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As(V) removal from arsenic wastewater by fibrous anion exchangers

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ABSTRACT

The aim of the present study was to investigate the removal of As(V) from arsenic wastewater by fibrous anion exchangers (Karacaron™ KC31 and SA). Our analysis indicated that the pristine KC31 was a free amine form, whereas the pristine SA was fully protonated. Fourier-transform infrared spectrometer and X-ray photoelectron spectroscopy analyses demonstrated that the protonated amine groups were responsible for the anion exchange of As(V). Batch experiments showed that in the removal of As(V), KC31 behaved differently from SA in response to pH change. The As(V) removal for KC31 was the highest at a pH of 3, whereas the As(V) removal for SA reached the maximum at a pH of 10. The fibers could be successfully regenerated with 0.1 M NaCl solution and reused over five adsorption–desorption cycles. Batch experiments in the high arsenic content wastewater (As(V) concentration = 98.798 mmol/L [7,402.3 mg/L]; pH = 2.9) demonstrated that KC31 was effective in the removal of As(V) from the arsenic wastewater, even in the presence of other anionic contaminants (chromate, sulfate, etc.). The As(V) removal capacity of KC31 (2.941 mmol/g) at the fiber dose of 2 g/L was higher than the As(V) removal capacities of anion exchangers (0.146–2.497 mmol/g) reported in the literature. Unlike KC31, the As(V) removal by SA from the arsenic wastewater was negligible, possibly due to the acidic pH of the wastewater along with the competitive effect of other anionic contaminants.

Keywords: Anion exchange; Arsenate; Arsenic wastewater; Fibrous anion exchanger; Modacryl fibers

1. Introduction

The pollution of water resources such as rivers, lakes, and ground waters by toxic pollutants is a wide-spread environmental problem around the world. Arsenic (As) is a toxic contaminant causing serious health problems, including skin changes, gastrointestinal symptoms, damage to nervous system, and cancer [1–5]. For arsenic, the WHO recommends a maximum contaminant level of 0.01 mg/L in drinking water. Arsenic contamination of water resources occurs through geochemical reactions, pesticide applications, and industrial activities [3]. Among the different valance states (−3 to 5), most arsenic occurs as As(III) and As(V) in water; As(III) exists in reducing environments and As(V) is predominant in oxidizing conditions [6,7].

Ion exchange is a water treatment process used to remove dissolved ions in the aqueous phase through exchange with ions in the solid phase. Basically, two types of ion exchange media, such as ion exchange resins and ion exchange fibers, have been used in water treatment practices. Ion exchange fibers have advantages over ion exchange resins, including larger specific surface areas, higher ion exchange capacities, and faster absorption/desorption rates [8]. Numerous researchers have used anion ion exchange resins for the removal of As(V) from aqueous solutions [9–17]. However, very few studies have been performed on the removal of As(V) with ion exchange fibers [18–21] and metal oxide–impregnated fibrous ion exchangers [22,23]. Ruixia et al. [18] prepared anion exchange fibers through the modification of

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polyacrylonitrile (PAN) fiber using hydrazine hydrate and amine functionalization of the modified fiber with ethylenediamine for the removal of As(V) from aqueous solutions. Dominguez et al. [19] synthesized anion exchange fibers using a vinylbenzyl chloride copolymer as a precursor and fiberglass fiber as a substrate through amine functionalization and hydrochloric acid treatment for As(V) removal from aqueous solutions. Vatutsina et al. [22] prepared hybrid fibrous sorbents through the impregnation of polypropylene-based and polyacrylic-based ion exchange fibers with hydrated ferric oxides for As(V) removal from drinking water. Smith et al. [23] impregnated polypropylene-based ion exchange fibers with hydrated ferric oxides for As(V) removal. These studies showed that the fibrous anion exchangers could be successfully applied for decontamination of As(V) from water. Furthermore, studies related to application of fibrous ion exchangers to As(V) removal from arsenic wastewater are scarce.

The aim of the present study was to characterize modacrylic anion exchange fibers in the removal of As(V) from high arsenic content wastewater. Batch experiments were conducted in synthetic As(V) solutions to examine the effects of the solution pH, regeneration, reaction time, and initial As(V) concentration on the removal of As(V). Fourier-transform infrared (FTIR) spectrometer and X-ray photoelectron spectroscopy (XPS) analyses were performed to characterize the fibers in the removal of As(V). Batch experiments were also performed for As(V) removal from the arsenic wastewater. The modacrylic fibers denote modified acrylic fibers made from acrylonitrile [24,25].

2. Materials and methods

2.1. Fibrous anion exchangers

The pristine KC31 and SA fibers (product name: Karacaron™, Kaneka Corporation, Osaka, Japan) were used in the experiments as received. The fibers were characterized using various techniques. Field emission scanning electron microscopy (FESEM, Supra 55VP, Carl Zeiss, Oberkochen, Germany) was used to obtain images of the fibers. Energy dispersive X-ray (EDX) spectrometer analysis was conducted using FESEM to characterize the element composition of the fibers. FTIR spectrometer (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) was used to obtain the infrared spectra before and after As(V) removal experiments. XPS (Sigma Probe, Thermo VG, East Grinstead, UK) scans with monochromatic Al Kα radiation were also performed before and after As(V) removal experiments.

2.2. Quantification of anion exchange capacity

Two separate experiments were performed following the method described in the literature [26]. In the first experiment, the pristine KC31 and SA fibers were used as received to quantify the number of functional groups containing chlorine (Cl) ions. A 0.3 g sample of each fiber was soaked in the 300 mL solution of 5% Na_2SO_4. After shaking for 6 h at 30°C, the solutions were separated from the fibers to measure Cl ion concentrations using ion chromatography (IC, ICS-3000, Dionex, Sunnyvale, CA, USA).

The second experiment was conducted to quantify the total number of functional groups (volumetric anion exchange capacity) for KC31 and SA. The fibers were immersed in 1 M hydrochloric acid (HCl) solution for 6 h and dried at 65°C in a drying oven (ThermoStable SOF-W 155, Daihan Scientific, Seoul, Korea). Then, the fibers were treated following the same procedures as the first experiment to measure Cl ion concentrations.

2.3. As(V) removal in synthetic solutions

The As(V) stock solution was prepared from sodium arsenate dibasic heptahydrate (Na_2HAsO_4, ACS reagent, Sigma-Aldrich, St. Louis, MO, USA) dissolved in deionized water. Batch tests were conducted using a 500 mL flask to investigate the removal of As(V) by the pristine KC31 and SA. Unless stated otherwise, all the experiments were performed in triplicate at a temperature of 30°C. The first experiment was performed to observe the effect of the solution pH on As(V) removal. The tests were performed at an initial As(V) concentration of 0.133 mmol/L (10 mg/L) with an anion exchange fiber dose of 1.0 g/L in 300 mL of solution. The pH of the solutions was adjusted using 0.1 M HCl and 0.1 M NaOH. The tubes were shaken at 150 rpm using a shaking incubator (Daihan Science, Seoul, Korea), and solution samples were collected after reacting for 6 h through centrifugation. The As(V) concentrations were analyzed via inductively coupled plasma–atomic emission spectroscopy (ICP-AES) (Optima-4300, PerkinElmer, Waltham, MA, USA).

The second experiment was conducted without pH adjustment (initial As(V) concentration = 0.133 mmol/L; pH = 7.5; fiber dose = 1.0 g/L; reaction time = 6 h) to examine the effect of regeneration. After the removal experiments, the anion exchange fibers were immersed in a 0.1 M NaCl solution and was shaken at 150 rpm for 3 h using the shaking incubator for the desorption of adsorbed As(V) ions. Then, the regenerated fibers were dried for 2 h at 65°C in a drying oven prior to reuse for the next adsorption–desorption cycle, which was repeated five times following the same procedures.

The third experiment was performed with pH adjustment to examine the influence of reaction time (fiber dose = 1.0 g/L; initial As(V) concentration = 0.133 mmol/L). It should be noted that the solution pH was adjusted to 3 for KC31 experiment based on the pH experiments, whereas the solution pH was adjusted to 10 for SA experiments. The fourth experiment was performed (fiber dose = 1.0 g/L; reaction time = 6 h) to examine the influence of the initial As(V) concentration in the range of 0.067–6.674 mmol/L (5–500 mg/L, solution pH = 7.5–8.6).

2.4. As(V) removal in high arsenic content wastewater

Batch tests were performed to examine the removal of As(V) from arsenic wastewater by the pristine KC31 and SA. The high arsenic content wastewater was generated during microwave exposure on gold ores in mineral processing, where nitric acid (HNO_3) was used as an absorbing solution for arsine gas. The characteristics of the arsenic wastewater were summarized in Table 1. Note that As(V) concentration in the arsenic wastewater was 98.8 mmol/L (7,402.3 mg/L) with a solution pH of 2.9. The heavy metal concentrations of the wastewater were measured by ICP-AES, whereas the anionic composition was analyzed using IC. The batch tests were conducted at the fiber dose of 2–20 g/L with reaction time of 6 h. The tubes were shaken at 150 rpm for 180 min using a shaking incubator, and then solution samples were collected through centrifugation. The As(V) concentrations were analyzed using ICP-AES.

Table 1
Characteristics of arsenic wastewater used in the experiments (mM)

pH	2.9
As	98.8
Cu	5.1
Zn	73.9
Na	212.1
K	58.9
Cr	53.9
Cl	10.2
NO_3	445.3
SO_4	11.7

2.5. Data analysis

The following equations for R^2, χ^2, and SAE were used to analyze the kinetic and equilibrium sorption data and confirm their fit to the model:

$$R^2 = \frac{\sum_{i=1}^{m}(y_c - \bar{y}_e)_i^2}{\sum_{i=1}^{m}(y_c - \bar{y}_e)_i^2 + \sum_{i=1}^{m}(y_c - y_e)_i^2}, \tag{1}$$

$$\chi^2 = \sum_{i=1}^{m}\left[\frac{(y_e - y_c)^2}{y_c}\right]_i, \tag{2}$$

$$\text{SAE} = \sum_{i=1}^{n}\left|y_c - y_e\right|_i, \tag{3}$$

3. Results and discussion

3.1. Characteristics of the fibrous anion exchangers

FESEM and digital images (Figs. 1(a) and (b)) showed that the fibers were yellowish and micron-sized anion exchangers (KC31 = 21.8 ± 6.1 μm, SA = 23.5 ± 6.6 μm). The EDX spectra (Figs. 1(c) and (d)) demonstrated that the fibers

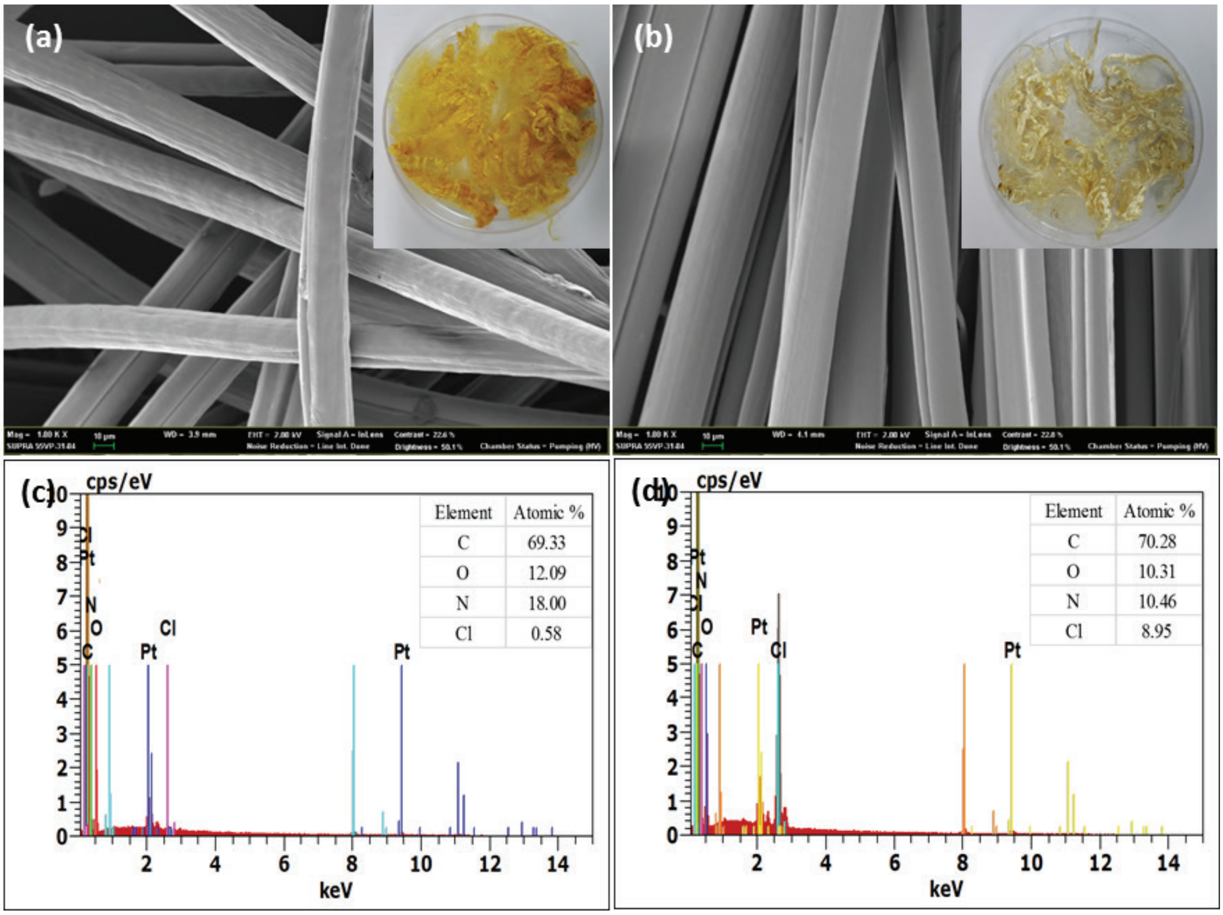

Fig. 1. Characteristics of KC31 and SA: (a) FESEM image of KC31 (bar = 10 μm, inset = digital image), (b) FESEM image of SA (bar = 10 μm, inset = digital image), (c) EDS pattern of KC31 (inset = atomic %), and (d) EDS pattern of SA (inset = atomic %).

were composed of carbon (C), oxygen (O), nitrogen (N), and chlorine (Cl). The fibers had a matrix of acrylonitrile (C_3H_3N)-vinyl chloride (C_2H_3Cl) copolymer functionalized with amine groups (NH_2).

The FTIR spectra of the anion exchange fibers before and after As(V) removal are shown in Fig. 2, and infrared band assignments are summarized in Table 2. In the KC31 and SA fibers before As(V) removal (Fig. 2(a)), C–H vibrations appeared at 2,933 and 2,925 cm^{-1}, respectively [27]. The peaks at 1,650 and 1,653 cm^{-1} corresponded to O=C–N–H (amide I), whereas the peaks at 1,555 and 1,556 cm^{-1} were assigned to O=C–N–H (amide II) [27,28]. The peaks at 2,239 and 2,241 cm^{-1} corresponded to C≡N vibrations from acrylonitrile [29], whereas the peaks at 677 and 669 cm^{-1} were assigned to C–Cl vibrations from vinyl chloride [30]. Amine groups (N–H) were detected from KC31 and SA at the peaks of 3,294 and 3,376 cm^{-1}, respectively, demonstrating that the KC31 and SA were functionalized through the amination reaction. In the FTIR spectra after As(V) removal (Fig. 2(b)), As–O vibrations were found from KC31 and SA at the peaks of 830 and 843 cm^{-1}, respectively [31], due to the association of As(V) ions with the ion exchange sites. Our results indicated that the secondary amines acted as functional groups on the ion exchange sites for KC31 and SA.

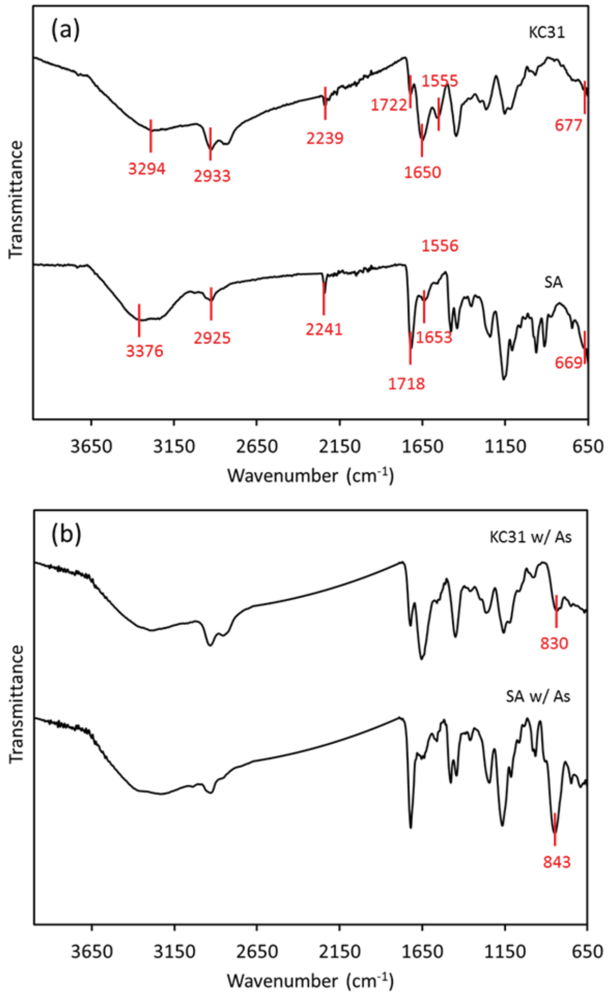

Fig. 2. FTIR spectra of KC31 and SA: (a) before As(V) removal and (b) after As(V) removal.

The XPS spectra of the anion exchange fibers before and after As(V) removal are shown in Fig. 3. In wide scans of KC31 and SA before As(VI) removal (Figs. 3(a) and (b)), the photoelectron peaks at the binding energies of 285 and 532 eV were attributed to C1s and O1s, respectively. In addition, the peak at 398 eV was assigned to N1s, which were contributed by acrylonitrile. The peaks at 196 and 255 eV were assigned to Cl2p and Cl2s, respectively, which came from the vinyl chloride. After the removal of As(V), the As3d peak at 45 eV appeared in a wide scan of KC31, SA, and SA2 (Figs. 3(c) and (d)). In high-resolution scans of the N1s region, changes were detected in the KC31 after the removal of As(V). Before As(V) removal, the peaks assigned to C≡N and C–N were found in KC31 at 399.2 and 400.5 eV, respectively (Fig. 3(e)). After As(V) removal, the N1s peak was shifted with the peaks of C≡N and C–N weakening, whereas a new peak assigned to C–N$^+$ (protonated amine) appeared at 402.2 eV (Fig. 3(g)). However, changes were not eminent for SA, and the peaks assigned to C≡N and C–N$^+$ were found before and after As(V) removal (Figs. 3(f) and (h)). These results demonstrated that the protonated amine groups were responsible for the ion exchange of As(V).

3.2. Effect of pH

The influence of the solution pH on the removal of As(V) by KC31 and SA is presented in Fig. 4. As(V) removal

Table 2
FTIR spectra obtained from KC31 and SA anion exchange fibers

Ion exchange fibers	Wave number (cm^{-1})		Assignment	Reference
	KC31	SA		
Before As(V) removal	3,294	3,376	N–H (amine)	[27]
	2,933	2,925	C–H	[27,29]
	2,239	2,241	C≡N	[27]
	1,722	1,718	C=O	[27]
	1,650	1,653	O=C–N–H (amide I)	[27,28]
	1,555	1,556	O=C–N–H (amide II)	[27,28]
	677	669	C–Cl	[30]
After As(V) removal	830	843	As–O	[31]

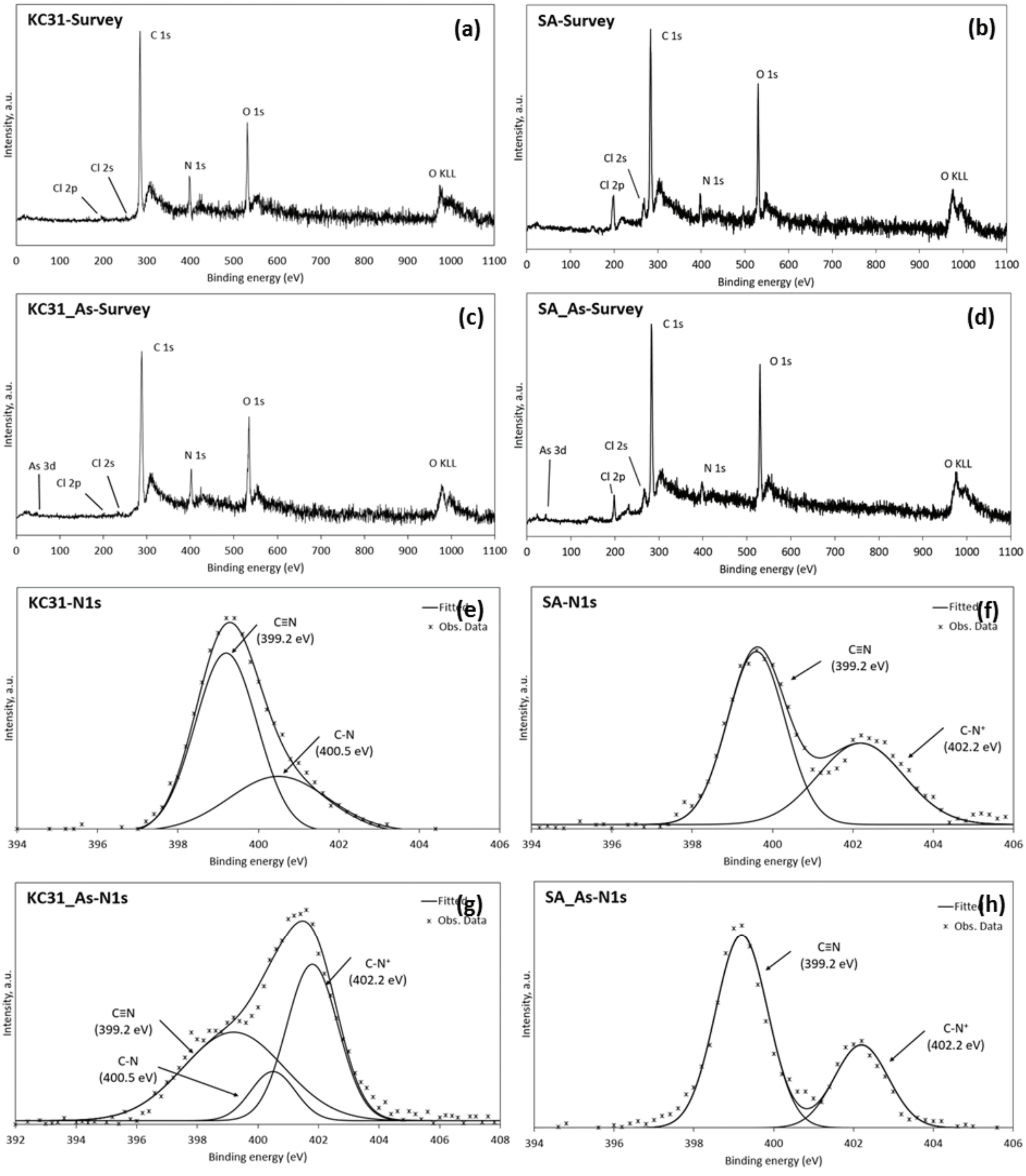

Fig. 3. XPS spectra of KC31 and SA before and after As(V) removal: (a) wide scan of KC31 before As(V) removal, (b) wide scan of SA before As(V) removal, (c) wide scan of KC31 after As(V) removal, (d) wide scan of SA after As(V) removal, (e) high-resolution scan in the N1s region of KC31 before As(V) removal, (f) high-resolution scan in the N1s region of SA before As(V) removal, and (g) high-resolution scan in the N1s region of KC31 after As(V) removal, (h) high-resolution scan in the N1s region of SA after As(V) removal.

by the exchange fibers was influenced by the solution pH. In the removal of As(V) by KC31, the removal capacity was very low (0.019 mmol/g) at a pH of 2 and increased sharply to 0.129 mmol/g at a pH of 3. Then, the removal capacity decreased gradually with an increase in the pH from 3 to 10 and dropped sharply to 0.002 mmol/g at a pH of 12. Similar findings were reported by Awual and Jyo [20], who demonstrated that As(V) removal by weak–base anion exchange fibers with primary amine groups decreased gradually with an increase in the pH from 3 to 8.

In the case of SA, the pH dependency of As(V) removal was very different from that of KC31 at the pH range of

3 to 10. The As(V) removal capacity was 0.001 mmol/g at a pH of 2. The As(V) removal was the highest at a pH of 10; the removal capacity increased gradually from 0.044 to 0.130 mmol/g with an increase in the pH from 3 to 10. Then, the removal capacity dropped sharply to 0.002 mmol/g at a pH of 12. Similar findings were reported by Jachula and Hubicki [16], who used polyacrylate (Amberlite IRA 458 and Amberlite IRA 958) and polystyrene (Amberlite IRA 402 and Amberlite IRA 900) anion exchange resins with quaternary ammonium functional groups for As(V) removal from aqueous solutions. These authors showed that As(V) removal by the anion exchange resins increased gradually as the solution pH increased from 4 to 10.

The discrepancy between KC31 and SA in the removal of As(V) with response to changes in the pH may be attributed to the different characteristics of the exchange fibers. In the pristine KC31, the amount of Cl ions available on the ion exchange sites was 0 mmol/g, indicating that the pristine KC31 did not have any exchangeable Cl ions on the amine functional groups. Therefore, the pristine KC31 anion exchanger was a free amine form with no HCl rinse. For the pristine SA, the ion exchange sites had 1.176 mmol/g of Cl ions, demonstrating that the pristine SA contained exchangeable Cl ions; the pristine SA anion exchanger was a chloride form with HCl rinse.

After HCl treatment in the laboratory, the KC31 anion exchanger contained 4.698 mmol/g of Cl ions, whereas the SA anion exchanger had 1.147 mmol/g of Cl ions. In the case of KC31, the free amine groups on the KC31 were protonated after HCl treatment. For SA, the amount of exchangeable Cl ions was very similar between the pristine fibers and the HCl-treated fibers, demonstrating that the ion exchange sites of the pristine SA were fully saturated with Cl ions. These results demonstrated that the protonated states of the ion exchange sites on the pristine KC31 and SA differed.

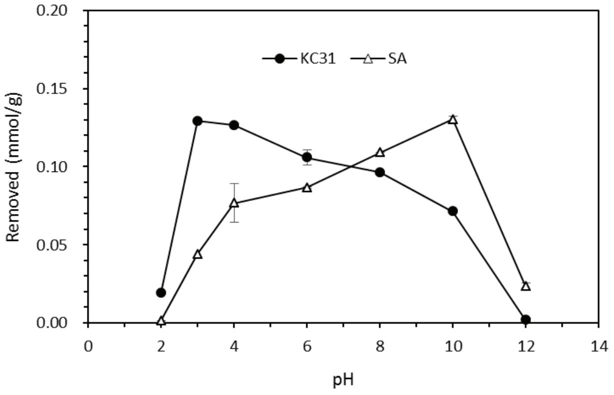

Fig. 4. Effect of solution pH on As(V) removal by KC31 and SA.

The pH dependency of As(V) removal by KC31 could be closely related to the number of protonated sites available for anion exchange. At the highly acidic pH of 2, the number of protonated sites with exchangeable Cl ions was very large, but As(V) removal was very low because of the speciation of As(V). Uncharged H_3AsO_4 was a major form of As(V) at a pH of 2, and As(V) removal by KC31 became very low. Among the tested pH levels, As(V) removal by KC31 was the highest at a pH of 3 because the number of protonated sites was large and anionic $H_2AsO_4^-$ was a dominant form. As the pH increased to 8, the protonated sites decreased, resulting in a decrease of As(V) removal. At a pH of 12, nearly all the amine groups were not protonated and, therefore, As(V) removal by KC31 became negligible.

As mentioned above, amine groups on the pristine SA were protonated along with exchangeable Cl ions. Above a pH of 7, a considerable amount of amine groups on SA was still protonated along with exchangeable Cl ions. Therefore, the increasing tendency of As(V) removal by SA with an increase in the pH between 3 and 10 could be mainly connected to the ionization of As(V) with a change in the pH. A monovalent $H_2AsO_4^-$ was dominant in the pH range of 3 to 6, whereas a divalent $HAsO_4^{2-}$ was dominant in the pH range of 8 to 10. The adsorbability of As(V) species to anion exchangers was in the increasing order of $H_3AsO_4 < H_2AsO_4^- < HAsO_4^{2-} < AsO_4^{3-}$ [32]. At the highly alkaline pH of 12, a trivalent AsO_4^{3-} was the dominant form of As(V); however, As(V) removal by SA became negligible because nearly all the amine groups were deprotonated.

3.3. Anion exchange and regeneration mechanisms

The schematic diagram of anion exchange reaction for As(V) are illustrated in Fig. 5. The anion exchange mechanism for As(V) on the surfaces of the fibers could be described as follows:

$$\text{R-Cl}^- + \text{H}_2\text{AsO}_4^- \rightarrow \text{R-H}_2\text{AsO}_4^- + \text{Cl}^- \tag{4}$$

$$2\text{R-Cl}^- + \text{HAsO}_4^{2-} \rightarrow \text{R}_2\text{-HAsO}_4^{2-} + 2\text{Cl}^- \tag{5}$$

At pH 3–6, the Eq. (4) was the major removal mechanism, while the Eq. (5) was the major mechanism at pH 8–10. Note that the As(V) removal by KC31 was the highest at pH 4, whereas the As(V) removal was the highest at pH 10 for SA.

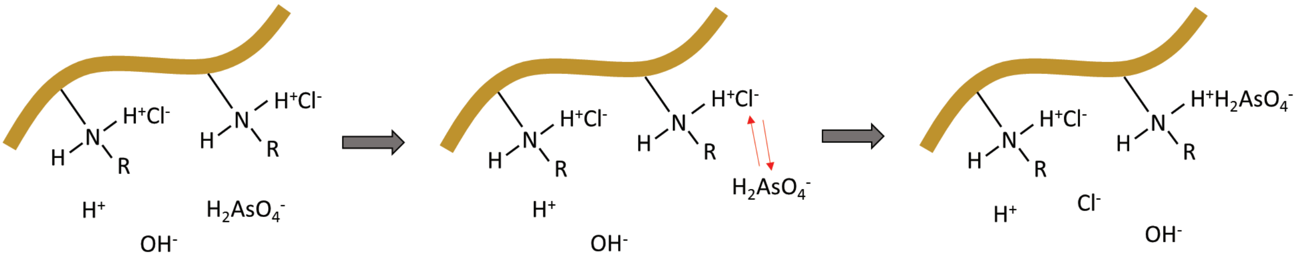

Fig. 5. Schematic diagram of anion exchange reaction between KC31/SA and As(V).

Regeneration of KC31 and SA with 0.1 M NaCl solution (initial As(V) concentration = 0.133 mmol/L, solution pH = 7.5) is presented in Table 3. During the regeneration and reuse over five cycles, the exchange fibers could maintain As(V) removal rate. For KC31, the percent removal was in the range of 74.9%–80.2% with the As(V) removal capacity of 0.100–0.107 mmol/g. For SA, the percent removal was in the range of 79.9%–83.2% with the As(V) removal capacity of 0.107–0.111 mmol/g. The regeneration mechanism could be described as follows:

$$\text{R-H}_2\text{AsO}_4^- + \text{NaCl} \rightarrow \text{R-Cl}^- + \text{H}_2\text{AsO}_4^- + \text{Na}^+ \quad (6)$$

$$\text{R}_2\text{-HAsO}_4^{2-} + 2\text{NaCl} \rightarrow 2\text{R-Cl}^- + \text{HAsO}_4^{2-} + 2\text{Na}^+ \quad (7)$$

Our results demonstrated that the exchange fibers could be successfully regenerated with NaCl solution.

3.4. Effects of reaction time and initial As(V) concentration

The influence of reaction time on the removal of As(V) by KC31 and SA is presented in Fig. 6, along with the kinetic sorption model fits. The sorption data were analyzed using the following kinetic sorption models [33]:

$$q_t = q_e(1 - e^{-k_1 t}) \text{ Pseudo first-order} \quad (8)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \text{ Pseudo second-order} \quad (9)$$

The corresponding model parameters are provided in Table 4. In the As(V) removal by KC31 and SA, the ion exchange reaction reached equilibrium within 30 min, demonstrating that the As(V) removal by the fibers was relatively fast process. The pseudo-second-order model exhibited the best fit to the kinetic data with the parameter values of q_e = 0.134–0.142 mmol/g and k_2 = 6.768–8.602 g/mmol/min (Table 4).

The influence of initial As(V) concentration on the removal of As(V) by KC31 and SA is presented in Fig. 7, along with the equilibrium sorption model fits. The sorption data were analyzed using the following equilibrium sorption models [34]:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \text{ Langmuir} \quad (10)$$

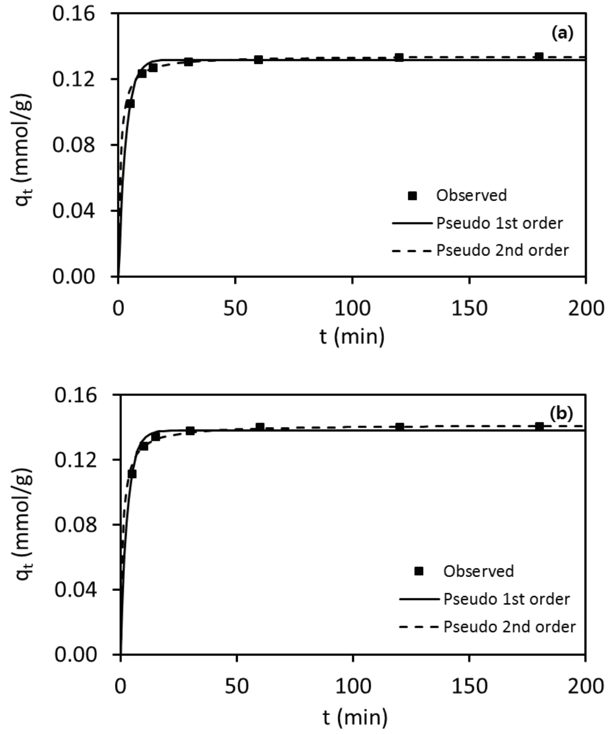

Fig. 6. Effect of reaction time on As(V) removal by KC31 and SA along with kinetic sorption model fits. Model parameters are provided in Table 4.

Table 3
Regeneration and reuse of KC31 and SA anion exchange fibers over five adsorption–desorption cycles

Cycle	KC31		SA	
	Removal rate (%)	Removal capacity (mmol/g)	Removal rate (%)	Removal capacity (mmol/g)
1	75.7	0.101	79.9	0.107
2	78.7	0.105	83.2	0.111
3	80.2	0.107	82.4	0.110
4	77.9	0.104	81.7	0.109
5	74.9	0.100	82.4	0.110

Table 4
Kinetic sorption parameters obtained from the model fitting to kinetic data

Ion exchange fibers	Pseudo-first-order model					Pseudo-second-order model				
	q_e (mmol/g)	k_1 (1/min)	R^2	χ^2	SAE	q_e (mmol/g)	k_2 (g/mol/min)	R^2	χ^2	SAE
KC31	0.132	0.321	0.958	0.0002	0.011	0.134	8.602	0.964	0.0007	0.010
SA	0.138	0.329	0.934	0.0003	0.015	0.142	6.768	0.978	0.0003	0.009

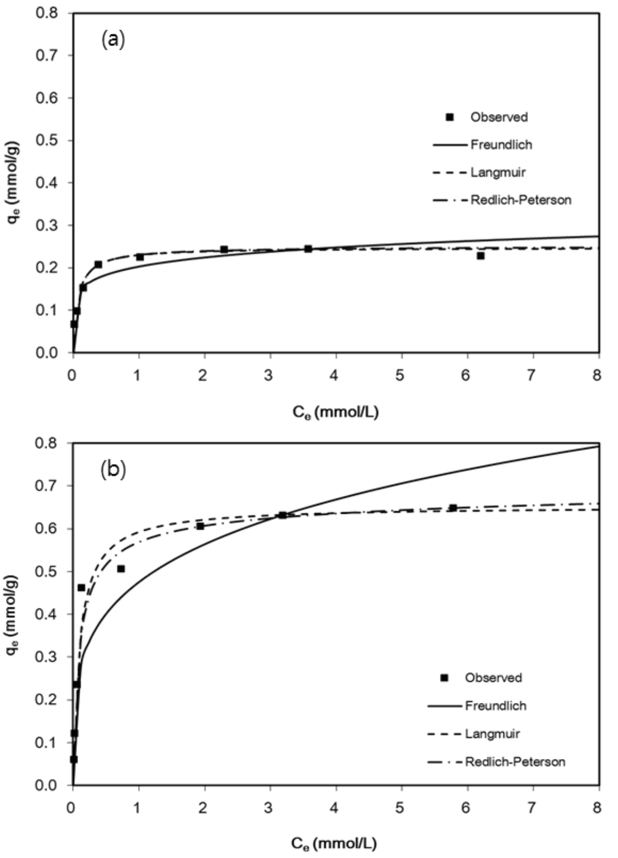

Fig. 7. Effect of initial As(V) concentration on As(V) removal by KC31 and SA along with equilibrium sorption model fits. Model parameters are provided in Table 5.

$$q_e = K_F C_e^{\frac{1}{n}} \text{ Freundlich} \tag{11}$$

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\,g}} \text{ Redlich} - \text{Peterson} \tag{12}$$

The corresponding model parameters are provided in Table 5. The Redlich–Peterson isotherm was most suitable for describing the equilibrium data with the parameter values of K_R = 3.368–7.075 L/g, a_R = 11.428–13.600 L/mmol, and g = 0.965–0.995 (Table 5). From the Redlich–Peterson model, the As(V) removal capacities (K_R/a_R) for KC31 and SA were 0.248 and 0.619 mmol/g, respectively, under the given experimental conditions (pH range = 7.5–8.6; initial As(V) concentration = 0.067–6.674 mmol/L).

3.5. As(V) removal from arsenic wastewater

The As(V) removal by KC31 from the high arsenic content wastewater are shown in Fig. 8. The As(V) removal rate increased from 17.4% to 87.5% as the fiber dose increased from 2 to 20 g/L, whereas the As(V) removal capacity decreased from 2.941 to 0.148 mmol/g. KC31 was effective in the removal of As(V) from the arsenic wastewater, even in the presence of other anionic contaminants

Table 5
Equilibrium isotherm parameters obtained from the model fitting to equilibrium data

Ion exchange	Freundlich isotherm					Langmuir isotherm					Redlich–Peterson isotherm						
fibers	K_F (L/g)	$1/n$	R^2	χ^2	SAE	Q_m (mmol/g)	K_L (L/mmol)	R^2	χ^2	SAE	K_R (L/g)	a_R (L/mmol)	K_R/a_R (mmol/g)	g	R^2	χ^2	SAE
KC31	0.203	0.144	0.863	0.031	0.165	0.248	13.453	0.967	0.129	0.084	3.368	13.600	0.248	0.995	0.968	0.127	0.084
SA	0.476	0.246	0.847	0.222	0.544	0.652	9.779	0.961	0.040	0.208	7.075	11.428	0.619	0.964	0.962	0.045	0.186

Table 6
As(V) removal capacity of anion exchangers reported in the literature

Anion exchanger	pH	As(V) removal capacity (mmol/g)	References
Coconut coir pith–based exchanger	7.0	0.167	[11]
Cellulose-based animated exchanger	6.0	2.497	[13]
Polystyrene exchanger (Amberlite IRA 900)	10.0	0.146	[16]
Polyethylene/polypropylene-based quaternized fibrous exchanger	7.0	1.112	[21]
Hydrated Zr(IV) oxide-impregnated polystyrene exchanger (Purolite A502P/A400)	7.0	0.267	[30]
Cellulose-based exchanger	6.0	1.451	[31]
Poly(ethylene mercaptoacetimide) exchanger	2.0	1.410	[32]
Manganese and iron (hydr)oxide-coated exchanger (D301)	5.0	1.711	[33]
Silica gel–based functionalized exchanger	7.0	0.591	[34]
Silica gel–based functionalized exchanger	7.5	0.186	[35]
KC31 fibrous exchanger	2.9	2.941	This study

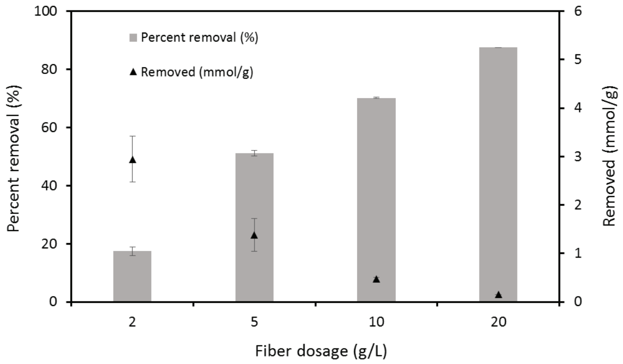

Fig. 8. As(V) removal by KC31 from the high arsenic content wastewater.

(chromate, sulfate, etc.). The As(V) removal capacity of KC31 (2.941 mmol/g) at the fiber dose of 2 g/L was higher than the As(V) removal capacities of anion exchangers (0.146–2.497 mmol/g) reported in the literature (Table 6) [11,13,16,21,35–40]. Unlike KC31, the As(V) removal by SA was negligible (data not shown), possibly due to the acidic solution pH of the arsenic wastewater (pH = 2.9) and the presence of other anionic contaminants, which were not favorable condition for SA to remove As(V).

4. Conclusions

In this study, we used the KC31 and SA fibers in the removal of As(V) from arsenic wastewater. The result indicated that the pristine KC31 was a free amine form, whereas the pristine SA was fully protonated. FTIR and XPS analyses indicated that the protonated amine groups were responsible for the anion exchange of As(V). Batch tests showed that in the removal of As(V), KC31 behaved differently from SA in response to pH change. In the regeneration tests, the fibers could be successfully regenerated over five adsorption–desorption cycles with NaCl solution. Batch experiments in the arsenic wastewater showed that KC31 was effective in the removal of As(V) from the arsenic wastewater, even in the presence of other anionic contaminants (chromate, sulfate, etc.). Unlike KC31, the As(V) removal by SA from the arsenic wastewater was negligible, possibly due to the acidic solution pH and the competitive effect of other anionic contaminants. This study demonstrates that the KC31 fibers could be used for the removal of As(V) from the acidic arsenic wastewater.

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Symbols

a_R — Redlich–Peterson constant related to the affinity of the ion exchange sites
C_e — Equilibrium concentration of contaminant in the aqueous phase
g — Redlich–Peterson constant related to the removal intensity
k_1 — Pseudo-first-order rate constant
k_2 — Pseudo-second-order rate constant
K_F — Freundlich constant related to the removal capacity
K_L — Langmuir constant related to the affinity of the exchange sites
K_R — Redlich–Peterson constant related to the removal capacity
$1/n$ — Freundlich constant related to the removal intensity
Q_m — Maximum removal capacity
q_t — Amount of As(V) removed at time t
R^2 — Determination coefficient
SAE — Sum of the absolute error
y_c — Removal capacity calculated from the model
y_e — Removal capacity measured from the experiment
$\bar{y}_e$ — Average measured removal capacity
χ^2 — Chi-square coefficient

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