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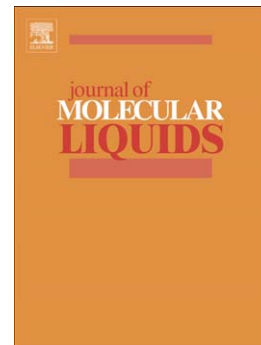
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SYNTHESIS OF DENIM WASTE-BASED ADSORBENTS AND THEIR APPLICATION IN WATER DEFLUORIDATION

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ABSTRACT. This study evaluates the application of denim fiber scraps as a precursor for the synthesis of adsorbents for water treatment via pyrolysis and their application in water defluoridation. The best pyrolysis conditions for the synthesis of this novel adsorbent have been identified and a metal doping route with different salts of Al^{3+} , La^{3+} and Fe^{3+} was proposed to improve its fluoride adsorption behavior. Different spectroscopic and microscopic techniques (i.e., FTIR, XPS, XRF, SEM) were used to characterize the precursor and adsorbents, and to analyze the surface interactions involved in the fluoride removal mechanism. Experimental results showed that these adsorbents were effective for fluoride adsorption showing uptakes up to 4.25 mg/g. The Si-O-metal-F interactions appear to be highly relevant for the fluoride removal. This study highlights the potential of denim textile waste as a raw material for the production of added-value products, thus minimizing their associated disposal cost. It also highlights the performance of denim textile waste as a precursor of adsorbents for addressing relevant environmental concerns such as fluoride pollution.

Keywords: Denim fiber scraps, fluoride, adsorption, water treatment

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1. INTRODUCTION

Activated carbon is recognized as a universal adsorbent for water pollution control due to its versatility in terms of efficiency, tailored physicochemical properties and excellent performance at different operational conditions [1]. To date, different studies have reported the preparation of a variety of carbon-based adsorbents for the removal of priority water pollutants including organic and inorganic compounds [2-5]. The synthesis and production of activated carbons for water treatment mainly rely on the use of lignocellulosic materials such as woods, agricultural residues and crops [1,6]. However, several authors have highlighted the relevance of identifying alternative precursor sources and the application of a proper method for the adsorbent production with the aim of reducing purification costs, especially in developing countries.

Wastes and sub-products of different industrial sectors can be used as alternatives in the preparation of low-cost adsorbents [1,7-10]. It is important to highlight that the application of waste materials for the synthesis of added-value products is an attractive approach due to environmental and economical issues involved in urban solid wastes management and disposal. In this sense, several urban wastes have been described in the literature for the preparation of adsorbents including tires, polymeric residues, sewage sludge, buffing dust and textiles [1,5,8,11,12]. These studies showed that the physicochemical properties of the synthesized material strongly depend on both the precursor and the synthesis conditions used.

Textile wastes can be classified as reusable materials with large potential for the production of value-added materials for water pollution control [8,11,13]. Solid waste management is a major issue in the textile industrial sector that can substantially increase production costs due to actual disposal strategies. For instance, the denim manufacturing industry is rated as one of the most polluting among all industrial sectors and its operations generate a significant volume of solid wastes that contain yarns and fibers loaded with dyes and various kinds of chemicals [13,14]. Overall, it has been estimated that textile residues comprise between 1 to 5 % of the composition of municipal solid wastes [15] and, consequently, they represent an important source of waste residues with large potential in materials science and energy related applications due to their high cellulosic content (cotton basis).

As stated above, several studies have analyzed the potential application of textile wastes as raw material for the preparation of adsorbents [8,11,16,17]. However, these studies have mainly focused on the determination of the synthesis conditions and the study of the physicochemical properties (e.g., textural parameters, functional groups) of the adsorbents, while the evaluation of these

adsorbents in water purification is scarce. The study of textile waste-based materials is fundamental for determining their capabilities and limitations in water purification processes.

In this paper, the synthesis of denim waste-based adsorbents via pyrolysis and their application in water defluoridation have been reported. Fluoride ions are considered priority toxic pollutants in the water used for human consumption. Indeed, different regions worldwide have reported the presence of natural occurring fluoride pollution in groundwater [18]. For instance, several cities in Mexico face severe environmental pollution problems due to high fluoride concentrations in the groundwater supply sources, with the corresponding toxicity effects for human beings [19]. Although there are commercial bone chars and activated aluminas available for the removal of this specific pollutant [20-23], these adsorbents lack an appropriate cost-performance trade-off. Consequently, the development of new highly-efficient adsorbents for water defluoridation is of paramount importance.

In the present study, the preparation of a novel adsorbent from denim fiber scraps using a pyrolysis process was evaluated and the best synthesis conditions to achieve a tailor-designed adsorbent were identified. Furthermore, a metal-doping procedure was used to improve the adsorption performance of these adsorbents and thermodynamic studies for water defluoridation were performed. XPS, XRF, SEM and FTIR studies were conducted to gain knowledge on the adsorbent surface chemistry and to understand the removal mechanism. Experimental results showed the potential use of a waste material from the denim industry to face a critical water pollution concern currently present in Mexico and other countries.

TILE WASTE MINIMISATION

2. METHODOLOGY

2.1. Denim wastes used as an adsorbent precursor

Denim fiber scraps were obtained from a local textile manufacturer located in Aguascalientes, Mexico. The physical appearance of these textile wastes, including their SEM micrograph, is shown in Figures 1a and 1c. These scraps were obtained from the outcome of a manufacturing process step, in which denim was washed with pumice stone. Thus, the obtained denim scraps are composed of cotton fiber loaded with indigo dyes (which causes its blue color). They also contain inorganic elements such as Si, Al, Mg and Fe [13]. These denim wastes were washed using deionized water, dried and stored for their further use in the preparation of fluoride adsorbents.

2.2 Pyrolysis of denim wastes

The preparation of denim-based adsorbents was performed via pyrolysis. Adsorbents were synthesized at different conditions using a factorial design of 20 experiments, as shown in Table 1.

These conditions include different temperatures (500 – 900 °C), residence times (2 and 4 h) and heating rates (5 and 10 °C/min). Specifically, 3 g of denim wastes were packed into a quartz sample holder and submitted to a thermal treatment with a Carbolite Eurotherm CTF 12165/550 tubular furnace, according to the pyrolysis conditions of Table 1. All adsorbents were synthesized using a N₂ flow rate of 100 mL/min. The impact of the selected pyrolysis variables on the adsorbent performance was determined with an ANOVA statistical analysis and the best conditions were identified after considering the fluoride uptake as the response variable for the experimental design. The denim-based adsorbents obtained according to Table 1 were washed with deionized water until a constant pH was reached and dried for 24 h prior their use in fluoride adsorption experiments. Removal tests were carried out by triplicate at batch conditions using fluoride solutions with an initial concentration of 50 mg/L. Conditions for these adsorption experiments were: 30 °C, pH 7, adsorbent-solution ratio of 5 g/L and equilibrium time of 120 h. The mean value from replicates of removal experiments was used for the data analysis.

Fluoride concentrations in aqueous solution were quantified with the ion selective electrode method [24] and a mass balance was employed for the calculation of the adsorption capacities (q , mg/g)

$$q = \frac{([F^-]_0 - [F^-]_f) \cdot V}{m} \quad (1)$$

where $[F^-]_0$ and $[F^-]_f$ are the initial and final fluoride concentrations obtained in the adsorption experiments (both given in mg/L), V is the volume of fluoride solution in L, and m is the adsorbent amount used in the removal experiments given in g, respectively.

2.3 Metal doping of denim-based adsorbents

Experimental results reported in Table 1 were used to identify the best pyrolysis conditions to achieve a tailor-designed adsorbent for fluoride adsorption. However, the effective removal of persistent water pollutants such as fluoride ions usually implies the application of specific activation strategies to improve the adsorbent performance. A metal doping procedure was tested using different salts of La³⁺, Al³⁺ and Fe³⁺. Note that the surface modification with multivalent metallic species offers several advantages for enhancing the fluoride uptakes in traditional materials such as activated carbons and bone char [23,25,26]. For the metal doping, 1 g of textile-based adsorbent was mixed with 10 mL of the metallic solution with an initial concentration of 200 mg/L. The mixture adsorbent-metallic solution was stirred at 150 rpm using different impregnation times and temperatures. Table 2 shows the experimental design used for this surface modification with metallic solutions. Metal-doped materials were washed with deionized water before being used in

the adsorption studies. The fluoride adsorption capacity of the modified adsorbents was the response variable of this experimental stage, while the studied variables were: the nature of the metallic salt (chloride, sulfate and nitrate) used for metal doping, the impregnation time (2 and 6 h) and temperature (30 and 60 °C). This experimental design allowed the analysis of the effect of the doping variables on fluoride uptake and the identification of the best conditions to achieve an optimum adsorption performance. Fluoride removal experiments were performed at the same conditions used in the experimental design of the pyrolyzed samples.

Fluoride adsorption isotherms and kinetics were determined for the best modified materials. These studies were performed at 30 °C and pH 7 using a mass-solution ratio of 5 g/L and an adsorbent particle size of ~ 0.67 mm. Equilibrium adsorption experiments were carried out using fluoride solutions with initial concentrations from 5 to 150 mg/L. The adsorption and intraparticle diffusion rates and the maximum adsorption capacities of selected adsorbents were calculated.

2.4 Analysis of surface interactions and characterization of denim-based adsorbents

Different spectroscopic and microscopic techniques were used to characterize the precursor and denim-based adsorbents including the analysis of surface interactions involved in the fluoride removal process. These techniques were Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDS) and X-ray fluorescence (XRF) spectroscopy. Nitrogen physisorption isotherms was also used to determine the textural parameters. A Bruker IFS 66/S spectrometer was utilized to perform FTIR analysis to characterize the functional groups of the samples, which were measured as pellets with KBr. FTIR Spectra were collected within a wavenumber range of 4000 - 400 cm^{-1} using a 4 cm^{-1} resolution per scan. The surface chemistry was also analyzed with a K-ALPHA (Thermo Scientific) X-ray photoelectron spectrometer. XPS spectra were recorded using monochromatized incident Al X-ray radiation (Al $K\alpha = 1486.6$ eV) yielding a focused X-ray spot of 400 μm diameter at 3 mA \times 12 kV. The morphology of raw textile precursor, pyrolyzed material and metal-doped adsorbents, prior and after fluoride removal, was observed by a SEM type JSM-840 JEOL microscope equipped with an EDS spectrometer (type UHV Dewar Si(Li), Bruker). This technique was also utilized to define the elemental composition of selected adsorbents. The samples were dispersed on an adhesive double-sided carbon tape and then mounted onto SEM cylinders for further coating with gold and charge dissipation during the analysis. The coated samples were observed using an electron beam energy of 20 keV. The elemental compositions of the metal-doped adsorbents were determined by XRF analysis using a sequential X-ray spectrometer (Philips Magix Pro), which was equipped with rhodium tube and beryllium window. Textural parameters of the

samples obtained at different pyrolysis conditions were determined from nitrogen adsorption-desorption isotherms at 77 K using an automatic Micromeritics TriStar 3000 analyzer. Prior to their analysis, 0.1 g of these samples was degassed under vacuum at 300 °C overnight.

3. RESULTS AND DISCUSSION

3.1 Analysis of pyrolysis conditions, metal doping of denim-based adsorbents and their application in water defluoridation

Figure 1b shows the typical appearance of the denim-based adsorbents obtained via pyrolysis whereas Figures 1d – 1f report SEM micrographs. All materials showed a non-porous structure with irregular shapes and rough texture. XRF results revealed that denim-based adsorbents contained different kind of oxides, see Figure 2. In particular, SiO₂, Al₂O₃, Fe₂O₃ and K₂O were the main oxides present in these samples. This implies that denim-based adsorbents contained a large fraction of silicon oxides (> 70 %) and minor fractions of other metal oxides (1 – 16 %).

Figure 3 shows the yields and fluoride adsorption capacities for the adsorbents obtained using the pyrolysis conditions reported in Table 1. The adsorbent production yield ranged from 80.2 to 82.3 % and, as expected, it slightly decreased with pyrolysis temperature. These yields are higher than those obtained for lignocellulosic-based adsorbents, which can be attributed to the presence of a high inorganic content in the textile precursor. Note that the yields of adsorbents obtained from the carbonization of different biomasses usually are very low (< 30 %) and, consequently, they impact the production costs. From an application point of view, the pyrolysis of denim wastes can be considered a high-yield route for the synthesis of alternative materials for water treatment.

Fluoride uptakes of the denim-adsorbents ranged from 0.05 to 1.5 mg/g at tested preparation conditions. These results showed that the pyrolysis conditions are of paramount importance for determining the adsorbent performance. Consequently, they should be carefully selected to improve the final uptake. According to the statistical analysis of this experimental design, the pyrolysis temperature is the variable with the major impact on the adsorbent properties (p-level < 0.01); the defluoridation performance of adsorbents decreased with an increase in the synthesis temperature. The best fluoride uptakes of denim-based materials were obtained for a pyrolysis temperature of 500 °C, residence time and heating rate of 2 h and 10 °C/min, respectively. These conditions provided the best compromise in terms of adsorbent yield and fluoride removal. The highest adsorption capacity obtained from Table 1 competes with fluoride uptakes reported for commercial bone chars [21,27] and other carbon-based adsorbents [28-30] whose fluoride uptakes ranged from 1 to 4 mg/g.

For illustration, Figure 4 shows the results for the textural parameters of selected samples. Denim-based adsorbents have low BET surface areas (9.5 – 14.5 m²/g) and total pore volumes (0.030 – 0.046 cm³/g). All nitrogen adsorption-desorption isotherms are rather similar and they correspond to a predominantly microporous structure with a certain contribution from larger pores [31]. At low relative pressures, these isotherms are Type I since the adsorption and desorption branches remain nearly horizontal and parallel after an initial nitrogen uptake, which is the characteristic behavior of microporous materials [31]. At intermediate and high relative pressures, there is a further increase in the adsorbed amount that is characteristic of a type IV isotherm together with a hysteresis loop. This behavior indicates the presence of larger pores in the mesoporous range [31]. Traditional adsorbents used for fluoride removal (e.g., bone char and other activated carbons) usually show surface areas higher than 100 m²/g [21,29,32]. Under this scenario, it could be expected that these textile-based adsorbents may be ineffective for the fluoride adsorption due their poor textural parameters. However, the excellent results obtained in this study unambiguously confirm the critical role of the surface chemistry in the removal of persistent water pollutants. These adsorption properties of denim-based adsorbents are associated to the presence of inorganic elements on their surface, especially Al and Fe oxides. Note that recent studies have reported low-area activated carbons (i.e., < 2 m²/g) with fluoride uptakes from 1 to 2 mg/g [30].

Figure 5 shows the fluoride adsorption capacities obtained for the adsorbents modified with different metallic solutions using the experimental conditions described in Table 2. Pollutant uptakes for metal-doped adsorbents ranged from 0.55 to 1.72 mg/g, for lanthanum-modified samples, from 0.63 to 2.47 mg/g for aluminum-modified samples, and from 0.12 to 1.47 mg/g for iron-modified samples, respectively. The impact of metal doping on adsorption properties is given by $Fe^{3+} < La^{3+} < Al^{3+}$ with an improvement of fluoride uptake up to 67 % for aluminum-modified samples. Fluoride ion is a hard base due to its high electronegativity and small ionic radius and, consequently, this anion has strong binding interactions with multivalent metallic species [26]. This fact explains the improved adsorption behavior of metal-modified denim-based adsorbents. Note that surface modification with multivalent metal ions offers several advantages for the preparation of fluoride adsorbents including better adsorbent yields and less severe activation conditions. ANOVA analysis for this specific experimental design indicated that the impregnation temperature used for metal doping was a relevant parameter to improve the fluoride uptake (i.e., p-level < 0.05). Indeed, these results showed that the efficiency of the surface modification with metals increased with the impregnation temperature. The best impregnation conditions for surface modification of these adsorbents were 60 °C and 6 h for lanthanum and aluminum solutions, and 60 °C and 2 h for iron solutions, respectively. Fluoride adsorption isotherms at 30 °C and pH 7 for the adsorbents

obtained with these metal doping conditions are reported in Figure 6. All adsorption isotherms correspond to a Langmuir-type shape. These isotherms showed that the highest fluoride removal was obtained with the aluminum-doped adsorbents (i.e., 4.25 mg/g), where the aluminum sulfate offered the best results. In fact, sulfate solutions were more effective than chloride and nitrate solutions for improving the adsorption properties of the denim-modified adsorbent. The Sips model fitted the fluoride adsorption isotherms and offered a satisfactory correlation of experimental data with low prediction errors (0.7 – 13.8 %), see Figure 6 and Table 3. This equation showed better correlation coefficients than those obtained for Langmuir and Freundlich isotherms.

Adsorption kinetics for fluoride removal using the best metal-doped adsorbents are reported in Figure 7a. Rates (k_1) for fluoride uptake ranged from 0.02 to 0.08 h⁻¹, where the Al-doped adsorbent showed the faster removal. Note that these rates were calculated with the pseudo-first order model, which showed the best data fitting. The diffusion analysis using Weber-Morris plot indicated that, as expected, the intraparticle diffusion was not the rate-limiting step for fluoride removal on these adsorbents. The multi-linearity behavior of Figure 7b suggested that several steps may be involved in the fluoride adsorption. In fact, there was a predominant adsorption of fluoride ions on the external surface of these adsorbents, which was indicated by the sharp section of the plots. Calculated fluoride diffusion rates (k_p) ranged from 0.19 to 0.34 mg/g h^{0.5} for tested adsorbents.

3.2 Characterization of denim-based adsorbents and surface interactions involved in the fluoride removal mechanism

FTIR spectroscopic measurements for raw samples and denim-based adsorbents are reported in Figure 8. Nomenclature used for these characterization results are as follows - Precursor: denim waste used for the preparation of the adsorbents; Pyrolyzed: best denim-material obtained from Table 1; C-Al: best aluminum-doped adsorbent; C-La: best lanthanum-doped adsorbent; and C-Fe: best iron-doped adsorbent. On the other hand, adsorbents loaded with fluoride ions were labeled as C-Al-F, C-La-F and C-Fe-F.

The main FTIR bands of pumice and cellulose compounds were identified in the raw sample (i.e., denim fiber scraps). The peak at 3700 cm⁻¹ corresponds to the stretching vibrations of OH bonds attached to polyhedral Al [33]. The broad band between 3000 and 3600 cm⁻¹ is due to the stretching of OH groups [34,35], while the band at 2925 cm⁻¹ and its shoulder at 2864 cm⁻¹ are related to CH stretching and bending vibrations [13]. The absorption bands at 1640 – 1520 cm⁻¹ can be associated to vibrations of OH groups of ketones, aldehydes, carboxylic acids and aromatic skeletal vibrations of cellulose [13,36]. The peaks at ~ 1320 – 1460 cm⁻¹ could be associated to OH bending and CH vibrations of pyran ring, while the band at 700 cm⁻¹ can be related to CH rocking

vibrations of cellulose composition [36,37]. The intense band located at 1040 cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of the Si-O-Si groups [34]. Note that the Si-O bending and Al-O stretching bands are located in the range $800 - 620\text{ cm}^{-1}$ [34,38,39]. The band associated with Si-O and Si-O-Fe stretching vibrations can be observed at 460 cm^{-1} [33]. It is clear that the presence of these groups in the FTIR spectrum are due to the minerals contained in the denim fiber scraps, which are derived from the washing with pumice stone [13,33].

FTIR spectra of the denim-based adsorbent showed some changes due to the pyrolysis process. The bands located at 3435 , 2925 , $1640 - 1520$ and $1460 - 1320\text{ cm}^{-1}$ that are related to water and organic groups decreased considerably, which can be explained in view of the decomposition of cellulose chains through dehydration, decarbonylation, ring-opening, glycosidic-bond breaking, aromatization and decarboxylation [39]. Note that the Si-O and Al-O groups remained unchanged after thermal treatment. With respect to the adsorbents doped with metallic ions, the bands associated to OH, Al-O and Si-O slightly shifted, while the band at 3700 cm^{-1} of the adsorbent treated with Fe solution disappeared. These findings imply the existence of some interactions between the metallic salts and the adsorbent surface [40]. The metal impregnation process caused the formation of new metallic interactions or oxide species leading to variations of the oxide contents [41]. Therefore, the relative content of Si, Al, Fe and K changed due to the possible substitution of some mobile cations (e.g., Na, Mg, K, Ca) for the trivalent ions (i.e., Al, La and Fe) on the adsorbent structure. For instance, the elemental composition (wt %) of the best Al-loaded adsorbent is O: 48.29, C: 21.23, Si: 17.12, Al: 6.97, K: 2.03, Na: 1.85, Fe: 1.1, Ca: 0.56, Mg: 0.45, S: 0.24 and P: 0.16 %. Note that FTIR spectra of the samples that underwent fluoride adsorption did not show remarkable changes in the bands.

Table 4 and Figure 9 show the results obtained from XPS characterization of denim-based adsorbents. The deconvolution spectrum for Si 2p of raw denim-based adsorbent showed two peaks that can be attributed to Si-O at 104.28 eV [42,43] and to Si-O-X at 102.62 eV [38] where X = Na, Al, Mg, K and Ca. These elements are present in the raw precursor used for the preparation of the adsorbents [13]. This result was consistent with the O 1s spectrum that indicated the presence of two different chemical states of oxygen, see Table 4. The peaks at 532.46 , 531.16 and 534.08 eV correspond to silica bonds (Si-O), the non-bridging oxygen (Si-O-X) and the O-H interactions from molecular water [38,43]. Changes in the deconvolution of Si 2p spectra were observed after metal doping of the denim-based adsorbents. These modified samples showed the presence of a symmetric single peak that can be associated with the incorporation of metallic ions (i.e., Al^{3+} , La^{3+} and Fe^{3+}) on the adsorbent surface forming new Si-O-X interactions, where X = Al, La and Fe [26,38,43-46]. The presence of Si-O-Al bonds was confirmed by the binding energies of the Al 2p

peak at 74.87 eV, see Table 4 and Figure 9 [44,46]. For the case of Fe-loaded adsorbents, the peaks of Fe 2p spectrum suggested the presence of interactions Si-O-Fe [47,48], while the XPS results for La-loaded adsorbent showed the peak energy for the Si-O-La bond [49-51].

After fluoride adsorption, some changes were observed in the intensity of the peaks associated with Si, Al, La and Fe bonds for all adsorbents and this result confirmed new interactions between fluoride and the surface metal species. It appears that fluoride ions interacted with metal-doped denim-based adsorbents via Si-O-X-F, where X = Al, Fe and La. At this point, it is important to highlight that peaks corresponding to F 1s appeared at 685.68, 686.33 and 685.42 eV (see Table 4 and Figure 9) for aluminum-, lanthanum- and iron-doped adsorbents, which could correspond to metal-fluoride bonds [26,40].

4. CONCLUSIONS

This study reports the application of denim fiber scraps for the synthesis of an effective and low-cost adsorbent for water defluoridation. Proper experimental conditions for the pyrolysis of these textiles wastes have been identified and a subsequent metal doping step has been proposed to modify their surface properties and to enhance the fluoride uptakes. These novel adsorbents showed a fluoride uptake up to 4.25 mg/g even though they had a very low surface area. This removal performance was higher than those reported for traditional adsorbents employed in fluoride adsorption from aqueous solution. Analysis of removal mechanism suggested that the interactions Si-O-X-F (X = Al, La or Fe) could play an important role for fluoride removal using these materials. In summary, results of this study show that denim-based adsorbents are promising for water treatment and purification. The valorization of denim waste wastes for the production of adsorbents can be a key factor to reduce both the operational cost of textile industry and the environmental impact in terms of solid waste generation.

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Figure captions.

Figure 1. Physical appearance of a) raw denim wastes (i.e., adsorbent precursor) and b) denim-based adsorbent and SEM images of c) precursor, d) denim-based adsorbent, e) aluminum-doped adsorbent and f) aluminum-doped adsorbent with fluoride ions.

Figure 2. XRF results for the denim-based adsorbents with and with loaded fluoride ions.

Figure 3. Yields and fluoride uptakes of denim-based adsorbents obtained via pyrolysis. Fluoride uptakes were determined using an initial fluoride concentration of 50 mg/L at pH 7 and 30 °C.

Figure 4. N₂ (●) adsorption – (○) desorption isotherms of selected denim-based adsorbents used for fluoride removal.

Figure 5. Fluoride uptakes of denim adsorbents modified with different metallic salts. Fluoride uptakes were determined using an initial fluoride concentration of 50 mg/L at pH 7 and 30 °C.

Figure 6. Adsorption isotherms of fluoride ions on denim-based adsorbents modified with metallic salts. Experimental conditions: 30 °C and pH 7.

Figure 7. a) Kinetics and b) intraparticle diffusion analysis for the adsorption of fluoride ions on denim-based adsorbents doped with metallic ions. Experimental conditions: 20 mg/L of fluoride concentration, 30 °C and pH 7.

Figure 8. FTIR spectra of raw precursor and denim-based adsorbents before (Pyrolyzed, C-Al, C-La, C-Fe) and after (C-Al-F, C-La-F, C-Fe-F) fluoride removal.

Figure 9. Deconvolution of XPS spectra of denim-based adsorbents before (Pyrolyzed, C-Al, C-La, C-Fe) and after (C-Al-F, C-La-F, C-Fe-F) fluoride removal.

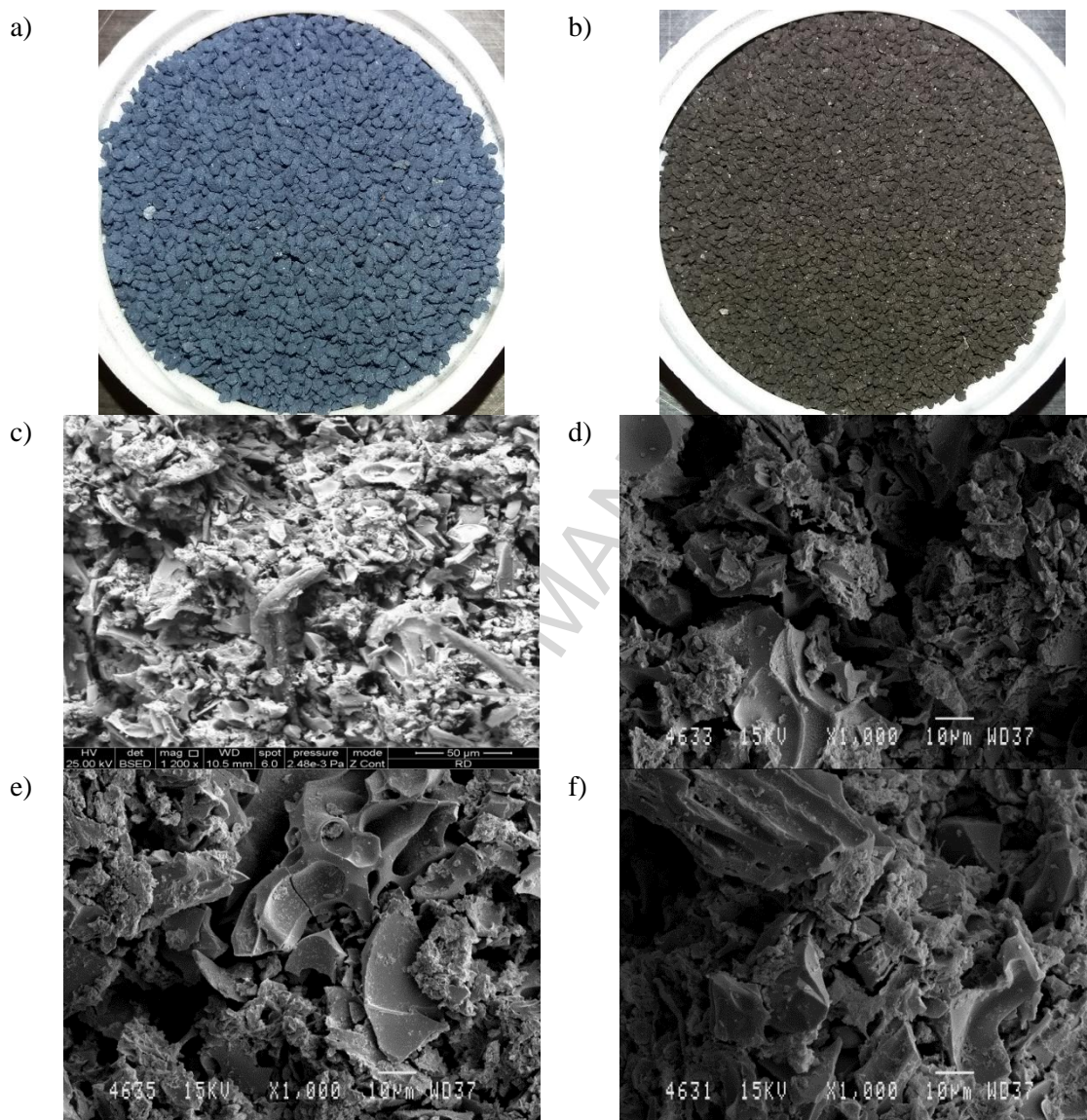


Figure 1.

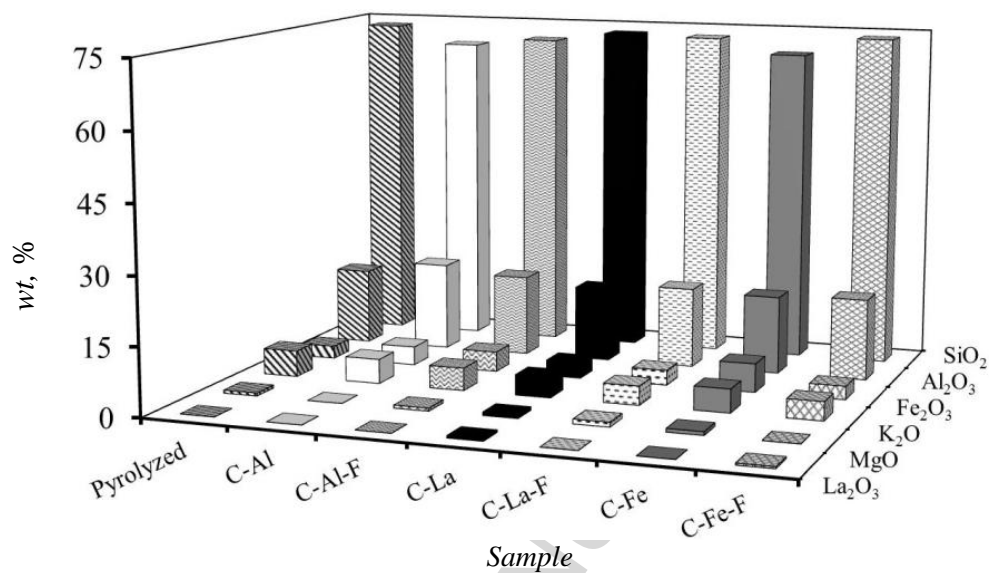


Figure 2.

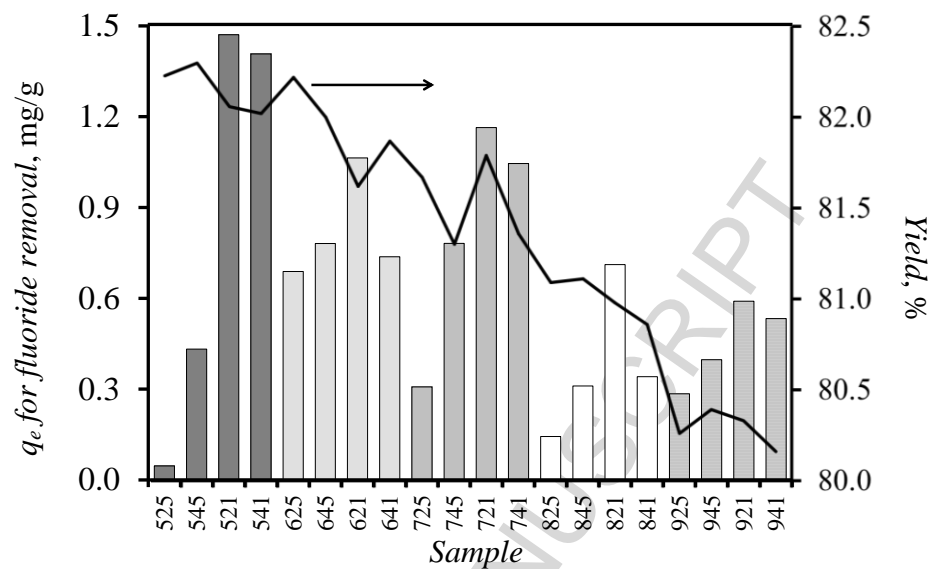


Figure 3.

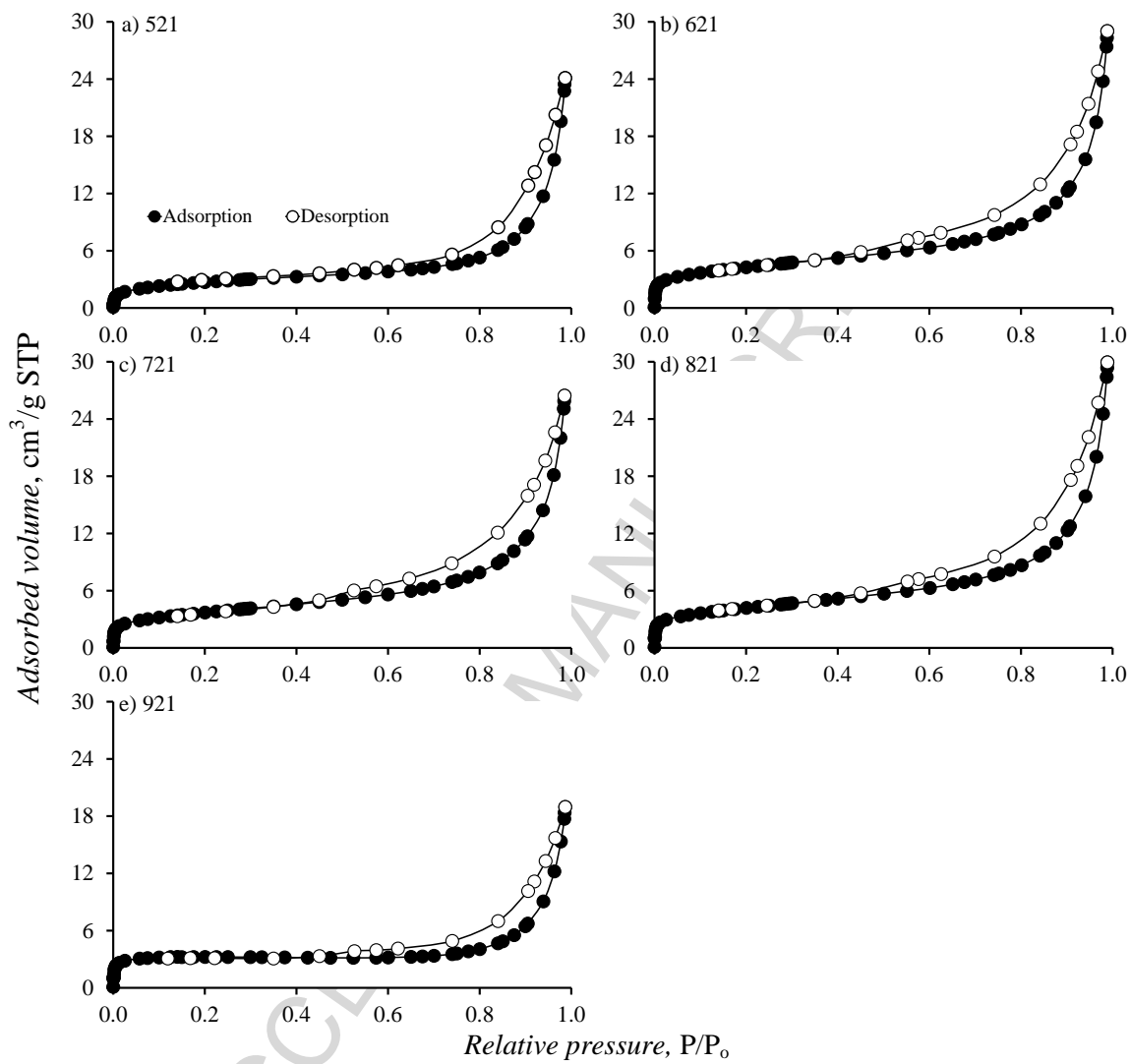


Figure 4.

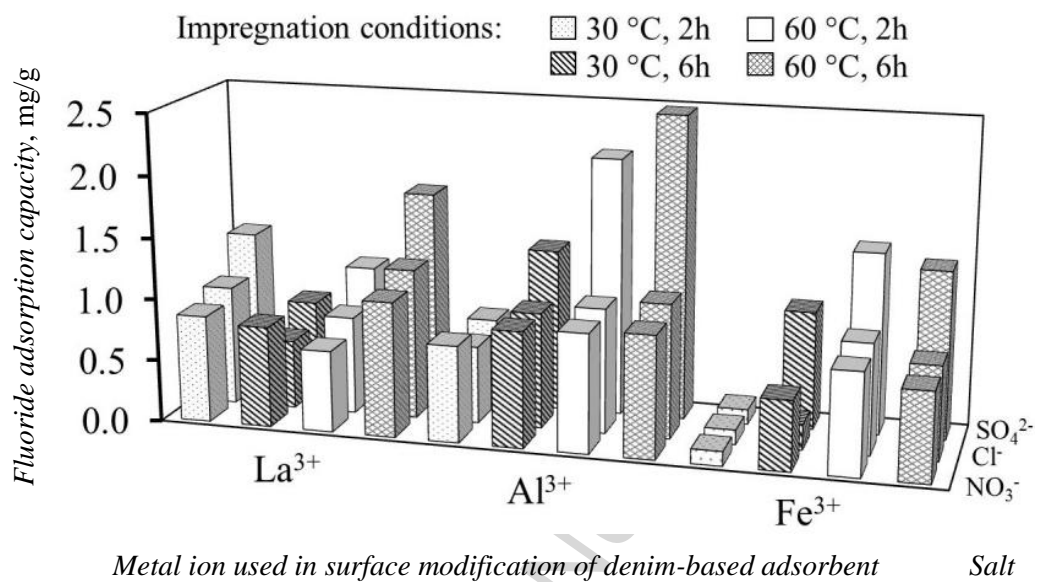


Figure 5.

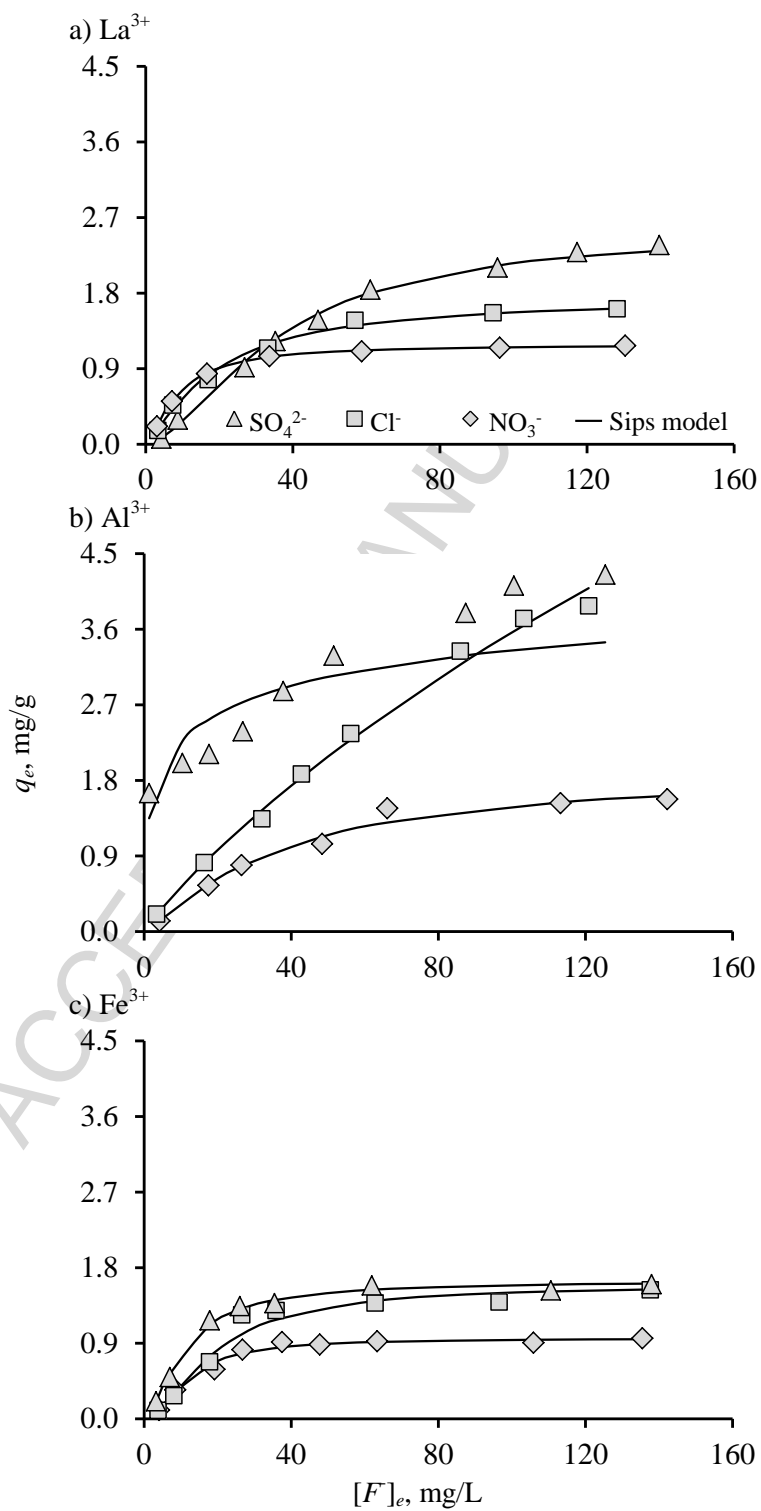


Figure 6.

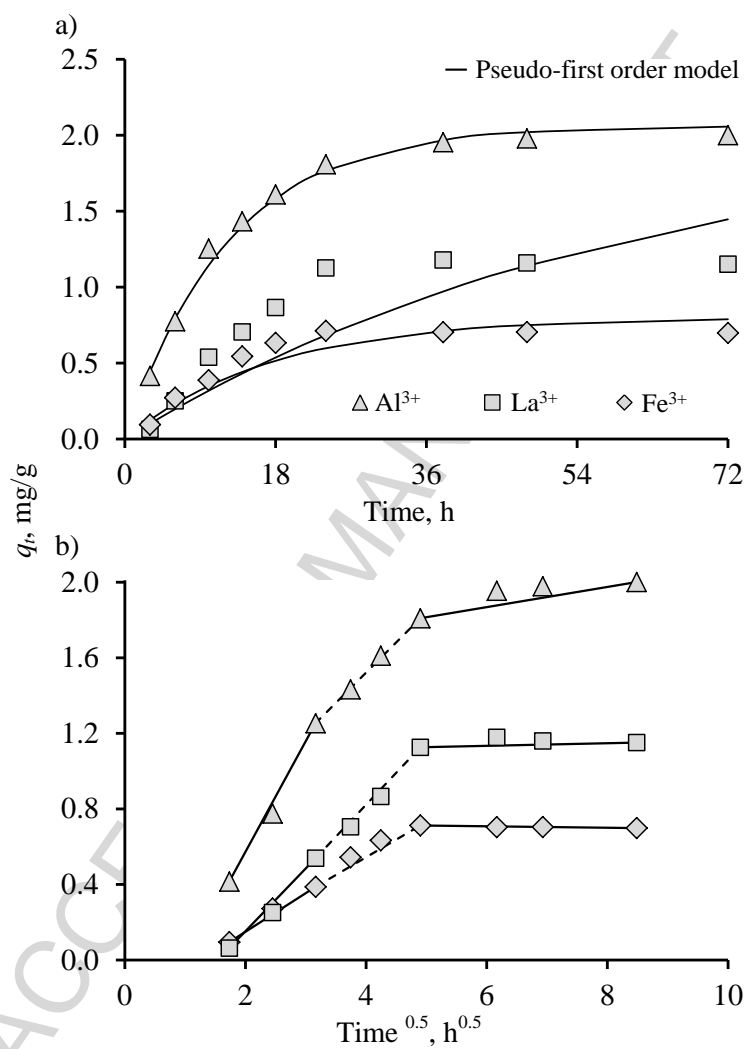


Figure 7.

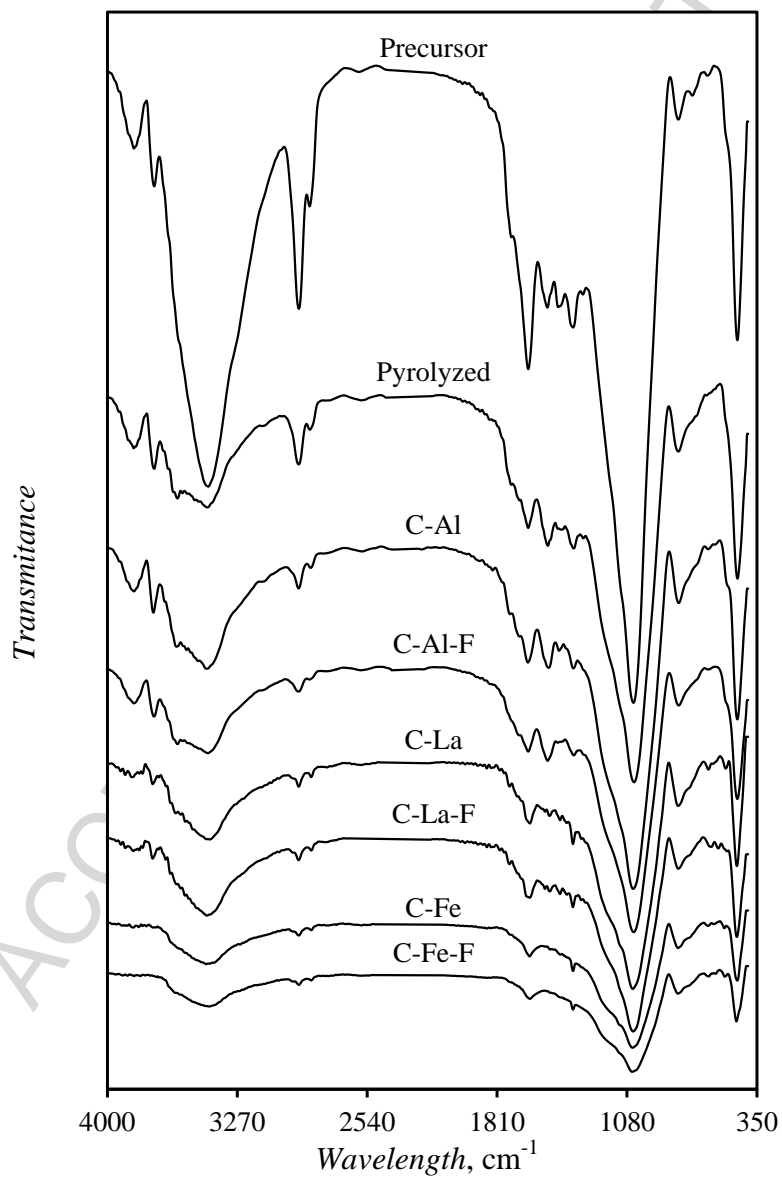


Figure 8.

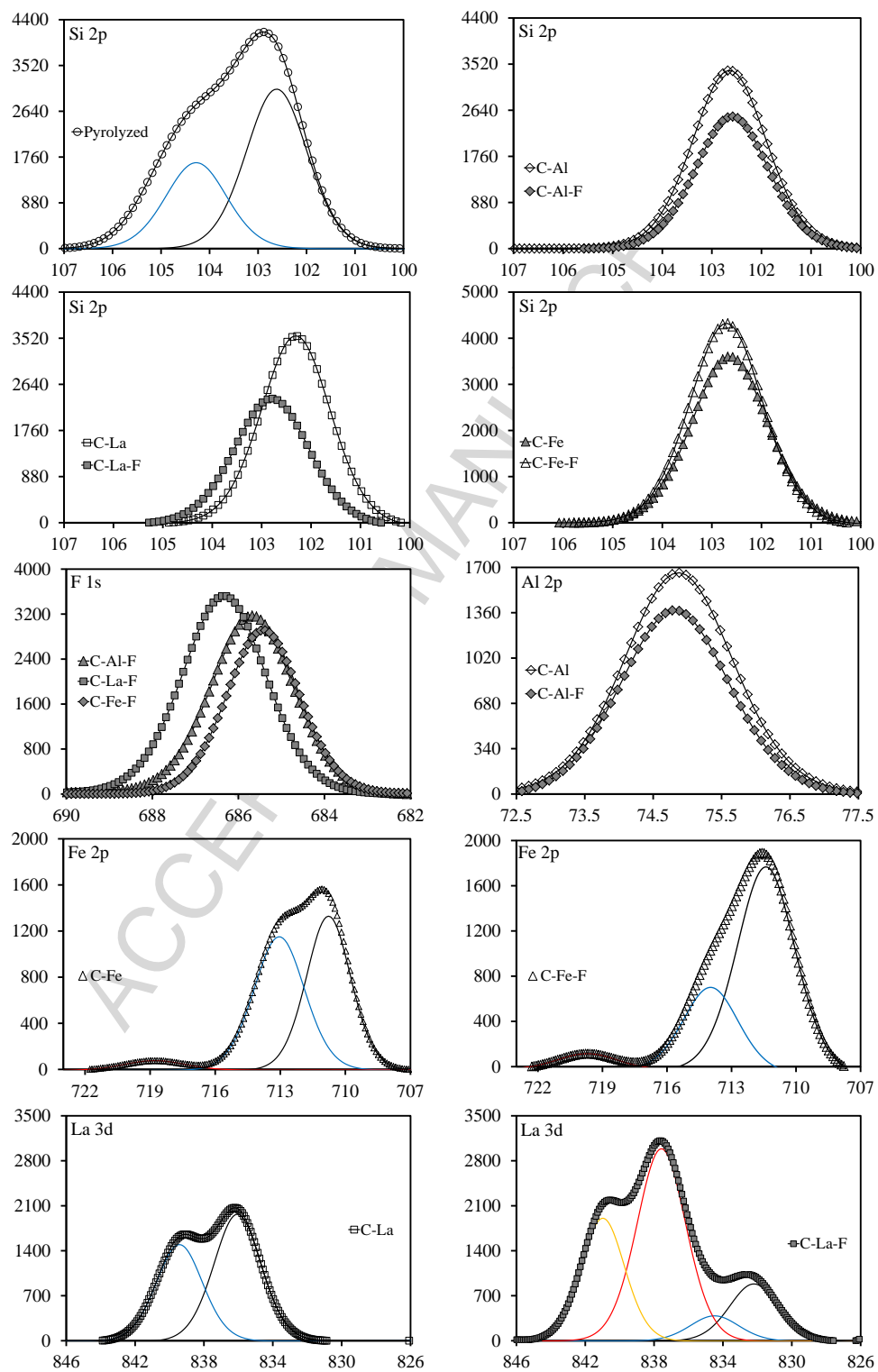


Figure 9.

Table captions.

Table 1. Experimental design used for the synthesis of denim-based adsorbents via pyrolysis. Nitrogen flow: 100 mL/min.

Table 2. Experimental design used for the surface modification of denim-based adsorbents using metallic salts of La^{3+} , Al^{3+} and Fe^{3+} .

Table 3. Results of Sips model for the correlation of fluoride adsorption isotherms using denim-based adsorbents modified with metallic salts of La^{3+} , Al^{3+} and Fe^{3+} .

Table 4. Results of XPS data analysis of denim-based adsorbents used in fluoride removal from aqueous solution.

Table 1.

| <i>Sample</i> | <i>Nomenclature</i> | <i>Pyrolysis conditions</i> | | |
|---------------|---------------------|-----------------------------|--------------------------|-----------------------------|
| | | <i>Temperature, °C</i> | <i>Residence time, h</i> | <i>Heating rate, °C/min</i> |
| 1 | 525 | 500 | 2 | 5 |
| 2 | 545 | | 4 | 5 |
| 3 | 521 | | 2 | 10 |
| 4 | 541 | 600 | 4 | 10 |
| 5 | 625 | | 2 | 5 |
| 6 | 645 | | 4 | 5 |
| 7 | 621 | 700 | 2 | 10 |
| 8 | 641 | | 4 | 10 |
| 9 | 725 | | 2 | 5 |
| 10 | 745 | 800 | 4 | 5 |
| 11 | 721 | | 2 | 10 |
| 12 | 741 | | 4 | 10 |
| 13 | 825 | 900 | 2 | 5 |
| 14 | 845 | | 4 | 5 |
| 15 | 821 | | 2 | 10 |
| 16 | 841 | 900 | 4 | 10 |
| 17 | 925 | | 2 | 5 |
| 18 | 945 | | 4 | 5 |
| 19 | 921 | 900 | 2 | 10 |
| 20 | 941 | | 4 | 10 |

Table 2.

| Experiment | Metallic ion | Type of metallic salt | Reaction conditions for metal doping | | |
|------------|------------------|-------------------------------|--------------------------------------|---------|---|
| | | | Temperature, °C | Time, h | |
| 1 | La ³⁺ | Cl ⁻ | 30 | 2 | |
| 2 | | NO ₃ ⁻ | | 6 | |
| 3 | | SO ₄ ²⁻ | | 2 | |
| 4 | | Cl ⁻ | | 60 | 6 |
| 5 | | NO ₃ ⁻ | | | 2 |
| 6 | | SO ₄ ²⁻ | | | 6 |
| 7 | | Cl ⁻ | 30 | | 2 |
| 8 | | NO ₃ ⁻ | | | 6 |
| 9 | | SO ₄ ²⁻ | | | 2 |
| 10 | | Cl ⁻ | | 60 | 6 |
| 11 | | NO ₃ ⁻ | | | 2 |
| 12 | | SO ₄ ²⁻ | | | 6 |
| 13 | Al ³⁺ | Cl ⁻ | 30 | | 2 |
| 14 | | NO ₃ ⁻ | | | 6 |
| 15 | | SO ₄ ²⁻ | | | 2 |
| 16 | | Cl ⁻ | | 60 | 6 |
| 17 | | NO ₃ ⁻ | | | 2 |
| 18 | | SO ₄ ²⁻ | | | 6 |
| 19 | | Cl ⁻ | 30 | | 2 |
| 20 | | NO ₃ ⁻ | | | 6 |
| 21 | | SO ₄ ²⁻ | | | 2 |
| 22 | | Cl ⁻ | | 60 | 6 |
| 23 | | NO ₃ ⁻ | | | 2 |
| 24 | | SO ₄ ²⁻ | | | 6 |
| 25 | Fe ³⁺ | Cl ⁻ | 30 | | 2 |
| 26 | | NO ₃ ⁻ | | | 6 |
| 27 | | SO ₄ ²⁻ | | | 2 |
| 28 | | Cl ⁻ | | 60 | 6 |
| 29 | | NO ₃ ⁻ | | | 2 |
| 30 | | SO ₄ ²⁻ | | | 6 |
| 31 | | Cl ⁻ | 30 | | 2 |
| 32 | | NO ₃ ⁻ | | | 6 |
| 33 | | SO ₄ ²⁻ | | | 2 |
| 34 | | Cl ⁻ | | 60 | 6 |
| 35 | | NO ₃ ⁻ | | | 2 |
| 36 | | SO ₄ ²⁻ | | | 6 |

Table 3.

| <i>Metal-doped adsorbent</i> | <i>Salt type</i> | <i>Parameters of Sips isotherm</i> ¹ | | | <i>E, %</i> |
|------------------------------|-------------------------------|-------------------------------------------------|----------------------|----------------------|-------------|
| | | <i>q_s, mg/g</i> | <i>b_s</i> | <i>n_s</i> | |
| La ³⁺ | NO ₃ ⁻ | 1.19 | 0.05 | 1.43 | 0.70 ± 0.4 |
| | Cl ⁻ | 1.76 | 0.02 | 1.27 | 4.56 ± 4.1 |
| | SO ₄ ²⁻ | 2.55 | 0.003 | 1.64 | 6.06 ± 6.9 |
| Al ³⁺ | NO ₃ ⁻ | 1.92 | 0.01 | 1.22 | 3.64 ± 4.4 |
| | Cl ⁻ | 21.21 | 0.003 | 0.89 | 3.39 ± 2.4 |
| | SO ₄ ²⁻ | 5.00 | 0.33 | 0.40 | 13.82 ± 6.2 |
| Fe ³⁺ | NO ₃ ⁻ | 0.96 | 0.01 | 1.86 | 4.69 ± 4.2 |
| | Cl ⁻ | 1.60 | 0.01 | 1.68 | 7.45 ± 5.6 |
| | SO ₄ ²⁻ | 1.64 | 0.02 | 1.58 | 3.52 ± 1.8 |

$${}^1 q_e = \frac{q_s b_s [F^-]_e^{n_s}}{1 + b_s [F^-]_e^{n_s}}$$

Table 4.

| Sample | O 1s | | | Si 2p | | | Al 2p | | | La 3d | | | Fe 2p | | | F 1s | | |
|-----------|----------|----------|-------|----------|----------|-------|----------|----------|-------|----------|----------|-------|----------|----------|-------|----------|----------|-------|
| | Peak, eV | FWHM, eV | At. % | Peak, eV | FWHM, eV | At. % | Peak, eV | FWHM, eV | At. % | Peak, eV | FWHM, eV | At. % | Peak, eV | FWHM, eV | At. % | Peak, eV | FWHM, eV | At. % |
| Pyrolyzed | 531.16 | 1.64 | 7.30 | 102.62 | 1.49 | 8.65 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 532.46 | 1.98 | 25.06 | 104.28 | 1.49 | 4.67 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 534.08 | 1.86 | 8.19 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 531.04 | 1.92 | 5.23 | 102.99 | 1.76 | 11.52 | 74.87 | 1.88 | 8.95 | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| C-Al-F | 532.31 | 1.92 | 35.44 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 534.45 | 1.92 | 3.35 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 531.75 | 1.92 | 20.37 | 103.32 | 1.74 | 9.14 | 74.81 | 1.88 | 8.12 | --- | --- | --- | --- | --- | --- | 685.68 | 2.24 | 2.49 |
| | 532.86 | 1.92 | 12.20 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| C-La | 535.25 | 1.92 | 1.196 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 531.04 | 2.02 | 19.88 | 102.31 | 1.65 | 10.54 | --- | --- | --- | 836.06 | 0.324 | 34 | --- | --- | --- | --- | --- | |
| | 532.31 | 2.02 | 26.00 | --- | --- | --- | --- | --- | --- | 839.43 | 0.318 | 26 | --- | --- | --- | --- | --- | |
| | 534.40 | 2.02 | 3.36 | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| C-La-F | 531.87 | 2.02 | 35.59 | 102.79 | 1.78 | 9.32 | --- | --- | --- | 832.20 | 0.337 | 20 | --- | --- | --- | 686.33 | 2.28 | 2.95 |
| | 533.46 | 2.02 | 11.20 | --- | --- | --- | --- | --- | --- | 834.49 | 0.337 | 09 | --- | --- | --- | --- | --- | |
| | --- | --- | --- | --- | --- | --- | --- | --- | --- | 837.58 | 0.337 | 66 | --- | --- | --- | --- | --- | |
| | --- | --- | --- | --- | --- | --- | --- | --- | --- | 840.98 | 0.299 | 38 | --- | --- | --- | --- | --- | |
| C-Fe | 530.91 | 1.92 | 7.96 | 102.64 | 1.80 | 13.69 | --- | --- | --- | --- | --- | --- | 710.78 | 2.41 | 0.31 | --- | --- | |
| | 532.20 | 1.92 | 36.30 | --- | --- | --- | --- | --- | --- | --- | --- | --- | 713.05 | 2.75 | 0.31 | --- | --- | |
| | 534.55 | 1.92 | 2.37 | --- | --- | --- | --- | --- | --- | --- | --- | --- | 718.79 | 3.37 | 0.02 | --- | --- | |
| | 531.05 | 1.92 | 8.31 | 102.71 | 1.74 | 13.35 | --- | --- | --- | --- | --- | --- | 711.39 | 3.19 | 0.48 | 685.42 | 2.00 | 1.37 |
| C-Fe-F | 532.27 | 1.92 | 32.60 | --- | --- | --- | --- | --- | --- | --- | --- | --- | 713.96 | 3.01 | 0.17 | --- | --- | |
| | 534.7 | 1.92 | 1.86 | --- | --- | --- | --- | --- | --- | --- | --- | --- | 719.7 | 3.37 | 0.03 | --- | --- | |
| | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |

Highlights

- Novel adsorbents for water defluoridation have been synthesized using denim wastes
- These novel adsorbents were effective for fluoride adsorption
- Si-O-metal-F interactions appear to be relevant for fluoride removal
- Denim textile wastes have potential for the production of added value products in water treatment

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