4th re-adsorption cycle. Interestingly, nano–magnetite might have a strong binding strength to stabilize La, providing less La dissolution. XRD, FTIR, SEM–EDS and N\(_2\) gas isotherms disclosed that nano–magnetite coating gave a considerable micropore clogging of PSAC, but increased mesopores due to the space creation between nano–magnetite particles. Nevertheless, LO/LH cemented the spaces of nano–magnetite to eliminate most pore structures and had an effective removal function of arsenate as LaAsO\(_4\) at pH 6.

Established on the results of batch tests, granular–sized MPSAC–La(0.36) has a potential to be a competitive and economic media because of extremely high sorption capabilities, easy magnetic separation and high regeneration rates.

### 4. Conclusion

In this study, highly–effective sorption materials for the removal of arsenate were prepared through magnetization of PSAC followed by La incorporation using a wetness impregnation and calcination. The isotherm study showed that the arsenate adsorption capacity and \(K_T\) value significantly increased with the increment of La impregnated to MPSAC. MPSAC–La(0.36) had about 16.5 or 1.6 times higher \(q_{\text{max}}\) (227.6 mg g\(^{-1}\)) for arsenate removal than PSAC or MPSAC. Especially, it had 230 times higher \(K_T\) than MPSAC, representing that La impregnation had much stronger sorption affinity for arsenate. The experimental results of pH effect on arsenate removal and speciation modeling revealed that arsenate is dominantly removed by precipitation at pH < 8 while it complexes on the surface of La(OH)\(_3\) at pH > 8. In addition, interestingly, nano–magnetite might have a strong binding strength to stabilize La, providing less La dissolution, XRD, FTIR, SEM–EDS and N\(_2\) gas isotherms disclosed that nano–magnetite coating gave a considerable micropore clogging of PSAC, but increased mesopores due to the space creation between nano–magnetite particles. Nevertheless, LO/LH cemented the spaces of nano–magnetite to eliminate most pore structures and had an effective removal function of arsenate as LaAsO\(_4\) at pH 6. Established on the results of batch tests, granular–sized MPSAC–La(0.36) has a potential to be a competitive and economic media because of extremely high sorption capabilities, easy magnetic separation and high regeneration rates.

### Acknowledgement

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### Appendix A. Supplementary material

Supporting information contains Langmuir, Freundlich and kinetic model equations and symbols definition. Titles for Tables...


