Chemically Modified Sawdust as Renewable Adsorbent for Arsenic Removal from Water

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S *Supporting Information*

ABSTRACT: Environmentally friendly and cost-effective adsorbent materials for arsenic extraction are needed for removing pollutants from groundwater. Here, lanthanum or zirconium oxide nanoparticle-incorporated sawdust was used for the removal of arsenic anions from water. The chemically modified sawdust was fully characterized and used for extraction of arsenic from water. The influences of ionic strength, pH, and interfering ionic pollutants toward the extraction efficiency of arsenic anions were investigated to understand the mechanism. ZrO_2-sawdust showed extraction capacities of 29 and 12 mg/g for arsenite and arsenate anions, respectively, while La_2O_3-sawdust extracted arsenite (22 mg/g) and arsenate (28 mg/g) anions efficiently. Desorption studies were performed on surface-modified sawdust to check the recyclability. La_2O_3-sawdust can be fully regenerated with no change in arsenic removal efficiency, while ZrO_2-sawdust retains ∼50% of its adsorption efficiency. Such modified renewable bioadsorbents are useful for developing environmentally friendly materials for water purification.

KEYWORDS: *Arsenic, Adsorption, Lanthanum, Zirconium, Glutamic acid, Sawdust, Isotherms, Kinetics*
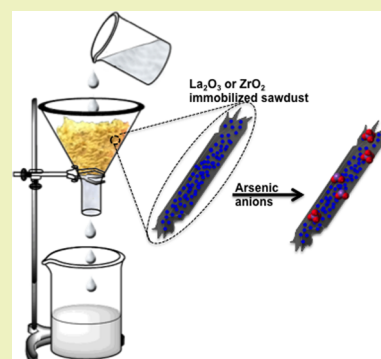
INTRODUCTION

Arsenic pollution in water is a worldwide problem[1−6] and causes significant health hazards such as damage to the central nervous system,[7] skin,[8] kidney,[9] and liver,[10] lung diseases,[11] and cancer.[12] Upon comparison of existing water treatment methods, extraction of pollutants with adsorbents is a simple and cost-effective process for removing arsenic and other pollutants from groundwater.[13] In general, many low-cost, natural, renewable, nontoxic, and biodegradable adsorbents are available in large quantities for potential applications for water purification.[14]

Agricultural waste materials such as spent grain,[15] onion-skin,[16] rice husks,[17] bark[18,19] and sawdust,[20−22] maize cobs,[23] wheat bran,[24] and insoluble starch[25] have been utilized for the removal of heavy metal salts from water. Sawdust has been used as an adsorbent for the removal of various pollutants from water, such as dyes, salts, and heavy metal cations and anions.[26] Overall, unmodified sawdust is suitable for the extraction of heavy metal cations owing to the presence of electron-rich groups on the surface.[27] Sawdust incorporated with ferric oxyhydroxides was used for arsenic removal with an arsenate adsorption capacity of 9.259 mg/g based on the Langmuir isotherm model.[28] For extraction of anions, electron-deficient functional groups such as quaternary nitrogen or metal centers must be incorporated on the surface of the sawdust.

Coating of transition metal oxides such as ZrO_2 and La_2O_3 on adsorbent surfaces helps to modulate the surface charges and enhances the extraction capacity toward arsenic anions.[29−31] On the other hand, $La(OH)_3$ has shown high efficiency toward extraction of arsenate anions.[32] Recently, we have reported the usage of ZrO_2-loaded apple peels for the extraction of chromium, arsenic, and phosphate anions.[33] La_2O_3-loaded zeolite and silica gel have also shown significant affinity for arsenate anions at neutral pH.[34,35]

From previous studies, it was difficult to find a single adsorbent that extracts both arsenite and arsenate anions efficiently. In addition, the large-scale production of modified samples for field implementation is usually difficult for reported materials. The aim of this project is to develop a cost-effective adsorbent from a renewable low-cost sawdust material through chemical modification of the surface for efficient removal of both arsenite and arsenate anions from water. Chemical modification of sawdust was achieved using a two-step process in which glutamic acid was grafted on the sawdust surface, followed by complexation of La or Zr oxide. The carboxyl group of glutamic acid is known to interact strongly with zirconia through Lewis acid−base pairing and with lanthanum hydroxide through ligand exchange.[36,37] Under neutral conditions, no leaching of La or Zr was detected during the extraction studies, as concentrations of La and Zr in water were below the ICP detection limit (<0.1 ppm).

La_2O_3- and ZrO_2-sawdusts were characterized using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FTIR) spectroscopy, elemental (CHNS) analysis, inductively coupled plasma−optical emission spectroscopy (ICP-OES), and X-ray diffraction

studies (XRD). Arsenite and arsenate anion extraction experiments were performed, and extraction efficiencies of modified sawdust were calculated and compared. Time-dependent studies, effect of pH, ionic strength, and role of interfering pollutants were completed to demonstrate extraction efficiency for arsenic pollutants and elucidate adsorption mechanism. An abstract art representing the concept of our investigation is given in Figure 1.
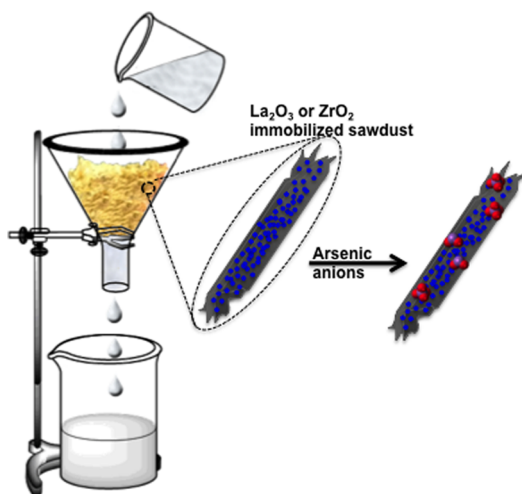
Figure 1. Removal of arsenic pollutants using chemically modified sawdust.

◼ EXPERIMENTAL SECTION

Materials. Hardwood sawdust was obtained from a local furniture workshop. Sodium hydroxide, sulfuric acid, glutamic acid, glutaraldehyde (50% w/v), phosphoric acid (85%), zirconyl chloride octahydrate, sodium arsenite ($NaAsO_2$) and sodium arsenate heptahydrate ($NaH_2AsO_4.7H_2O$), and lanthanum nitrate hexahydrate were purchased from Sigma-Aldrich Pte, Ltd. Ammonia solution (25%) was purchased from Merck and used as received.

Preparation of Arsenic and Other Anions Stock Solutions. Aresenite and arsenate stock solutions (1000 ppm) were prepared using sodium arsenite ($NaAsO_2$) and sodium arsenate heptahydrate ($NaH_2AsO_4.7H_2O$), respectively. Sodium sulfate (Na_2SO_4), potassium nitrate (KNO_3), and trisodium phosphate hydrate ($Na_3PO_4.12H_2O$) were purchased from Sigma-Aldrich Pte, Ltd. and were used to prepare sulfate, nitrate, and phosphate anion stock solutions (1000 ppm).

Preparation of Glutamic Acid Sawdust and Coating with ZrO_2/La_2O_3. Sawdust was mixed with deionized water, sonicated, and filtered; the process was repeated several times until the water washings become clear. Lignin was removed by soaking the dried sawdust in NaOH solution (200 mL, 2 M) for 24 h, followed by washing with deionized water, soaking in a H_2SO_4 (200 mL, 1% v/v) solution, washing with water, and drying in an oven at 50 °C. To further functionalize the sawdust, glutamic acid (2 g, 13.6 mmol) was dissolved in 100 mL water along with phosphoric acid (2 mL, 2% v/v) and was mixed with sawdust (2 g, 0.02 g/mL), followed by a slow addition of glutaraldehyde (2 mL, 2% v/v). The solution was allowed to stir for 24 h and was then filtered, and the solid residue was washed with water (150 mL).

To load Zr or La oxide on the surface, sawdust (1 g) was stirred in water (30 mL) together with zirconyl chloride octahydrate (5 g) for ZrO_2-sawdust or lanthanum nitrate hexahydrate (5 g) for La_2O_3-sawdust for 24 h. The functionalized sawdust was filtered and placed inside an ammonia chamber for 3 h to prepare Zr oxide or La oxide immobilized on the surface.[31,38] The material was washed with water (200 mL) and dried at 50 °C.

Characterization of Sawdust. FTIR spectra of the sawdust before and after functionalization were recorded within the range of 4000−400 cm^{-1} using a Bruker ALPHA FT-IR spectrophotometer using KBr as matrix. Elemental (CHNS) analyses were done on the sawdust samples before and after functionalization using an Elementar Vario Micro Cube instrument. X-ray diffraction (XRD) patterns of the sawdust were recorded using Bruker-AXS: D8 DISCOVER with a GADDS powder X-ray diffractometer with a Cu Kα (λ = 1.54 Å) source at 40 kV and 40 mA over a range of 2Θ angles from 1° to 90° using a step size of 1°. The morphologies of the sawdust were examined using a JEOL JSM-6701F field emission scanning electron micrograph (SEM). Energy dispersive X-ray spectroscopy (EDS) was used for identification of elements on the surface of sawdust. Percentages of Zr and La in the sawdust were measured using a dual-view Optima 5300 DV inductively coupled plasma optical emission spectroscopy (ICP-OES) system. The La and Zr components of the sawdust, arsenite, and arsenate anions adsorbed on the sawdust were further identified using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra[DLD] using mono Al Kα as the photoexcitation source). C 1s (C−C bond) was calibrated at 284.5 eV.

Time-Dependent Studies. La_2O_3- or ZrO_2-sawdust (0.024 g) was dispersed in an arsenite or arsenate solution (12 mL, 10 ppm) to determine the amount of arsenic adsorbed at a low concentration similar to arsenic pollutants found in groundwater. For kinetics studies, an arsenite or arsenate solution (12 mL, 80 ppm) was mixed with sawdust (0.012 g) and stirred at pH 7. The minimum concentration of sawdust in solution was used in order to find the maximum amount adsorbed (q_e). All arsenic adsorption studies were done using an orbital shaker at 250 rpm. Time point collections of samples were done at 0.25, 0.5, 1, 2, 4, 8, and 24 h. Samples (1.5 mL) were collected, diluted to 7 mL, and filtered prior to ICP analysis.

Concentration-Dependent Studies. The pH of arsenite or arsenate solutions (10 mL, 100 ppm) was adjusted to 7 by adding the appropriate amounts of 0.1 M HCl solution, and the solution was diluted to get the concentrations at 10, 20, 30, 40, 50, 60, and 80 ppm. La_2O_3- or ZrO_2-sawdust (0.01 g) was dispersed in the above solutions and put on a mechanical shaker. Samples (1.5 mL) were taken after 24 h, diluted to 7 mL, and filtered prior to ICP analysis.

pH and Ionic Strength Studies. In order to understand the effect of pH on extraction efficiency, the pH of arsenite and arsenate salt solutions (5 mL, 10 ppm) were adjusted to 3, 5, 7, 9, and 11 using appropriate amounts of either a NaOH or HCl solution (0.1 M). La_2O_3- or ZrO_2-sawdust (0.01 g) was added to the solution and stirred. Samples (1.5 mL) were collected after 24 h, diluted to 7 mL, and filtered prior to ICP analysis. Ionic strength of solutions was adjusted by adding appropriate amounts of NaCl salt into arsenic solutions to make the final concentrations of NaCl as 584 and 5840 ppm. Extractions were done to understand the role of ionic strength toward removing arsenic pollutants from water.

Desorption Studies and Recycling of Sawdust. Arsenic adsorbed on the surface of ZrO_2-sawdust was desorbed using NaOH (10 mL, 1 M) and La_2O_3-sawdust using HNO_3 (10 mL, 1 M) and by shaking the mixture for 24 h using an orbital shaker at 250 rpm. The samples (1.5 mL) were collected, diluted to 7 mL, filtered, and submitted for ICP analysis to calculate the percentage of arsenic desorbed. Owing to the release of La/Zr oxide nanoparticles from the surface during the desorption process, the sawdust was reloaded with La oxide or Zr oxide using the same procedure described above, filtered, washed, and dried at 50 °C, followed by second cycle of adsorption studies using a fresh arsenite or arsenate salt solution.

◼ RESULTS AND DISCUSSIONS

Sawdust Characterization. The composition of sawdust mainly consists of cellulose and lignin.[39] Lignin was removed to provide a larger surface area for the adsorption of arsenic from water. Removal of lignin from the sawdust FTIR spectra (Figure 2) showed that a few peaks disappeared upon treatment of the sawdust with 2 M KOH and 1% H_2SO_4, which included an aromatic C−H stretch from lignin (2964
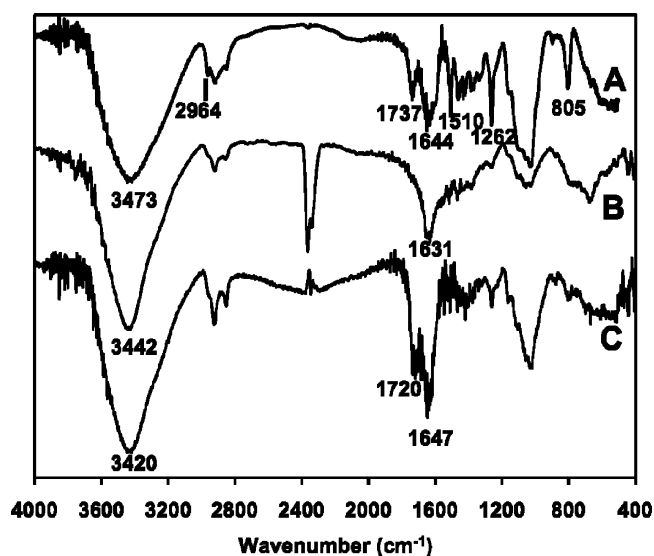
Figure 2. FTIR spectra of sawdust (A) before and (B) after treatment with a NaOH solution, followed by dilute H_2SO_4 and glutamic acid-modified sawdust (C).

cm^{-1}), aromatic C=C bending (1644 cm^{-1}, 1737 cm^{-1}), aromatic C=C stretch (multiplet near 1510 cm^{-1}), methoxy C–O stretch (1262 cm^{-1}), and aromatic C–H bending (805 cm^{-1}), which indicates removal of lignin.

After the removal of lignin, sawdust (S-OH) was functionalized using glutamic acid (glutamic-NH$_2$) and glutaraldehyde (OHC-Glu-CHO) as shown in eq 1.

S-OH + OHC-Glu-CHO + glutamic-NH$_2$

$\rightarrow$ S-O-CH-Glu-C-NH-glutamic   (1)
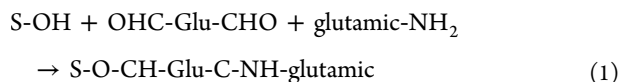
Transformation from raw sawdust to glutamic acid-grafted sawdust was confirmed by the appearance of a carboxylic acid C=O stretch peak at 1720 cm^{-1} and an imine C=N stretch peak at 1647 cm^{-1} (Figure 2C). Elemental analysis (Table S1, Supporting Information) showed an increase in N content from 0.33% to 1.08% upon grafting with glutamic acid.

The raw sawdust fibers used in this study have different sizes and shapes with dimensions of approximately 1–5 mm in length and 1 mm in width, which makes it easy to handle during the water purification process (Figure 3). Color change from brown to pale yellow was also observed after surface modification of the sawdust (Figure 3B). As expected, the surface functionalization with glutamic acid and metal oxide incorporation on the sawdust did not change the morphology (Figure 3). The presence of a large number of functional groups on the surface of sawdust enhances the reaction with glutamic acid and incorporation of La oxide or Zr oxide on the surface.

EDS, XRD, and ICP were used to identify and quantify nanoparticles present on the sawdust surface. EDS (Figure S1 and S2, Supporting Information) and ICP (Table S2, Supporting Information) showed that La and Zr atoms were present on the surface of modified sawdust at about 8%. The incorporation of La oxide or Zr oxide on the sawdust surface was varied to fine-tune the extraction efficiencies toward arsenic anions (Table S2, Supporting Information). The La oxide nanoparticles deposited on the sawdust were identified as a mixture of La_2O_3 and $La(OH)_3$ using XRD measurements (Figure S3B, Supporting Information).[40] No prominent
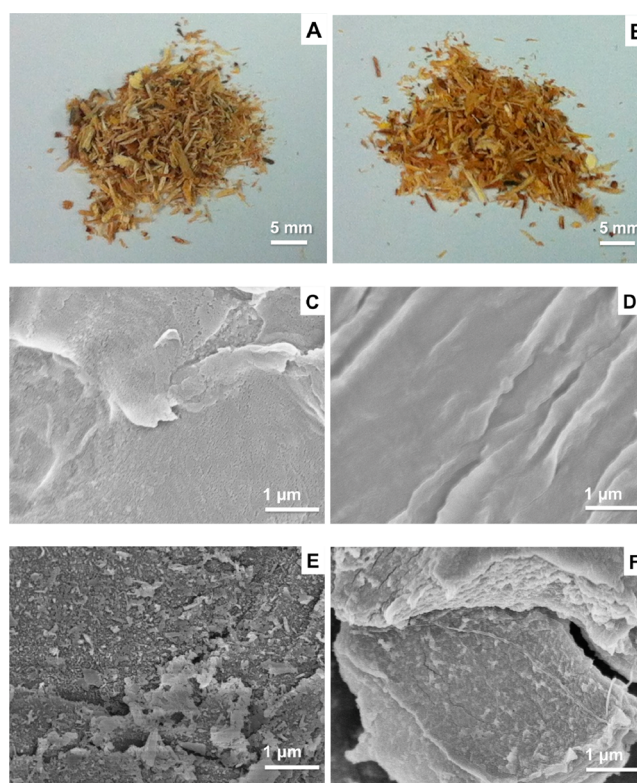
Figure 3. Optical micrographs of (A) unmodified and (B) modified sawdust. SEM micrographs of surface of (C) unmodified, (D) glutamic acid-modified, (E) La_2O_3-sawdust, and (F) and ZrO_2-sawdust.

crystalline peaks were identified in the XRD data (Figure S3C, Supporting Information) of Zr oxide nanoparticles on ZrO_2-sawdust, which could be due to their amorphous nature.[41]

Time-Dependent Studies. To understand the kinetics of arsenic adsorption onto the La_2O_3- and ZrO_2-sawdusts surfaces, the data were analyzed using both pseudo-first- and pseudo-second-order kinetic models.[42,43] Pseudo-first-order model in the linear form is expressed as follows

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \qquad (2)$$

The rate constant (k_1) and maximum amount adsorbed (q_e) were determined experimentally by plotting $\log(q_e - q_t)$ against t.

Similarly, the pseudo-second-order model in the linear form is expressed as follows

$$t/q_t = t/q_e + 1/(k_2 \times q_e^2) \qquad (3)$$

The rate constant (k_2) and maximum amount adsorbed (q_e) were determined experimentally by plotting t/q_t against t.

La_2O_3-sawdust removed 95% of arsenite and arsenate anions from solutions at a concentration of 10 ppm after 1 h. However, ZrO_2-sawdust only removed ~85–90% of arsenite and arsenate anions after 24 h. It is conceivable that two different mechanisms may be involved in the arsenic adsorption on the surface, resulting in different rates of adsorption at lower arsenic concentration. Electrostatic interaction is the dominant adsorption mechanism for La_2O_3-sawdust at low arsenic concentration (i.e., ~ 10 ppm). Time-dependent arsenic removal studies (Figure 4) using ZrO_2-sawdust showed that arsenite and arsenate extraction rate was slower as compared to La_2O_3-sawdust. ZrO_2-sawdust showed a preferential adsorption
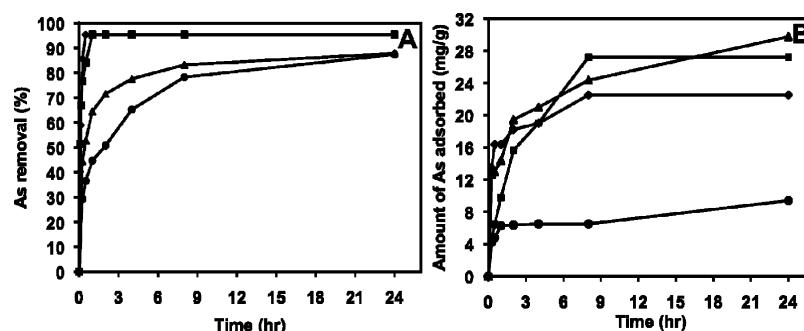
Figure 4. Time-dependent studies of arsenic extraction using (A) 10 ppm and (B) 80 ppm solution of arsenite and arsenate salts using La_2O_3- and ZrO_2-sawdusts. ◆ La_2O_3-sawdust—arsenite; ■ La_2O_3-sawdust—arsenate; ▲ ZrO_2-sawdust—arsenite; and ● ZrO_2-sawdust—arsenate. The measurements were done at pH 7 and in room temperature.
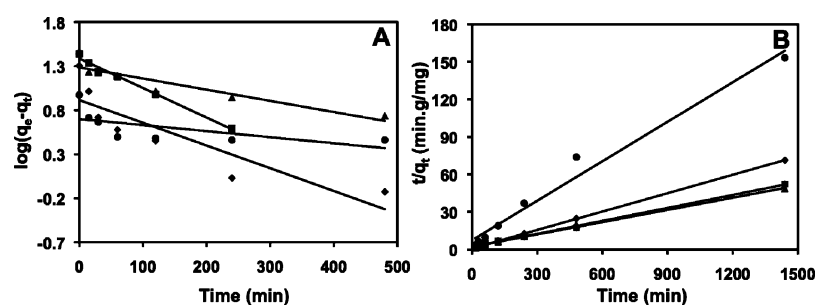
Figure 5. (A) Pseudo-first-order and (B) pseudo-second-order kinetics plots for arsenite and arsenate adsorption on La_2O_3- and ZrO_2-sawdusts. ◆ La_2O_3-sawdust—arsenite; ■ La_2O_3-sawdust—arsenate; ▲ ZrO_2-sawdust—arsenite; and ● ZrO_2-sawdust—arsenate.

of arsenite anions, while La_2O_3-sawdust favored the arsenate anion adsorption on the surface (Figure 4B).[31,32]

Data collected from arsenic anions adsorption by La_2O_3- and ZrO_2-sawdusts fit better to the pseudo-second-order kinetics model with the predicted q_e value closer to the experimental q_e value (Figure 5 and Table 1). The rate-controlling mechanism for arsenic adsorption on La_2O_3- and ZrO_2-sawdusts is deduced to be chemisorption.[44]

Table 1. Pseudo-First-Order and Second-Order Kinetics Parameters for Arsenite and Arsenate Adsorption on La_2O_3- and ZrO_2-Sawdusts under Ambient Conditions

kinetic models	kinetic parameters	La_2O_3-sawdust		ZrO_2-sawdust	
		arsenite	arsenate	arsenite	arsenate
	q_e (exp) (mg/g)	22.51	27.54	26.80	9.39
pseudo-first-order	q_e (mg/g)	8.25	24.43	19.36	5.02
	k_1 (min^{-1})	0.006	0.008	0.003	0.002
	R^2	0.7739	0.9886	0.8362	0.3879
pseudo-second-order	q_e (mg/g)	20.37	28.90	30.67	9.50
	k_2 (g/mg min)	0.003	0.0006	0.0005	0.002
	R^2	0.9999	0.9987	0.9999	0.9792

Concentration-Dependent Studies. Two isotherm models are widely used to describe the adsorption process: Langmuir and Freundlich isotherms (Figure 6).[45] The Langmuir isotherm is based on three assumptions: (1) Adsorption is limited to monolayer coverage. (2) Homogeneous surface sites bind one solute molecule. (3) Binding of a molecule by a given site is independent of whether its neighboring site is occupied or not.[46] The following linear

form was used in plotting Langmuir isotherms, with C_e/Q_e values as y-axis and C_e values as x-axis, in order to find K_L and Q_m

$$C_e/Q_e = 1/(K_L \times Q_m) + (C_e/Q_m) \tag{4}$$

where Q_e is amount of extracted arsenic in mg/g, Q_m is the maximum adsorption capacity at monolayer coverage in mg/g, K_L is the Langmuir adsorption constant related to heat of adsorption, and C_e is initial concentration of adsorbate in solution.

Favorability of the adsorption process is described by separation factor (R_L)

$$R_L = 1/(1 + K_L \times C_0) \tag{5}$$

C_0 is initial adsorbate concentration (mg/L). $R_L > 1$ indicates unfavorable adsorption, $R_L = 1$ corresponds to linear adsorption process, $0 < R_L < 1$ indicates favorable adsorption, and $R_L = 0$ means irreversible adsorption.

The second model, the Freundlich isotherm, is often used to describe multilayer adsorption on heterogeneous surface.[47] For analyzing the data, the following linearized form of the Freundlich isotherm is used

$$\ln Q_e = 1/n \ln C_e + \ln K_F \tag{6}$$

where K_F and n are the Freundlich constant and adsorption intensity, respectively. $\ln Q_e$ values (y-axis) were plotted against $\ln C_e$ (x-axis) to calculate n and K_F.

R^2 values for adsorption of arsenite salts on La_2O_3- and ZrO_2-sawdusts are higher for the Freundlich isotherm, while adsorption of arsenate salts is better described by the Langmuir isotherm (Table 2). This is due to the presence of the arsenate group as an anionic moiety at pH 7 while arsenite exists as neutral. Adsorption of arsenate beyond monolayer adsorption
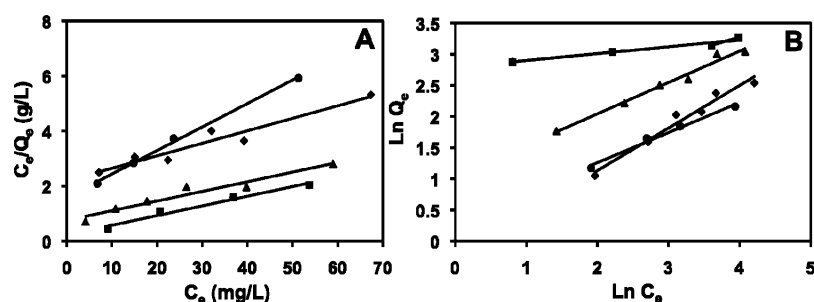
Figure 6. (A) Langmuir and (B) Freundlich isotherm plots for arsenite and arsenate extraction using La$_2$O$_3$- and ZrO$_2$-sawdusts. ◆ La$_2$O$_3$-sawdust—arsenite; ■ La$_2$O$_3$-sawdust—arsenate; ▲ ZrO$_2$-sawdust—arsenite; and ● ZrO$_2$-sawdust—arsenate. Time was kept constant at 24 h, with changes in adsorbate concentration from 10 to 80 ppm as variable, adsorbate equilibrium concentration after adsorption (C_e) from 10 to 70 ppm, pH 7, and room temperature.

Table 2. Langmuir and Freundlich Parameters for Arsenite and Arsenate Anion Extraction Using La$_2$O$_3$- and ZrO$_2$-sawdusts[a]

isotherm models	parameters	La$_2$O$_3$-sawdust		ZrO$_2$-sawdust	
		arsenite	arsenate	arsenite	arsenate
Langmuir	Q_m (mg/g)	22.03	28.41	28.57	11.71
	K_L	0.021	0.155	0.046	0.054
	R_L	0.376	0.075	0.213	0.188
	R^2	0.9320	0.9757	0.9411	0.9972
Freundlich	K_F (mg/g)	1.26	16.19	2.82	1.34
	$1/n$	0.6830	0.1120	0.5028	0.4833
	R^2	0.9681	0.9547	0.9799	0.8966

[a]Time was kept constant at 24 h, with adsorbate concentration from 10 to 80 ppm as variable, pH 7, and room temperature.

would not be favorable due to repulsion of negative charges. For both sawdust samples, $1/n$ values were below 1 indicating chemisorption.[48] R_L values for both sawdust samples were in between 0 to 1, which implies a favorable adsorption process. The Langmuir adsorption capacities are 22 mg/g (arsenite) and 28 mg/g (arsenate) for La$_2$O$_3$-sawdust and 29 mg/g (arsenite) and 12 mg/g (arsenate) for ZrO$_2$-sawdust and match with the experimental q_e values of 22 mg/g (arsenite) and 28 mg/g (arsenate) for La$_2$O$_3$-sawdust and 27 mg/g (arsenite) and 9 mg/g (arsenate) for ZrO$_2$-sawdust. Such details are useful to calculate the amount of adsorbent required to remove a certain concentration of arsenic pollutants from water. La$_2$O$_3$-sawdust showed better performance than ZrO$_2$-sawdust as both arsenite and arsenate were removed with higher adsorption capacities (22 mg/g arsenite, 28 mg/g arsenate).

Langmuir capacities of La$_2$O$_3$- and ZrO$_2$-sawdusts were also compared with those of other low-cost agricultural waste-based adsorbents in (Table S3, Supporting Information).[49−54] Both La$_2$O$_3$- and ZrO$_2$-sawdusts have relatively higher adsorption capacities than other known adsorbents at pH 7. They can be used without additional processing conditions to purify natural groundwater at a pH range of 6.5−8.5. Other good reasons for selecting sawdust among other biomass based adsorbents for arsenic removal include good mechanical properties, low rate of biodegradation and no release of soluble contaminants into water.

pH and Ionic Strength Effect. The effect of pH on the extraction of arsenite anion using La$_2$O$_3$-sawdust is similar to the reported method for arsenite anion extraction by Ce(IV)−La(III) hydroxide binary adsorbent.[55] The adsorption mechanism was described to be a mixture of inner-sphere surface

complexation and electrostatic interaction. La$_2$O$_3$-sawdust contains both La(OH)$_3$ and La$_2$O$_3$ as shown by its XRD spectrum (Figure S3B, Supporting Information). Strong electrostatic interaction between La^{3+} of La(OH)$_3$ and arsenic anions, followed by anion exchange, play important roles in the extraction. Changes in pH, however, did not affect arsenate anion extraction behavior of La$_2$O$_3$-sawdust.

Only at pH 11 is arsenate anion adsorption dropped to ∼30%, which is likely due to repulsion of negatively charged surface of the adsorbent and anionic arsenic species. Extraction of arsenite anions using ZrO$_2$-sawdust decreased at pH 9 owing to the formation of negative charges on the adsorbent surface and repulsion between adsorbent and adsorbate. Similar correlation was also observed for the arsenate anion, which showed higher extraction efficiency at a lower pH of 3−5.

Increase in ionic strength also affected the extraction of arsenite and arsenate anions by La$_2$O$_3$-sawdust, which confirms that electrostatic interaction plays a significant role in the extraction process (Figure 7B).[56] The arsenate extraction using La$_2$O$_3$-sawdust decreased at 0.01 M NaCl concentration and increased again at 0.1 M NaCl. Increase in ionic strength can reduce coulomb repulsive forces by inducing a more positive net surface charge of the sawdust,[57] which caused an increase in arsenate extraction. Increase in ionic strength, however, did not have any effect on extraction of arsenite and arsenate anions by the ZrO$_2$-sawdust. This could be due to inner-sphere complex formation as a potential adsorption mechanism.[58] In summary, ZrO$_2$-sawdust and La$_2$O$_3$-sawdust adsorbs arsenic through electrostatic interaction and ligand exchange on ZrO$_2$.[31,32,59]

Arsenite anion extraction using La$_2$O$_3$-sawdust can be affected by the presence of interfering anions such as PO$_4^{3−}$ > NO$_3^−$ > SO$_4^{2−}$ (Figure 7C−E). However, extraction of arsenate anions by La$_2$O$_3$-sawdust is relatively stronger and more selective than other anions. Arsenite and arsenate anion extraction using ZrO$_2$-sawdust showed little interference from NO$_3^−$ and SO$_4^{2−}$ anions (Figure 7C and D). However, arsenate adsorption was decreased to about 11% due to the presence of competing PO$_4^{3−}$ anions. The La$_2$O$_3$- and ZrO$_2$-sawdusts extract arsenic anions well in the presence of phosphate anions in water. Arsenite can be removed using ZrO$_2$-sawdust, while arsenate can be removed using La$_2$O$_3$-sawdust at 60−80% removal.

X-ray Photoelectron Spectroscopy. The characteristic peaks on the XPS spectra (Figure 8A and B) have shown that the dominant species on the surface of La$_2$O$_3$- and ZrO$_2$-sawdusts are La$_2$O$_3$ and ZrO$_2$.[60,61]

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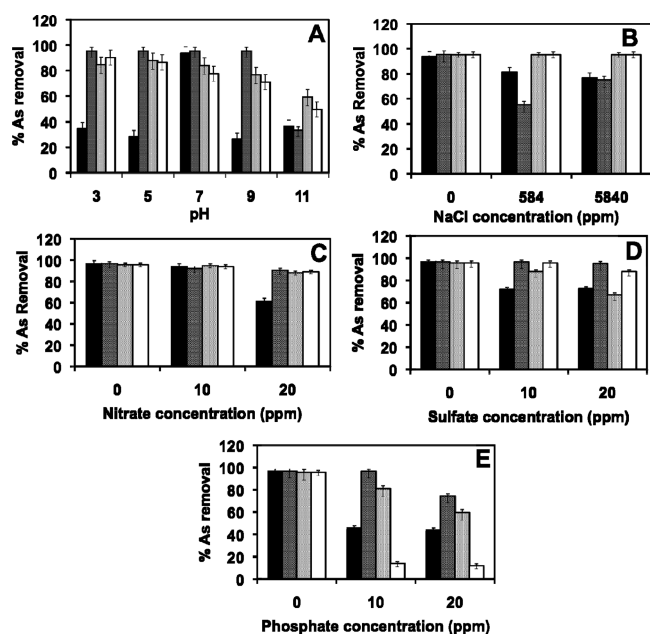
Figure 7. Effect of (A) pH and ionic strength by addition of (B) NaCl salt, (C) nitrate, (D) sulfate, and (E) phosphate anion concentration on arsenite and arsenate anion removal using La_2O_3- and ZrO_2-sawdust materials. ■ La_2O_3-sawdust–arsenite; (dark gray box) La_2O_3-sawdust–arsenate; (light gray box) ZrO_2-sawdust–arsenite; and □ ZrO_2-sawdust–arsenate. Extractions were done at ambient conditions.

Arsenite and arsenate anions bonded to La_2O_3- and ZrO_2-sawdusts still maintained the same oxidation states (Figure 8C–F). Arsenate is known to have ~1 eV higher binding energy than arsenite anions.[62] The values can sometimes shift to slightly higher binding energy when the arsenite and arsenate ions are bonded to metal oxide.[63]

Arsenic Desorption Studies. Desorptions of arsenite and arsenate anions from La_2O_3- and ZrO_2-sawdusts were carried out using 1 M HNO_3 and 1 M NaOH, respectively. The desorption process occurred by ionization and release of the La oxide from La_2O_3-sawdust and replacement of arsenic anion by OH^- ion on ZrO_2-sawdust.[64,65] Data from the desorption studies were summarized in Table S4 of the Supporting Information. La_2O_3-sawdust can be successfully regenerated without any change in efficiency by reloading of La oxide on the sawdust. In contrast, arsenic binding on ZrO_2-sawdust is strong; only about 30% of arsenite and arsenate can be desorbed using 1 M NaOH. As a result, subsequent arsenic adsorption was decreased to about 50% upon reloading of ZrO_2.

■ CONCLUSION

In summary, renewable low-cost sawdust material was used as an efficient adsorbent for both arsenite and arsenate anions using surface engineering. La or Zr oxide was incorporated on the sawdust surface and used for extraction of arsenic anions from water. At pH 7, the Langmuir adsorption capacities of La_2O_3-sawdust were 22 and 28 mg/g for arsenite and arsenate, respectively, while those observed for ZrO_2-sawdust were 29 for arsenite and 12 mg/g for arsenate. In comparison to similar sawdust-based adsorbent materials reported in the literature, the surface-modified sawdust showed higher adsorption capacities and can be used to remove both arsenite and arsenate anions. In addition, such modified sawdust can be used
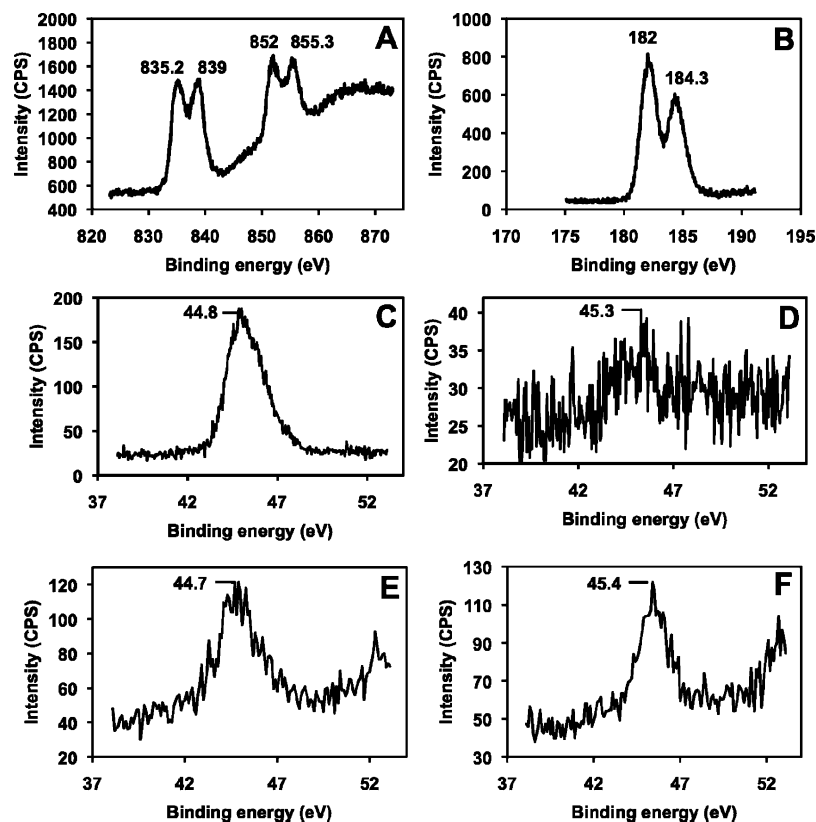
Figure 8. XPS spectra of (A) La_2O_3 on La_2O_3-sawdust, (B) ZrO_2 on ZrO_2-sawdust, (C) arsenite and (D) arsenate anions adsorbed on La_2O_3-sawdust, and (E) arsenite and (F) arsenate anions adsorbed on ZrO_2-sawdust. The extractions were done in ambient conditions.

directly at neutral pH 7. Electrostatic interaction is the dominant adsorption mechanism for La_2O_3-sawdust, while ZrO_2-sawdust binds arsenic through ligand exchange with surface hydroxyl groups. La_2O_3- and ZrO_2-sawdusts showed better selectivity toward arsenate and arsenite anions in the presence of other interfering anions such as nitrate, sulfate, and phosphate anions. La_2O_3-sawdust, which is a suitable adsorbent for both arsenite and arsenate, can be fully regenerated by washing with dilute nitric acid and reloading with La oxide. Additional work is in progress to improve the extraction efficiency of sawdust for all anions.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Supporting characterization data of the adsorbents and extra information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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