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ORIGINAL PAPER

Removal of heavy metals and arsenic from aqueous solution using textile wastes from denim industry

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Abstract In this study, the denim fiber scraps were reused as an alternative low-cost sorbent for the removal of heavy metals Pb^{2+}, Cd^{2+}, Zn^{2+} and arsenic from aqueous solutions. Results showed that this textile waste was an effective sorbent for the removal of these heavy metal ions and offered a better removal performance than those reported for other synthetic and natural sorbents such as activated carbons and zeolites. On the other hand, raw and metal-loaded denim wastes were also useful for the removal of arsenic (V) from aqueous solutions and their sorption capacities were higher than 1.5 mg/g. In particular, the presence of Pb^{2+} ions on the surface of denim wastes improved significantly its arsenic (V) sorption performance. In summary, the reuse of denim textile wastes in wastewater treatment can be considered as an eco-friendly application that could be useful for waste management and also for reducing the production costs in this important industrial sector.

Keywords Water pollutants · Denim fiber scraps · Sorption · Waste management

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Introduction

The manufacturing processes in the textile and dyeing industries are characterized by their significant impact on environment because of the use of large volumes of water and the generation of wastes that are traditionally considered as sources of environmental pollutants (Mo et al. 2009; Huang et al. 2011). The type and physicochemical properties of wastes and pollutants generated by these industrial sectors depend on the characteristics of the textile factory facilities (i.e., the processes and technologies used the types of chemicals and fibers employed). In particular, solid residues are generated from different unit operations involved in textile manufacturing processes such as the preparation, bleaching, dyeing, sizing and finishing. A wide variety of chemicals and raw materials is used in these industrial operations (Ozturk et al. 2009). However, the main wastes generated by the textile manufacturing operations are sliver, yarn, woven and fiber scraps (Halimi et al. 2008), which may contain different inorganic and organic compounds and dyes depending on their source.

The textile manufacturing industry is a relevant economic activity in Mexico, and it generates a significant amount of textile wastes. These wastes are usually handled improperly, and their final disposal significantly increases the production costs. Currently, the improper waste management remains as an important environmental problem in the Mexican textile industry. Additionally, the amount of solid waste generated is steadily increasing due to the continuous growing of this industrial sector. Therefore, new alternatives for reusing and disposing of the textile residues and wastes should be studied and analyzed.

The principles of cleaner production approach provide an attractive basis for the reuse to not only reduce the

environmental impact but also to obtain significant financial savings in the textile industries of Mexico and other developing countries. Recent studies reported the reprocessing of textile industry wastes in the textile sector processes (Halimi et al. 2008), while other studies explored the reuse of these wastes for other applications, e.g., for improving properties of building materials (Briga-Sá et al. 2013) or in energy recovery (Ryu et al. 2007). However, it is important to highlight that wastes used in these studies have been obtained mainly from sub-operations, e.g., the treatment of textile effluents (Li et al. 2005), and not from primary operations of textile manufacturing.

In particular, an alternative for minimizing the solid wastes generated from textile industries is their reuse in the field of wastewater and water treatment. The utilization of wastes from one industry to the wastewater treatment of other industry has been recognized as attractive approach for waste minimization and for reducing industrial costs caused by the disposal of these residues (Dhaouadi and M'Henni 2008). Recently, clothing textile residues and wastes have been used for the preparation of sorbents, which could be used in the wastewater treatment (Williams and Reed 2003, 2004; Nahil and Williams 2010, 2012). However, no attempts have been performed for reusing raw textile residues and wastes in the removal of water pollutants. These textile residues and wastes can be obtained directly from the textile manufacturing process, and, consequently, they have an interesting composition due to the use of different fibers and both inorganic and organic compounds (e.g., dyes).

Based on this fact, this study has focused on the reusing of fiber wastes obtained from denim industry for the removal of priority pollutants from water. Specifically, fiber scraps loaded with indigo-derivative dyes obtained from the denim washing with pumice stone have been used as sorbent of lead (Pb^{2+}), cadmium (Cd^{2+}) and zinc (Zn^{2+}) ions and arsenic (V) from aqueous solution. These pollutants are considered toxic in the context of wastewater and water treatment. Several sorbents have used for heavy metal removal including activated carbons, polymers, zeolites, clays and other materials (Nadaroglu et al. 2010; Dhir and Srivastava 2011; Celebi et al. 2012; Kalkan et al. 2012; Kamsonlian et al. 2012; Nadaroglu and Kalkan 2012; Saka et al. 2012; Saqib et al. 2013; Dubey et al. 2013; Nadaroglu et al. 2013). Denim wastes have not been applied in the removal of toxic pollutants from water. Thus, this study proposes their reuse and application for water treatment. The main objective of this study was to determine the potential of denim fiber scraps as a low-cost sorbent for the removal of heavy metal ions and arsenic (V) from aqueous solution. This study has been performed at Water Engineering and Technology Laboratory of Instituto Tecnólogico de Aguascalientes (Aguascalientes, Mexico) during 2013.

Materials and methods

Description and characterization of textiles wastes resulted from the denim manufacturing industry

Textile wastes were obtained from industrial operations of a local denim industry located in Aguascalientes, Mexico. These wastes were fiber scraps dyed with indigo-derivative dyes obtained from the denim washing with pumice stone, which is used to provide the esthetic finish and strength of denim fabric. It is estimated that one ton per week of these wastes is generated by this local industry of Aguascalientes. For illustration, Fig. 1 shows the physical appearance of the denim fiber scraps obtained directly from the industry. SEM images are also reported in Fig. 1, which were obtained with a FE-SEM system (Quanta FEG 650, FEI). For SEM analyses, solid particles were dispersed on a graphite adhesive tab placed on an aluminum stub and no further coating was required. A semi-quantitative analysis of denim waste samples was obtained by EDX, and an average of three punctual analyses on the sample surface at 20 μm was reported. Raw denim fiber scraps were washed with deionized water. Washing stopped when a constant pH was reached. The scraps were then dried at 110 °C for 24 h. The fiber scraps were crushed and sieved to obtain a particle size of 18–20 mesh fractions. These textile wastes were used for sorption experiments of heavy metals and arsenic (V) in aqueous solution, and the experimental procedure used in removal experiments is described in the following sections.

The textural characteristics of denim fiber scraps were determined from N_2 adsorption–desorption isotherms at 77 K using an automatic TriStar 3000 analyzer (Micromeritics). Content of C, H, N and S of this textile waste was determined using an elemental analyzer LECO CHNS-932, and the oxygen content was obtained with a LECO VTF-900. On the other hand, the point of zero charge (pH_{PZC}) was determined using NaCl solutions with concentrations from 0.01 to 1.0 N. A sample dosage of 4 g/L was used in this quantification with solutions with different initial pHs (i.e., 3–9), which were adjusted with 0.1 M HCl and 0.1 M NaOH. These experiments were performed at 30 °C, the solution was equilibrated for 24 h, and the final pH was measured (Faria et al. 2004). In addition, the pH of denim wastes was determined using 10 g of denim fiber scraps. Textile wastes were boiled in 100 mL of deionized water for 1.5 min. The slurry was then filtered, and the pH of the filtrate was measured at 50 °C. Finally, FT-IR spectra of denim waste samples were obtained with a DIGILAB FT-

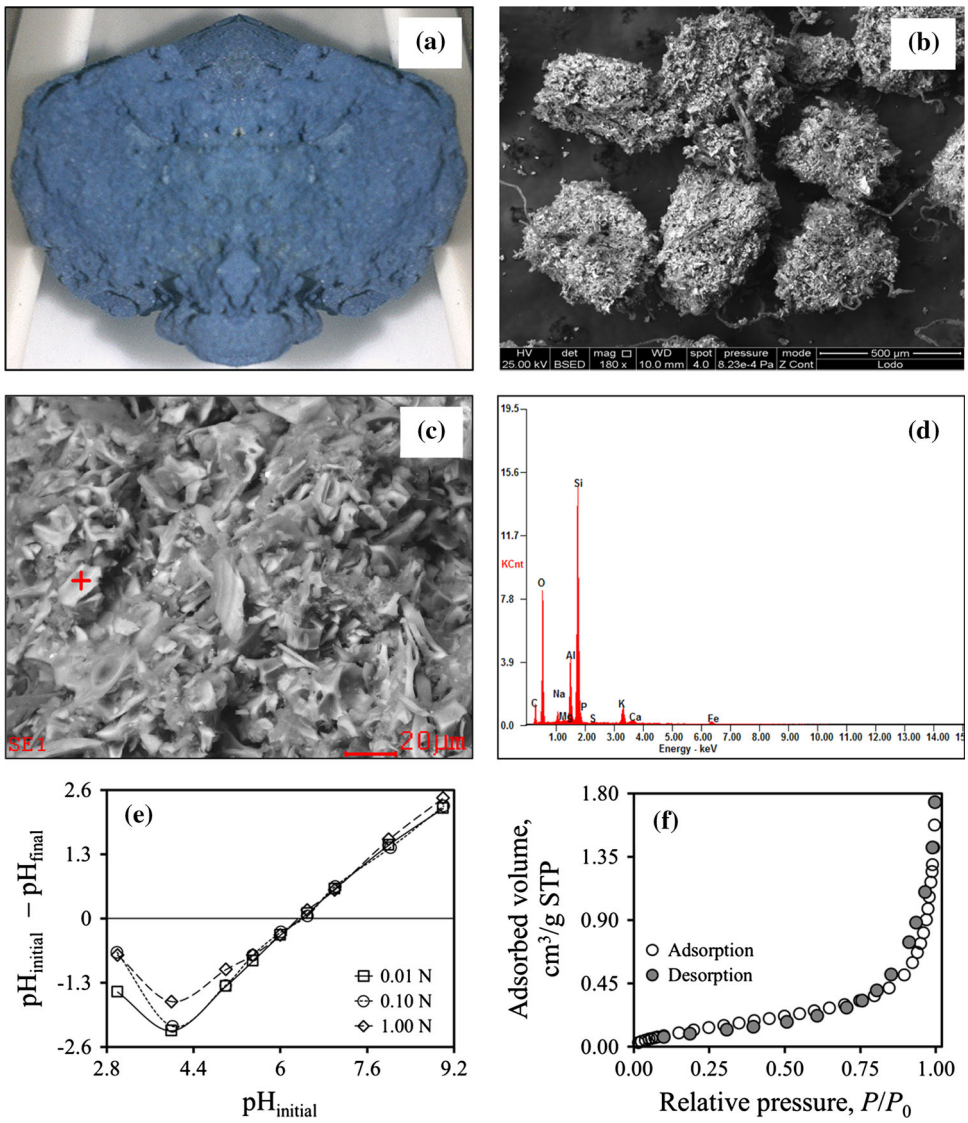

Fig. 1 **a** Physical appearance, **b** SEM images (500 μm), **c**, **d** EDX analysis, **e** pH of zero charge and **f** N_2 adsorption–desorption isotherms at 77 K of denim fiber scraps used in the removal experiments of heavy metal ions and arsenic (V) from aqueous solution

IR spectrometer employing a deuterated triglycine sulfate (DTGS) detector to collect the IR spectra in the 4,000–500 cm^{-1} spectral range.

Evaluation of the performance of denim fiber scraps as sorbent for the removal of heavy metals

Denim fiber scraps were used in kinetic and equilibrium sorption experiments of heavy metal ions. These experiments were performed using aqueous solutions of Pb^{2+}, Cd^{2+} and Zn^{2+}, which were prepared from nitrate salts (analytical grade) of these metals and deionized water. Batch sorption experiments were performed using a sorbent dosage of 1 g/L at 30 °C and different conditions of pH (i.e., 3–5). Kinetic experiments were performed using different initial metal concentrations from 40 to 120 mg/L. These experimental conditions were considered for all tested heavy metals. Metal sorption rates were calculated from kinetic experiments using traditional kinetic sorption models.

On the other hand, the metal uptakes of textile wastes were determined from the sorption isotherms obtained at 30 °C and different conditions of solution pH: 3–5. Solutions with initial metal concentrations from 10 to 170 mg/L were used, and the equilibrium time of sorption experiments was determined from kinetic studies. A mass balance was employed for the calculation of metal sorption capacities

$$q = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 and C_t are the initial and final concentration of metal ion in the sorption experiment given in mg/L, V is the volume of metal solution in L, and m is the amount of denim fiber scraps used in the removal experiments given

in g, respectively. Experimental sorption capacities were modeled using different isotherm models, which include Langmuir, Freundlich and Sips equations.

For all the sorption experiments, the quantification of heavy metals was performed using a Perkin Elmer AAnalyst 100 atomic absorption spectrometer with linear calibrations curves. All experiments were performed in triplicate, and the mean values were used for the calculation of metal uptakes and data analysis.

Sorption experiments of arsenic (V) on denim fiber scraps loaded with heavy metal ions

Arsenic (V) sorption experiments were performed using both raw and metal-loaded denim fiber scraps. Specifically, a comparative study of the arsenic (V) sorption capacities was performed between samples of raw denim wastes, and those samples of denim fiber scraps obtained from the removal experiments of heavy metal ions (i.e., metal-loaded denim fiber scraps). This comparative study was performed to determine the effect of metal loaded on the denim wastes with respect to its arsenic (V) sorption capacity. Batch sorption experiments were performed at 25 °C and using an arsenic (V) solution with an initial concentration of 30 mg/L. A sorbent dosage of 10 g/L was used in these experiments, and two conditions of pH were considered: 7 and 9. In these experiments, metal-loaded denim fiber scraps were obtained from the sorption experiments using initial metal concentrations of 25, 50 and 100 mg/L. The equilibrium time for arsenic (V) experiments was 24 h, and the uptakes were calculated using Eq. (1) where pollutant concentrations were also quantified using atomic absorption spectroscopy.

Results and discussion

Removal of heavy metal ions

Results of sorption kinetic for all tested heavy metals at different pH conditions are reported in Fig. 2. Overall, the sorption rates depend on the solution pH and the initial concentration of metal ions. For all cases, the uptake of metals is fast during the first hours (i.e., 4 h) of the sorption process at batch conditions where 60–90 % of the metallic ions present in solution is removed. Note that pH has a significant impact on the performance of denim wastes for the removal of heavy metal ions. It is clear that the removal of heavy metals decreased with a decrement of the solution pH. Since the concentration of protons increases at a low pH, they compete with the metal ions for occupying the sorption sites of the denim fiber scraps, thus affecting the removal of heavy metal ions. On the other hand, the pH_{PZC} value of denim fiber scraps is 6.39 ± 0.05 and the pH value of this sorbent is 6.59 ± 0.15 (Fig. 1; Table 1). Below the pH_{PZC} value, the surface of denim fiber scraps is positively charged and, consequently, the sorbent tends to attract anions and to repel cations. Based on the fact that the removal of heavy metals was studied on denim fiber scraps at $pH < pH_{PZC}$, the extent of metal sorption decreases with a pH decrement. These results suggest that the coulombic interactions between the heavy metal ions and the surface charge of denim fiber scraps contribute to the sorption process. In summary, the positive surface charge of denim wastes and the concentration of H^+ in solution cause a decrement of the heavy metal uptakes at low pH. Herein, it is important to remark that sorption experiments have been performed at $pH < 6$ to avoid the precipitation of heavy metals due to the formation of hydrolyzed metal species.

Sorption rates of all heavy metals on denim fiber scraps were calculated using the pseudo-first and pseudo-second order kinetic models. The kinetic parameters determined from metal sorption experiments, using a nonlinear regression approach, and a relative least squares objective function (F_{obj}), are reported in Table 2. Results of kinetic data fitting indicate that the pseudo-first order model offers the best correlation coefficients for all tested heavy metals. Specifically, the values of correlation coefficients (R^2) are >0.9 and the metal uptakes calculated by this model are close to those metal uptakes determined in sorption experiments. Therefore, the pseudo-first order model is more appropriate for modeling the sorption kinetics obtained in this study. Sorption rate constants (k_1) ranged from 0.11 to 1.08 for Pb^{2+}, from 0.07 to 1.17 for Cd^{2+} and from 0.08 to 0.79 h^{-1} for Zn^{2+}, respectively.

Kinetic data were also used to analyze the rate controlling steps affecting the sorption kinetics of heavy metal ions on denim wastes. Specifically, a linear regression analysis of the plot $q_t - t^{1/2}$ was performed for the kinetic data obtained in this study. For illustrative purposes, Fig. 3 shows this linear regression analysis for kinetic data obtained at pH 5. Overall, all regression plots of $q_t - t^{1/2}$ showed a multi-linearity behavior and, consequently, it is expected that several steps may be involved in the sorption mechanism of heavy metal ions on denim wastes. These linear plots have a sharp section, which also indicates a sorption stage of heavy metal ions on the external surface of textile wastes. Note that the results of N_2 adsorption–desorption isotherms (Fig. 1) indicated that the denim fiber scraps can be considered as a nonporous sorbent with a low-specific surface area (i.e., 9 m^2/g). Therefore, it is expected that the type and quantity of functional groups of the external surface of denim fiber scraps are relevant for the removal of heavy metal ions.

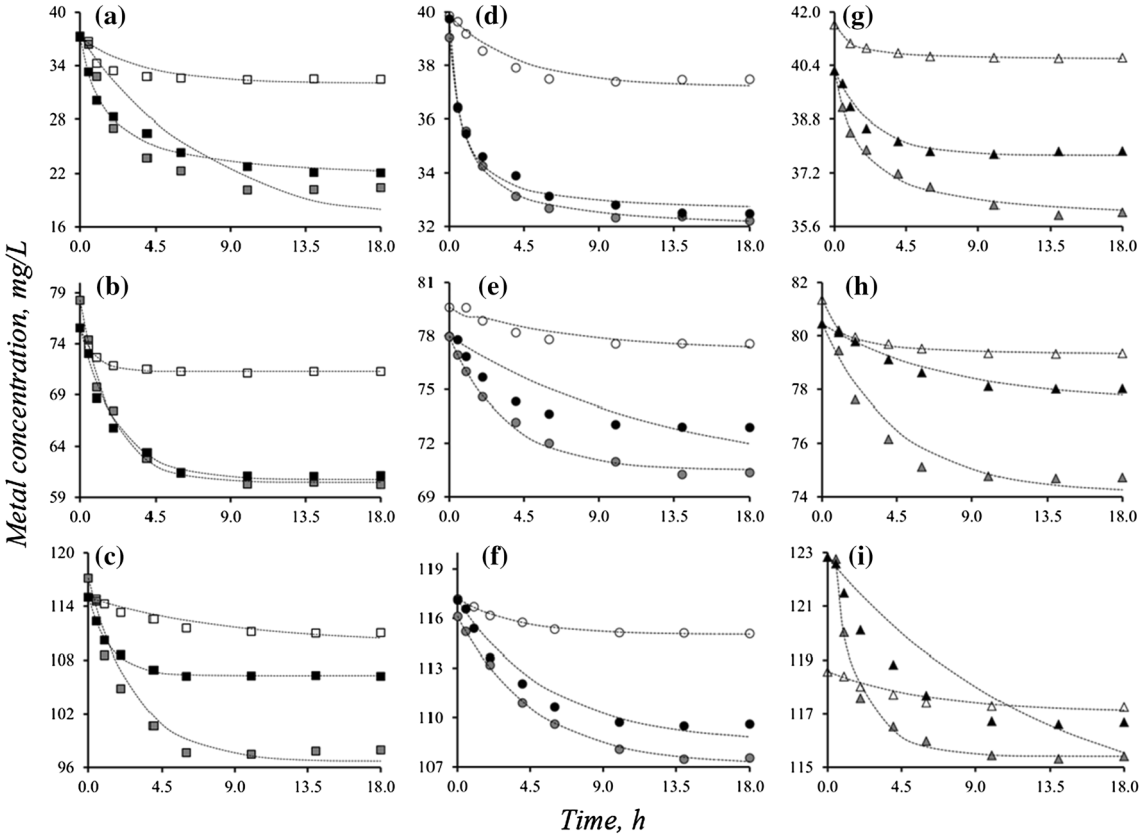

Fig. 2 Sorption kinetics of **a–c** Pb^{2+}, **d–f** Cd^{2+} and **g–i** Zn^{2+} ions on denim fiber scraps at 30 °C. Solution pH: 3 (*open square*, *open circle*, *open triangle*); 4 (*filled black square*, *filled black circle*, *filled black triangle*) and 5 (*filled gray square*, *filled gray circle*, *filled gray triangle*)

Table 1 Physicochemical parameters of denim fiber scraps

Element	Content (%)	Parameter	Value	Element	Value (Wt%)[b]
Carbon	10.09	pH	6.59 ± 0.15	C	18.57
Hydrogen	1.70	pH_{PZC}	6.39 ± 0.05	O	38.21
Nitrogen	0.74			Na	1.82
Sulfur	N.D.[a]	SBET, m^2/g	9.00	Mg	0.35
Oxygen	6.77	V_t, cm^3/g	0.049	Al	7.26
				Si	27.93
				P	0.15
				S	0.27
				K	3.06
				Ca	0.80
				Fe	1.55

[a] Non detected

[b] Average of three determinations

Figure 4 shows the sorption isotherms of all heavy metals on denim fiber scraps at tested pH conditions. These isotherms confirm the pH effect on the sorbent performance and indicate that there is an increment of 160–186 % in the maximum metal uptakes when the solution pH increased from 3 to 5. Specifically, the maximum sorption capacities ranged from 11.0 to 30.3 for Pb^{2+}, from 4.3 to 11.2 for Cd^{2+} and from 5.4 to 15.4 mg/g for Zn^{2+} at tested experimental conditions. It is interesting to remark that the maximum uptakes of Zn^{2+} ions on denim fiber scraps are similar at pH 3 and 4: 5.4 and 5.9 mg/g, respectively. However, the sorption performance

Table 2 Results of data correlation of sorption kinetics of heavy metal ions on denim fiber scraps

Metal	C_o (mg/L)	pH	Kinetic sorption models[a]							
			k_1, h^{-1}	q_{te} (mg/g)	R^2	F_{obj}	k_2 (g/mg h)	q_{te} (mg/g)	R^2	F_{obj}
Pb^{2+}	40	3	0.27	5.18	0.54	0.75	0.03	6.98	0.41	0.86
		4	0.63	13.67	0.92	0.08	0.04	16.17	0.98	0.02
		5	0.13	21.28	0.72	0.88	0.01	33.46	0.66	0.95
	80	3	1.08	4.26	0.99	0.01	0.29	4.69	0.96	0.02
		4	0.45	14.79	0.97	0.10	0.02	18.13	0.92	0.16
		5	0.52	17.78	0.99	0.03	0.03	21.14	0.97	0.05
	120	3	0.11	5.25	0.88	0.53	0.01	8.55	0.85	0.57
		4	0.74	8.70	0.99	0.01	0.08	9.93	0.97	0.03
		5	0.35	20.45	0.94	0.21	0.01	25.95	0.86	0.30
Cd^{2+}	40	3	0.24	2.67	0.92	0.26	0.05	3.68	0.85	0.35
		4	1.17	6.53	0.84	0.08	0.21	7.26	0.97	0.02
		5	0.87	6.43	0.95	0.05	0.15	7.21	0.99	0.01
	80	3	0.14	2.44	0.93	0.06	0.03	3.62	0.89	0.08
		4	0.29	7.46	0.99	0.01	0.03	9.72	0.99	0.01
		5	0.07	8.14	0.71	1.13	0.01	14.44	0.68	1.16
	120	3	0.27	2.17	0.99	0.02	0.08	2.82	0.96	0.05
		4	0.21	9.01	0.99	0.01	0.01	12.36	0.99	0.02
		5	0.17	8.66	0.94	0.28	0.01	12.80	0.90	0.34
Zn^{2+}	40	3	0.77	0.97	0.93	0.02	0.99	1.07	0.99	0.01
		4	0.41	2.51	0.95	0.13	0.12	3.11	0.88	0.22
		5	0.59	3.82	0.92	0.08	0.14	4.53	0.98	0.02
	80	3	0.79	1.90	0.87	0.03	0.51	2.12	0.98	0.01
		4	0.13	2.93	0.96	0.06	0.02	4.46	0.94	0.08
		5	0.22	6.31	0.92	0.15	0.02	8.69	0.86	0.20
	120	3	0.16	1.53	0.90	0.23	0.05	2.27	0.85	0.23
		4	0.08	9.82	0.76	1.03	0.01	17.33	0.74	1.06
		5	0.51	7.42	0.98	0.01	0.06	8.69	0.95	0.04

[a] Pseudo-first order model: $q_t = q_{te}\left(1 - e^{-k_1 t}\right)$ and Pseudo-second order model: $q_t = \frac{q_{te}^2 k_2 t}{1 + q_{te} k_2 t}$

of the textile waste for this metal increased drastically at pH 5. Several studies have reported that the sorption behavior of heavy metal ions may be attributed to the physicochemical properties of these pollutants such as the ionic and hydrated ionic radii, hydration energies and electronegativity (Gupta et al. 2012). In particular, Pb^{2+} has the highest electronegativity of the studied heavy metal ions and, based on the fact that the electrostatic interactions between metallic species and denim wastes could play a relevant role in sorption process, it is expected that Pb^{2+} ions could be more strongly attracted to the surface of denim fiber scraps. This finding is consistent with results reported in previous studies, e.g., Gupta et al. (2012).

On the other hand, Langmuir, Freundlich and Sips isotherm models have been used for the correlation of sorption isotherms of heavy metals on textile wastes. The results of data fitting, using also a nonlinear regression approach, are reported in Table 3. Both Langmuir and Freundlich models showed a poor performance for modeling the experimental results of equilibrium sorption studies, while Sips model showed the best correlation coefficients ($R^2 > 0.94$) for isotherm data modeling (Table 3). Therefore, Sips is the best isotherm equation for modeling the sorption data obtained in this study.

In summary, raw denim fiber scraps showed competitive sorption capacities for the removal of heavy metal ions. In fact, this textile waste may show a better removal performance than those reported for other natural and synthetic sorbents. Table 4 shows a comparison of sorption capacities of different materials used for heavy metal removal. For example, the Pb^{2+} uptakes of denim fiber scraps are higher than those reported for carbons obtained from plum kernels (5.4 mg/g) and jacaranda fruit (7.0 mg/g) (Treviño-Cordero et al. 2013), natural clays (25.0 mg/g) (Irani et al. 2011) and they are close to the metal uptakes reported for limestone (40 mg/g) (Rangel-Porras et al. 2010) and

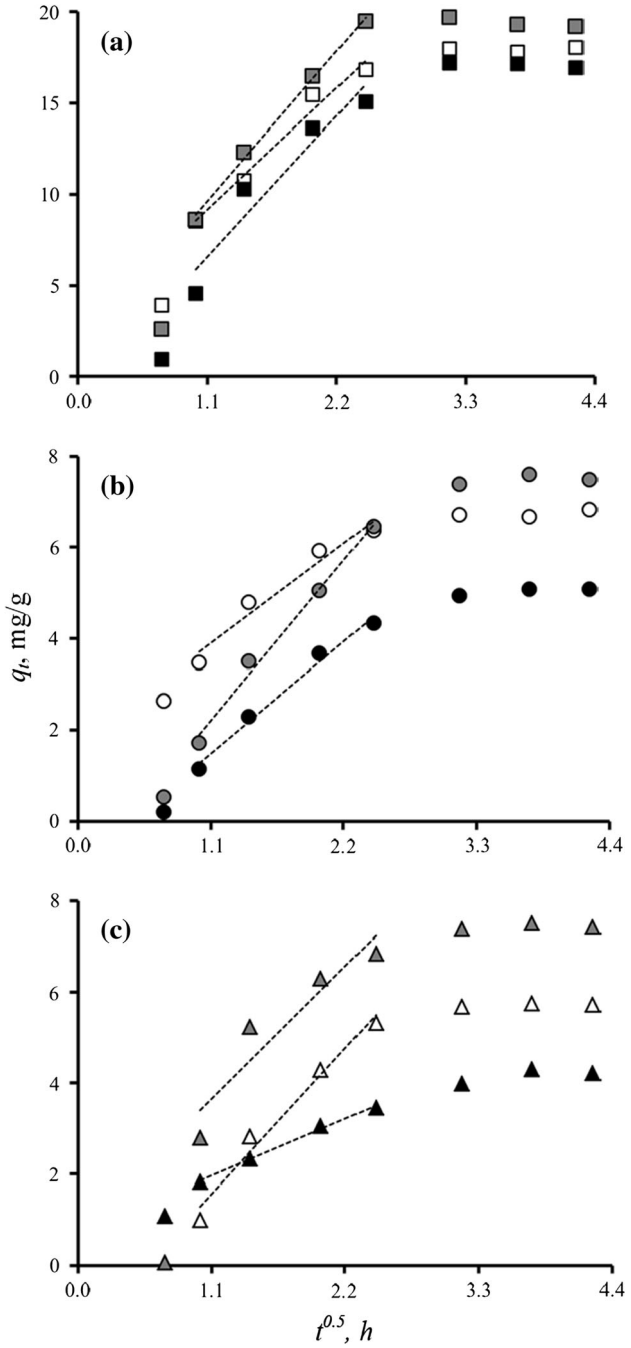

Fig. 3 Linear analysis of kinetic data for the removal of **a** Pb^{2+}, **b** Cd^{2+} and **c** Zn^{2+} ions on denim fiber scraps at pH 5 and 30 °C. Initial metal concentration: (*filled black square*, *filled black triangle, filled black circle*) 40 mg/L (*open square*, *open triangle, open circle*) 80 mg/L and (*filled gray square*, *filled gray triangle, filled gray circle*) 120 mg/L

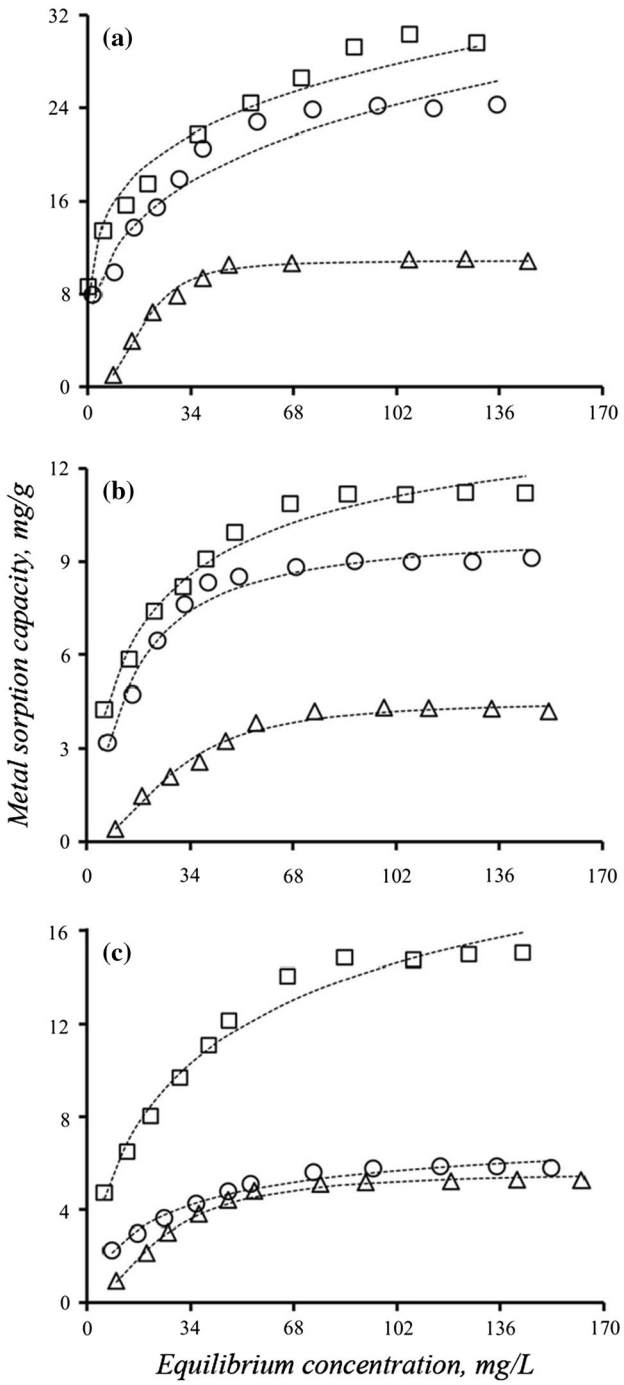

Fig. 4 Sorption isotherms of **a** Pb^{2+}, **b** Cd^{2+} and **c**Zn^{2+} ions on denim fiber scraps at 30 °C. Solution pH: (*open triangle*) 3 (*open circle*) 4 and (*open square*) 5. Initial metal concentration: 10–170 mg/L

modified corncobs (43.4 mg/g) (Tan et al. 2010). With respect to Cd^{2+} removal, the denim fiber scraps showed higher sorption capacities than those obtained for limestone: 1.3 mg/g (Rangel-Porras et al. 2010), commercial activated carbon modified with egg shell wastes: 5.7 mg/g (Guijarro-Aldaco et al. 2011) and kraft lignin: 8.2 mg/g (Šćiban et al. 2011). Finally, the maximum Zn^{2+} sorption capacity of this textile waste is similar to that obtained for lemon grass: 15.9 mg/g (Zuo et al. 2012) and it is higher than those reported for aquatic macrophyte: 6.8 mg/g (Lesage et al. 2007), tea waste: 8.9 mg/g (Wasewar et al. 2009) and kraft lignin: 1.76 mg/g (Šćiban et al. 2011). It is

Table 3 Results of sorption isotherm modeling for the removal of heavy metal ions on denim fiber scraps

	Metal	Pb^{2+}			Cd^{2+}			Zn^{2+}		
	pH	3	4	5	3	4	5	3	4	5
Langmuir	q_m (mg/g)	0.30	6.16	9.83	0.10	2.02	2.71	0.35	1.25	2.69
$q_e = \frac{K_L q_m C_e}{1+K_L C_e}$	K_L (L/mg)	1.28	3.36	4.45	1.25	3.04	3.25	1.72	3.01	2.68
	R^2	0.18	0.93	0.96	0.57	0.76	0.91	0.62	0.91	0.93
	F_{obj}	1.46	0.08	0.05	0.91	0.17	0.06	0.53	0.06	0.05
Freundlich	K_f	23.18	24.21	20.91	9.81	10.54	12.22	8.22	6.78	17.25
$q_e = K_f C_e^{1/n_1}$	n_1	0.01	0.12	1.73	0.01	0.07	0.08	0.02	0.06	0.05
	R^2	0.51	0.88	0.34	0.77	0.96	0.97	0.87	0.98	0.97
	F_{obj}	1.07	0.35	0.62	0.59	0.03	0.04	0.20	0.03	0.07
Sips	q_s (mg/g)	10.91	185.94	10,848.65	4.53	9.99	14.83	5.76	7.84	25.50
$q_e = \frac{q_m a_s C_e^n}{1+a_s C_e^n}$	a_s	3×10^{-4}	0.03	1×10^{-3}	1×10^{-3}	0.05	0.11	0.01	0.08	0.08
	n	2.78	0.33	0.23	1.99	1.15	0.71	1.73	0.78	0.64
	R^2	0.99	0.94	0.96	0.98	0.97	0.98	0.99	0.98	0.97
	F_{obj}	0.02	0.08	0.05	0.04	0.03	0.02	0.01	0.02	0.03

clear that raw denim fiber scraps can be considered an alternative and promising sorbent for the removal of heavy metal ions from aqueous solution.

Removal of arsenic (V) on the metal-loaded denim fiber scraps

Results of sorption experiments of arsenic (V) using both raw and metal-loaded denim fiber scraps are reported in Fig. 5 at pH 7 and 9. These results show that the presence of heavy metal ions adsorbed on the surface of denim fiber scraps improves the arsenic (V) uptakes. Metal-loaded denim wastes may show an increment of arsenic (V) sorption capacities from 1.6 to 70 % where the presence of Pb^{2+} ions on sorbent surface increases significantly the sorption performance of raw denim fiber scraps (Fig. 5). Overall, the arsenic (V) sorption capacities of metal-loaded denim fiber scraps increase with the quantity of metal ions adsorbed on the surface of textile waste and they follow the trend: $Pb^{2+} > Cd^{2+} > Zn^{2+}$. Note that the metal ion with the highest electronegativity has more impact on the arsenic (V) sorption performance of metal-loaded denim fiber scraps. It appears that the presence of Zn^{2+} ions on sorbent surface does not affect significantly the arsenic (V) uptakes of this textile waste. On the other hand, the arsenic (V) uptakes decreased when the solution pH increased from 7 to 9 for both raw and metal-loaded denim fiber scraps. This decrement of sorption capacities is more evident for Pb^{2+}-loaded denim samples where a decrement from 21 to 25 % in the removal efficacy has been observed. Arsenic removal experiments (V) have been performed at $pH > pH_{PZC}$, and, consequently, the surface of metal-loaded denim fiber scraps is negative causing the repulsion of the dissolved arsenic species, which are $HAsO_4^{-2}$ at pH: 6.76–11.6 (Streat et al. 2008). Again, it appears that electrostatic interactions between the dissolved arsenic species and the denim fiber scraps are playing an important role in the sorption process.

Finally, it is interesting to observe that denim fiber scraps, with and without metal loaded on its surface, showed arsenic (V) sorption capacities higher than those reported for other sorbents reported in the literature (Table 4). For example, the raw and Pb^{2+}-loaded denim wastes showed a better performance for arsenic (V) removal (1.96 and 3.3 mg/g, respectively) than those reported for powdered eggshell: 1.92 mg/g (Oke et al. 2008) and iron-modified carbon material: 1.25 mg/g (Vitela-Rodriguez and Rangel-Mendez 2013) at pH 7. Note that previous studies have shown that the doping of sorbent surfaces using metallic species has emerged as an effective approach for improving the sorption properties of materials employed for arsenic removal from water (Deliyanni and Bandosz 2011; Vitela-Rodriguez and Rangel-Mendez 2013). Results of this study confirmed these findings, and it is clear that the presence of heavy metal ions on surface of denim fiber scraps improves their sorption properties for the removal of arsenic (V) from aqueous solution. Therefore, the denim fiber scraps can be used for the removal of heavy metal ions from industrial effluents and, after their saturation with metallic species, these metal-loaded denim wastes can be reused for the removal of arsenic (V).

Characterization of denim fiber scraps

Particularly, the textile wastes used in this study are solid particles of blue color constituted by some thin fibers (Fig. 1a, b). Table 1 shows the elemental composition of denim fiber scraps, and, according to the results obtained by

Table 4 Comparison of sorption capacities reported in the literature for the removal of Pb^{2+}, Cd^{2+}, Zn^{2+} and arsenic from aqueous solution

Pollutant	Sorbent	Sorption capacity (mg/g)	Reference
Pb^{2+}	Modified corncobs	43.4	Tan et al. (2010)
	Fly ash	18.8	Ahmaruzzaman (2011)
	Natural clays	25.0	Irani et al. (2011)
	Carbon obtained from jacaranda fruit	7.0	Treviño-Cordero et al. (2013)
	Carbon obtained from plum kernels	5.4	Treviño-Cordero et al. (2013)
Cd^{2+}	Limestone	1.3	Rangel-Porras et al. (2010)
	Bagasse fly ash	6.19	Ahmaruzzaman (2011)
	Commercial activated carbon modified with egg shell wastes	5.7	Guijarro-Aldaco et al. (2011)
	Kraft lignin	8.2	Šćiban et al. (2011)
	Bacteria-modified red mud	83.0	Kalkan et al. (2013)
	Methylobacterium extorquens-modified silica fume waste	166.7	Nadaroglu et al. (2013)
Zn^{2+}	Aquatic macrophyte	6.8	Lesage et al. (2007)
	Tea waste	8.9	Wasewar et al. (2009)
	Rice husk ash	14.3	Ahmaruzzaman (2011)
	Commercial activated carbon modified with egg shell wastes	10.48	Guijarro-Aldaco et al. (2011)
	Lemon grass	15.9	Zuo et al. (2012)
As(V)	Granular activated carbon	2.5	Di Natale et al. (2008)
	Powdered eggshell	1.92	Oke et al. (2008)
	Apricot stone based activated carbon	0.034	Tuna et al. (2013)
	Fe^{2+}-loaded activated carbon	2.02	Tuna et al. (2013)
	Iron-modified carbon	1.25	Vitela-Rodriguez and Rangel-Mendez (2013)

EDX analysis (Fig. 1c, d), these textile wastes have inorganic elements such as Si, Al, Na, P, Ca, Fe and others. The presence of these elements can be associated with the chemical reagents employed in the denim washing with pumice stone (Wang et al. 2008). Note that the carbon content is due to the fiber composition (cotton) and to the

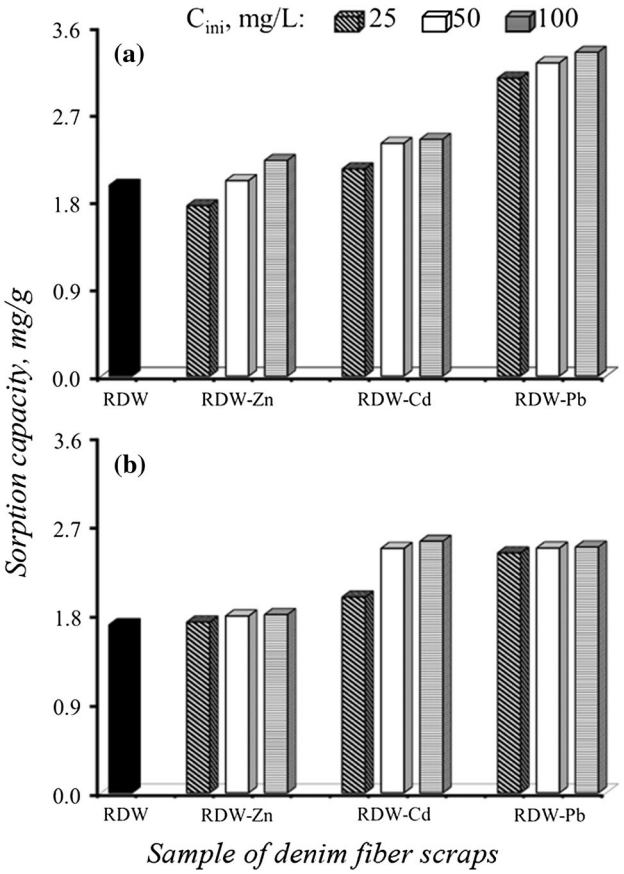

Fig. 5 Sorption of arsenic (V) using both raw (RDW) and metal-loaded denim fiber scraps (RDW-Zn, RDW-Cd, RDW-Pb) at 30 °C. Solution pH: **a** 7 and **b** 9

indigo-derivative dyes loaded onto these fibers. Additionally, the high content of Si (~28 %), Al (7.26 %) and K (3.06 %) found in the denim fiber scraps is caused by the stone washing process because the pumice stone is composed of SiO_2 (65.21 %), Al_2O_3 (15.50 %), CaO (2.51 %), MgO (0.86 %), Na_2O (1.81 %), K_2O (2.68 %) and Fe_2O_3 (2.61 %) (Asgari et al. 2012). In this context, the FT-IR spectra of raw denim fibers confirmed this finding (Fig. 6) because the principal bands of silicon compounds of pumice were identified at 460 and ~800 cm^{-1} and a strong peak around 1,047 cm^{-1}, which can be associated with the Si–O bending strength vibrations and the Si–O stretching vibrations (Ersoy et al. 2010). Also, a broadband located at 3,423 cm^{-1} was observed, which corresponds to O–H stretching vibration in hydroxyl functional groups, and the band at 2,922 cm^{-1} and its shoulder at 2,856 cm^{-1} could be attributed to νC–H and δC–H (ν = stretching and δ = bending) absorption bands that may be associated with methyl and methylene groups (Deng et al. 2010; Tian et al. 2011). The band at 1,630 cm^{-1} can be attributed to C=O vibrations of ketones, aldehydes or carboxylic acids. Finally, it is important to highlight that an important

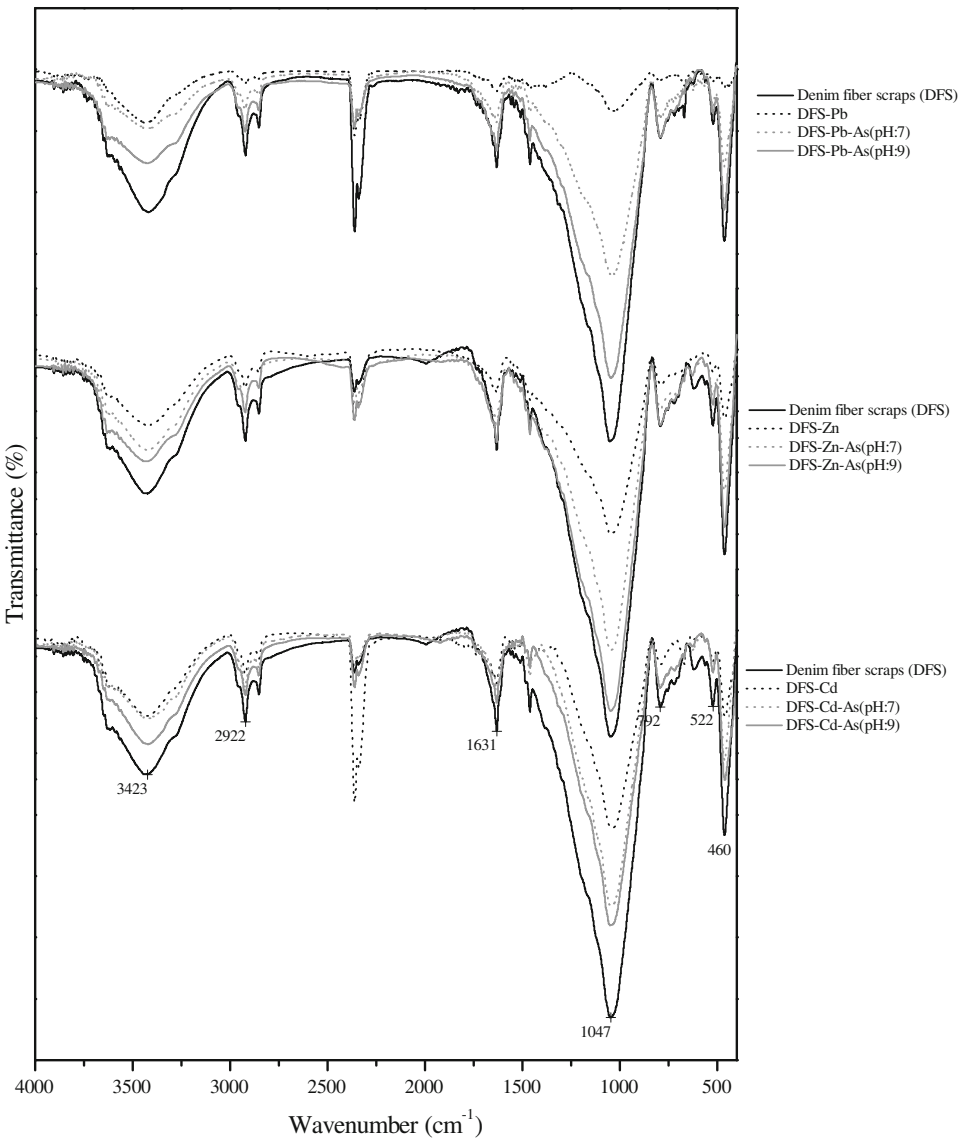

Fig. 6 FT-IR spectra of denim fiber scraps with and without loaded heavy metal ions and arsenic (V)

difference could not be observed between the principal peaks of the raw denim fiber scraps and these textile wastes loaded with the heavy metals and arsenic compounds (Fig. 6).

Conclusion

This study reports the application of denim fiber scraps for the removal of heavy metal ions and arsenic (V) from aqueous solution. Results showed that these denim wastes can be reused as an effective and low-cost sorbent for the removal of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from aqueous solution. In fact, this textile waste showed metal uptakes higher than those reported for other synthetic and natural sorbents including commercial activated carbons and zeolites. On the other hand, both raw and metal-loaded denim fiber scraps can be useful for the removal of arsenic (V) from aqueous solution. In particular, the presence of heavy metal ions, especially Pb^{2+} ions, on the surface of denim wastes improved their sorption performance for arsenic (V). Results of this study suggested that the electrostatic interactions between denim wastes and these toxic pollutants may play an important role in the sorption process. Finally, it was shown that the reuse of denim residues and wastes as sorbents of priority water pollutants offers several advantages such as a free availability and low-cost treatment and also contributes to the waste management in the textile industrial sector.

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