




Communication

# Wheat Straw as a Bio-Sorbent for Arsenate, Chromate, Fluoride, and Nickel

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**Abstract:** Batch-type experiments were used to study As(V), Cr(VI), F<sup>-</sup>, and Ni<sup>2+</sup> sorption/desorption on wheat straw. For the lowest concentration added (0.5 mmol·L<sup>-1</sup>), the sorption sequence was F<sup>-</sup> > Ni<sup>2+</sup> > Cr(VI) >> As(V) (93%, 61%, 29%, 0.3%), but changed to Ni<sup>2+</sup> > F<sup>-</sup> > Cr(VI) >> As(V) when 3.0 and 6.0 mmol·L<sup>-1</sup> were added (with 65%, 54%, 25%, 0%, and 68%, 52%, 27%, 0% sorption, respectively). Overall, As(V) showed the lowest sorption, whereas it was 25–37% for Cr(VI), 61–68% for Ni<sup>2+</sup>, and 52–93% for F<sup>-</sup>. For As(V), pH in the equilibrium solution was always above the pH of the point of zero charge (pH<sub>PZC</sub>) for wheat straw, decreasing sorption efficiency. For Cr(VI), pH was below pH<sub>PZC</sub>, but not enough to reach high sorption. For F<sup>-</sup>, pH in the equilibrium was above pH<sub>PZC</sub>, which could reduce sorption. For Ni<sup>2+</sup>, pH in the equilibrium was always below pH<sub>PZC</sub>, which made sorption difficult. The satisfactory fitting of Cr(VI), F<sup>-</sup>, and Ni<sup>2+</sup> data to the Freundlich model suggests multilayer-type adsorption. Desorption was high for F<sup>-</sup>, whereas Ni<sup>2+</sup> showed the lowest desorption. This research could be especially relevant when focusing on the use of wheat straw as a bio-sorbent, and in cases where straw mulching is used.

**Keywords:** As(V); Cr(VI); F<sup>-</sup>; Ni<sup>2+</sup>; retention/release; straw

## 1. Introduction

Public health issues, phytotoxicity and overall pollution concerns have been related to As(V) [1,2], Cr(VI) [3,4], F [5,6], and Ni [7].

To fight heavy metal, metalloid, and F<sup>-</sup> pollution, different waste and by-products have been studied as bio-sorbents [8,9], including mussel shell [10–12] and wood industry waste [13]. As indicated by Malik et al. [14], some cellulosic materials (as wheat straw) can be effective low-cost sorbents. In addition, 315.9 million tons per year of agricultural residue are generated in the European Union [15], and total (world basis) cereal straw generation is estimated to be 1580 million tons per year [16], which should stimulate its recycling [17].

Previous research has aimed at straw as a means for reducing erosion in sloped soils affected by forest fires [18–20], or as a sorbent to fight heavy metals pollution [21–23]. In addition, Rao et al. [24] found that straw mulching could reduce the loss of heavy metals in runoff. We have previously studied cadmium, copper, and lead sorption on wheat straw [17], with a main focus on sustainability in vineyards. However, as far as we know, no previous studies have dealt with As(V), Cr(VI), F<sup>-</sup>

and Ni<sup>2+</sup> retention on wheat straw, adding concentrations up to 6 mmol·L<sup>-1</sup> to each one. This could be relevant, taking into account that wheat straw recycled in agriculture (or used to reduce soil erosion) could facilitate temporary retention of different elements by contacting the sorbent when transported within percolating waters or runoff, thus alleviating peaks of concentration associated with pollution risks.

In light of this, the objective of this work was to study As(V), Cr(VI), F<sup>-</sup>, and Ni<sup>2+</sup> retention/release on wheat (*Triticum aestivum*) straw, adding up to 6 mmol·L<sup>-1</sup> of each element. The results of the study could provide useful information regarding the potential of wheat straw to immobilize these anions and cations, which could help to reduce the eventual risks of soil and water contamination.

## 2. Materials and Methods

### 2.1. Characteristics of the Wheat Straw

The wheat straw used was from a local provider (Cospeito, Lugo, Spain). It was dried, milled, and sieved (not washed), using particles between 2.0 and 0.5 mm (representing 95% of the initial weight before milling) for analyses. Samples corresponding to the same batch of the wheat straw here used were previously characterized by Coelho et al. [17]. Its main characteristics are presented in Supplementary Materials.

### 2.2. Sorption/Desorption Experiments

Wheat straw samples (2.5 g each) were weighed and added with 30 mL of a 1 M NaNO<sub>3</sub> solution (used as background electrolyte to control ionic strength), with increasing individual concentrations (0.5, 1.5, 3.0 and 6.0 mmol·L<sup>-1</sup>) of one of the following substances: As(V), Cr(VI), F<sup>-</sup> or Ni<sup>2+</sup>, respectively, prepared from Na<sub>2</sub>HAsO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KF (Panreac, Barcelona, Spain), and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich, St. Louis, MO, USA). These suspensions were stirred for 24 h, centrifuged (at 4000 rpm for 15 min, with equivalence to 6167 × g), and filtered through acid washed paper with a pore size of 2.5 μm. On the filtrate, As, Cr, and Ni were determined by means of ICP-MS (Varian 820-MS, Varian, Palo Alto, CA, USA); F was quantified by using an ion selective electrode (Orion Research, Jacksonville, FL, USA), with the addition of a total ionic strength adjuster and the buffer TISAB IV; pH was measured by using a pH-meter (model 2001, Crison Instruments, Barcelona, Spain); dissolved organic carbon (DOC) was determined by UV-visible spectrometry (UV-1201, Shimadzu, Kyoto, Japan). Sorbed As(V), Cr(VI), Ni<sup>2+</sup>, and F<sup>-</sup> were calculated as the difference between added concentration of each element and the concentration remaining in the 24 h equilibrium solutions.

Desorption was determined after sorption experiments, adding 30 mL of 0.01 M NaNO<sub>3</sub> to each sample, then stirring (24 h), centrifuging (4000 rpm for 15 min, equivalent to 6167 × g), and filtering through acid washed paper. As, Cr, F, Ni, pH, and DOC, were determined as above. All determinations were carried out in triplicate.

### 2.3. Data Analyses

Descriptive statistics, as well as adjustment to adsorption models, were carried out by means of the statistical package SPSS 21 (IBM, New York, NY, USA).

Equation (1) was used to calculate adsorbed quantities (Q<sub>e</sub>) for As(V), Cr(VI), F<sup>-</sup>, and Ni<sup>2+</sup>:

$$Q_e = V (C_0 - C_f)/m \quad (1)$$

where Q<sub>e</sub> = quantity of each element adsorbed at the equilibrium (mg·g<sup>-1</sup>), m = mass of wheat straw used as adsorbent (g), C<sub>0</sub> = initial concentration in solution for each element (mg·L<sup>-1</sup>), C<sub>f</sub> = final concentration in solution for each element (mg·L<sup>-1</sup>), and V = volume of solution (L).

The fitting of sorption data to the Langmuir and Freundlich models was investigated. However, fitting to the Langmuir model was not possible due to error values being too high for adjustment.

Equation (2) corresponds to the Freundlich model:

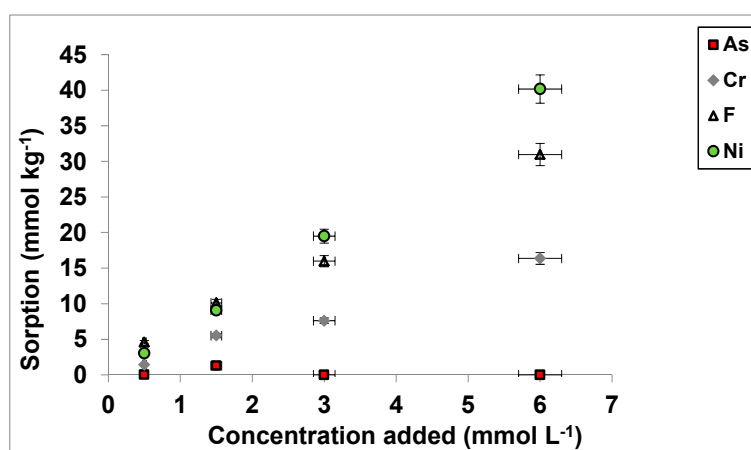
$$Q_{eq} = K_F C_e^{1/n} \quad (2)$$

where  $Q_{eq}$  = quantity adsorbed of each element ( $\text{mmol}\cdot\text{kg}^{-1}$ ),  $K_F$  = Freundlich constant (which is related to the energy of adsorption),  $C_e$  = concentration of each element at the equilibrium ( $\text{mmol}\cdot\text{L}^{-1}$ ), and  $n$  = constant related to the adsorption intensity.

### 3. Results and Discussion

#### 3.1. As(V), Cr(VI), $F^-$ , and $Ni^{2+}$ Sorption as a Function of Concentrations Added

Figure 1 shows that sorption ( $Q_e$ ) for the lowest initial concentration added ( $0.5 \text{ mmol}\cdot\text{L}^{-1}$ ) was in the order  $F > Ni > Cr \gg As$ , with values of 4.6, 3.0, 1.4, and  $0.01 \text{ mmol}\cdot\text{kg}^{-1}$ , corresponding to percentage sorption (with respect to the concentration added) from 93.4% to 0.3% (Table 1). When the highest initial concentrations ( $3.0$  and  $6.0 \text{ mmol}\cdot\text{L}^{-1}$ ) were added, the sequence changed to  $Ni > F > Cr \gg As$ . The specific values for  $3.0 \text{ mmol}\cdot\text{L}^{-1}$  added were 19.5, 16.0, 7.6, and  $0.0 \text{ mmol}\cdot\text{kg}^{-1}$ , corresponding to percentage sorption from 65.2% to 0%. For  $6 \text{ mmol}\cdot\text{L}^{-1}$  added, the values were 40.2, 31.0, 16.4, and  $0.0 \text{ mmol}\cdot\text{kg}^{-1}$ , corresponding to percentage sorption from 67.5% to 0%. The scale of electronegativity of the elements investigated ( $F > As > Ni > Cr$ ) was not coincident with the sorption sequences found for any of the concentrations added.



**Figure 1.** As(V), Cr(VI),  $F^-$ , and  $Ni^{2+}$  sorption ( $\text{mmol}\cdot\text{kg}^{-1}$ ) for different concentrations added ( $\text{mmol}\cdot\text{L}^{-1}$ ) of each element. Average values (with error bars) for 3 replicates, with coefficients of variation always  $<5\%$ .

**Table 1.** As, Cr, F, and Ni percentage sorption on wheat straw for different concentrations added ( $C_0$ ) (0, 0.5, 1.5, 3.0, and  $6.0 \text{ mmol}\cdot\text{L}^{-1}$ ).

$C_0$	0.5	1.5	3.0	6.0
	<b>Sorption (%)</b>			
As(V)	0.3	8.5	0	0
Cr(VI)	29.1	36.9	25.5	27.4
$F^-$	93.4	68.4	54.1	52.3
$Ni^{2+}$	61.3	60.7	65.2	67.5

Note: Average values for 3 replicates, with coefficients of variation always  $<5\%$ .

Table 1 and Figure 1 show that the lowest sorption corresponded to As(V), especially when the highest As(V) concentrations ( $3$  and  $6 \text{ mmol}\cdot\text{L}^{-1}$ ) were added. Regarding Cr(VI), rather low sorption

percentages were found, with the highest (36.9%) being obtained when  $1.5 \text{ mmol}\cdot\text{L}^{-1}$  was added, then declining with increasing concentrations.  $\text{F}^-$  showed rather high sorption results, although with decreasing percentages (from 93.4% to 52.3%) as a function of increasing  $\text{F}^-$  concentrations added.  $\text{Ni}^{2+}$  showed notable sorption and an opposite trend to that of  $\text{F}^-$ , with sorption percentage increasing when the highest  $\text{Ni}^{2+}$  concentrations (3 and  $6 \text{ mmol}\cdot\text{L}^{-1}$ ) were added. We have previously studied [10–13,25–28] the effects of different concentrations, pH, incubation time, and other variables on As(V), Cr(VI),  $\text{F}^-$ , and/or  $\text{Ni}^{2+}$  retention on other sorbent materials, but it should be also performed for wheat straw in future works.

It must be taken into account that As(V), Cr(VI), and F are present in solution in the form of anions, whereas nickel is in cationic form ( $\text{Ni}^{2+}$ ). F in solution is found in the form of fluoride ( $\text{F}^-$ ) [29], and Cr(VI) is an oxyanion that can be found as  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{Cr}_2\text{O}_7^{2-}$  depending on the pH [30].

Low As(V) sorption efficiency can be related to the solution pH. In fact, pH value was between 7.0 and 7.6 in the equilibrium solution when the various As(V) concentrations were added (Table 2), always being above the  $\text{pH}_{\text{PZC}}$  value for wheat straw (6.68), implicating a predominance of negative charges on the surface of the adsorbent, thus decreasing As(V) sorption efficiency. For As(V), sorption was low at low added concentrations, and there was no As(V) sorption at higher added concentrations. According to Mohan and Pittman [31], As(V) in the presence of competing anions such as phosphate ( $\text{PO}_4^{3-}$ ) has decreased adsorption, as P tends to cause specific adsorption by inner-sphere complexes, hindering ion exchange [32]. However, in the present study, where each element was added individually to the straw, and where phosphate was not added, phosphate sorption did not take place on wheat straw. In fact, wheat straw released  $37.7 \text{ mg L}^{-1}$  P without adding P (i.e., just adding 30 mL of the 1 M  $\text{NaNO}_3$  solution, stirring, centrifuging, filtering, and quantifying P using UV–visible spectroscopy (UV-1201, Shimadzu, Kyoto, Japan) (data not shown).

**Table 2.** Solution pH and DOC ( $\text{mg}\cdot\text{L}^{-1}$ ) after As, Cr, F, and Ni sorption on wheat straw, for different concentrations added ( $C_0$ ).

$C_0$	As(V)	Cr(VI)	$\text{F}^-$	$\text{Ni}^{2+}$
$\text{mmol}\cdot\text{L}^{-1}$	pH			
0.5	7.0 ( $\pm 0.1$ )	6.2 ( $\pm 0.1$ )	8.0 ( $\pm 0.2$ )	5.5 ( $\pm 0.1$ )
1.5	7.4 ( $\pm 0.1$ )	6.3 ( $\pm 0.1$ )	7.9 ( $\pm 0.2$ )	5.7 ( $\pm 0.1$ )
3	7.5 ( $\pm 0.1$ )	6.4 ( $\pm 0.1$ )	7.1 ( $\pm 0.1$ )	5.8 ( $\pm 0.1$ )
6	7.6 ( $\pm 0.2$ )	6.6 ( $\pm 0.1$ )	7.1 ( $\pm 0.1$ )	5.9 ( $\pm 0.1$ )
$\text{mmol}\cdot\text{L}^{-1}$	DOC ( $\text{mg}\cdot\text{L}^{-1}$ )			
0.5	423.2 ( $\pm 11.5$ )	256.4 ( $\pm 8.3$ )	337.8 ( $\pm 9.2$ )	289.5 ( $\pm 8.7$ )
1.5	494.3 ( $\pm 14.2$ )	272.3 ( $\pm 8.7$ )	355.4 ( $\pm 9.4$ )	213.6 ( $\pm 6.8$ )
3.0	486.0 ( $\pm 13.8$ )	298.3 ( $\pm 9.1$ )	379.9 ( $\pm 10.1$ )	192.2 ( $\pm 5.9$ )
6.0	487.6 ( $\pm 13.6$ )	319.3 ( $\pm 9.4$ )	403.3 ( $\pm 11.6$ )	158.6 ( $\pm 5.1$ )

Note: Average values ( $\pm$ standard deviation) for 3 replicates, with coefficients of variation always  $<5\%$ .

Regarding Cr(VI), strongly acidic environments promote protonation of active groups of bio-sorbents (in fact, carboxylic, hydroxyl, and amine functional groups were detected on the surface of this wheat straw—see Supplementary Materials, as well as Coelho et al. [17]), which will acquire positive charges and attract anionic Cr(VI) species ( $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{CrO}_4^{2-}$ ) [33]. For the wheat straw here studied, the pH values in the equilibrium solutions were not strongly acidic, suffering an increase from 6.1 to 6.6. However, these values are acidic enough to be below its  $\text{pH}_{\text{PZC}}$  (6.68), suggesting a predominance of positive charges on the surface of the adsorbent material, although it did not allow for a high Cr(VI) sorption efficiency.

For As(V) and Cr(VI), an increase in the pH of the equilibrium solution took place as the added concentration of these elements increased. The same was observed by Fernández-Pazos et al. [25]

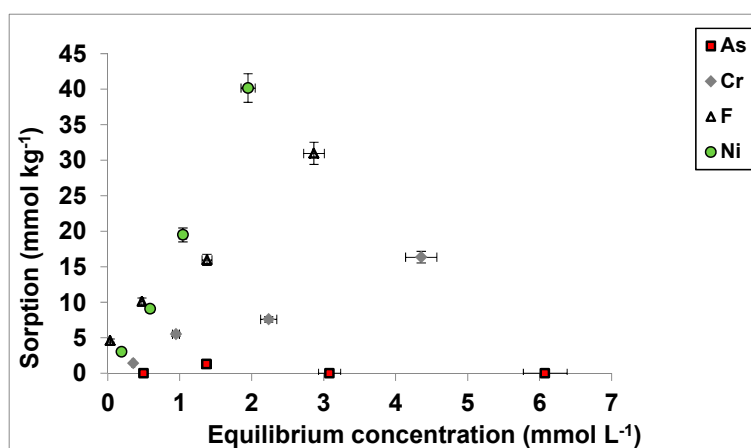
studying chromium sorption and by Seco-Reigosa et al. [11] studying arsenic sorption. This behavior may occur when the samples adsorb Cr(VI) and As(V) predominantly by electrostatic attraction between the adsorbent surface and the anionic species of these elements, releasing  $\text{OH}^-$  and causing an increase in pH [10,34,35]. In the present study, some pH increases took place even when 3 and 6  $\text{mmol L}^{-1}$  As(V) were added (with no As(V) sorption taking place on straw for these added concentrations), suggesting that additional causes could contribute to raising pH.

In the case of F, pH decreased from 8.0 to 7.1 in the equilibrium solution (Table 2). However, these pH values are above the  $\text{pH}_{\text{PZC}}$  of wheat straw (6.68), which causes a dominance of negative charges on the surface of the sorbent (as in the case of As), and this could reduce  $\text{F}^-$  sorption. Some studies reported the release of  $\text{OH}^-$  during the adsorption of  $\text{F}^-$ , which caused an increase in pH [29,34,36]. However, this did not occur in the present study with wheat straw, with a slight acidification of the environment and variable reduction of DOC levels taking place in the solution with increasing concentrations of added F. The absence of pH increases can be explained by  $\text{F}^-$  sorption taking place by means of H bonds or van der Waals forces, without the release of  $\text{OH}^-$  groups [35,37,38]. Another possibility is the formation of precipitates including  $\text{F}^-$  and different elements present in wheat straw, resulting in complexes such as  $\text{CaF}_2$  or  $\text{TiF}$  [39]. Organic matter can adsorb  $\text{F}^-$  through polyvalent cations or through H bonds, which can justify the absence of increase of DOC in solution (Table 2).

For  $\text{Ni}^{2+}$ , increasing concentrations added were associated with increasing pH values in the equilibrium solutions (although always being below the  $\text{pH}_{\text{PZC}}$  value of wheat straw, thus favoring positive surface charges, which made sorption of  $\text{Ni}^{2+}$  difficult) and with decreasing DOC values. The progressive pH increase could be due to cationic exchange releasing basic cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the surface of the sorbent, cations that could facilitate precipitation of organic matter (carboxylic acids were detected on this wheat straw—see Supplementary Materials) and the subsequent decrease in DOC values.

### 3.2. As(V), Cr(VI), $\text{F}^-$ and $\text{Ni}^{2+}$ Sorption Curves

Sorption curves are presented in Figure 2. As in Figure 1, these plots show almost a total absence of retention in the case of As, rather high sorption for Ni and F, and moderate sorption for Cr. The layouts of Ni, F, and Cr show a linear trend, without signs of stabilization.



**Figure 2.** Sorption curves for As, Cr, F, and Ni. Average values (with error bars) for 3 replicates, with coefficients of variation always <5%.

Accordingly, the fitting of sorption data was not possible in the case of the Langmuir model due to error values being too high for adjustment. The parameters of the Freundlich model are shown in

Table 3. The satisfactory fitting of Cr, F, and Ni data to the Freundlich model suggests multilayer-type adsorption on wheat straw for these elements.

**Table 3.** Parameters of the Freundlich model related to sorption on wheat straw.

Pollutant	$K_F$ (mmol·kg <sup>-1</sup> )	$n$	$R^2$
As	-	-	-
Cr	4.3 ± 0.7	0.89 ± 0.13	0.978
F	15.1 ± 1.7	0.65 ± 0.12	0.970
Ni	18.2 ± 0.3	1.19 ± 0.03	0.999

Note: -: error values too high for fitting.

Corroborating previous findings mentioned above, Table 3 shows that  $K_F$  values follow the sequence Ni > F > Cr, whereas the order of the Freundlich  $n$  parameter was Ni > Cr > As, with only that of Ni being >1. The  $n$  parameter indicates the reactivity of the active sites of the adsorbent, which is related to its heterogeneity. According to Khezami and Capart [40], and Foo and Hameed [41], values of  $n > 1$  are a strong indication of the presence of high energy sites. These values can also suggest the occurrence of cooperative sorption, involving strong interactions between the molecules of the adsorbate itself.

### 3.3. As, Cr, F, and Ni Desorption from Wheat Straw

Table 4 shows high F desorption, which can be due to weak bonds such as van der Waals forces. In the opposite side, the lowest desorption corresponded to Ni, which can be related to the strong affinity that cationic metals have with the carboxyl groups present in the adsorbent [42].

**Table 4.** As, Cr, F, and Ni desorption in mmol·L<sup>-1</sup> (and mmol·kg<sup>-1</sup> between brackets) from wheat straw for different concentrations added.

$C_0$	As	Cr	F	Ni
mmol·L <sup>-1</sup>	Desorption			
0.5	0.17 (1.74)	0.14 (1.39)	0.23 (2.24)	0.10 (0.99)
1.5	0.60 (5.99)	0.46 (4.59)	0.55 (5.40)	0.28 (2.81)
3.0	-	0.92 (9.19)	1.58 (15.65)	0.53 (5.31)
6.0	-	2.29 (22.76)	3.51 (34.67)	1.06 (10.51)

Notes: Average values for 3 replicates, with coefficients of variation always <5%; -: experiment not performed due to an absence of sorption.

Table 5 shows alkalization of the solution when the elements were desorbed, suggesting that OH<sup>-</sup> was released in parallel with these elements. DOC in solution increased with Cr and F desorption (which can be in relation to the facilitated release of organic matter due to alkalization) and decreased with Ni desorption (probably in relation to precipitation of organo-metal compounds).

In the present work, desorption studies mainly focused on the retention of the studied pollutants on wheat straw; however, additional research would be needed to deepen an understanding of the mechanism involved, especially if regeneration of the sorbent is a main objective.



**Table 5.** pH and DOC in equilibrium solutions after As, Cr, F, and Ni desorption from wheat straw.

$C_0$	As	Cr	F	Ni
$\text{mmol}\cdot\text{L}^{-1}$	pH			
0.5	6.24 ( $\pm 0.1$ )	5.74 ( $\pm 0.1$ )	5.45 ( $\pm 0.1$ )	5.51 ( $\pm 0.1$ )
1.5	6.14 ( $\pm 0.1$ )	5.77 ( $\pm 0.1$ )	5.54 ( $\pm 0.1$ )	5.65 ( $\pm 0.1$ )
3.0	-	6.16 ( $\pm 0.1$ )	5.6 ( $\pm 0.1$ )	5.50 ( $\pm 0.1$ )
6.0	-	6.35 ( $\pm 0.1$ )	6.19 ( $\pm 0.2$ )	5.8 ( $\pm 0.1$ )
$C_0$	As	Cr	F	Ni
$\text{mmol}\cdot\text{L}^{-1}$	DOC ( $\text{mg}\cdot\text{L}^{-1}$ )			
0.5	194.7 ( $\pm 8.4$ )	108.5 ( $\pm 4.1$ )	114.7 ( $\pm 3.8$ )	111.2 ( $\pm 2.7$ )
1.5	249.2 ( $\pm 9.6$ )	121.0 ( $\pm 4.3$ )	127.6 ( $\pm 3.2$ )	114.2 ( $\pm 3.1$ )
3.0	-	216.3 ( $\pm 6.9$ )	135.0 ( $\pm 4.2$ )	115.5 ( $\pm 2.9$ )
6.0	-	249.0 ( $\pm 6.7$ )	168.9 ( $\pm 4.9$ )	80.8 ( $\pm 1.2$ )

Notes: Average values ( $\pm$  standard deviation) for 3 replicates, with coefficients of variation always  $<5\%$ ; -: experiment not performed due to absence of sorption.

### 3.4. Implications of the Research

In this work, it was found that wheat straw sorption potential is rather high for Ni and F (which could be useful in cases of pollution due to these elements), whereas it was low for Cr(VI), and almost non-existent for As(V). Wheat straw has also previously shown its potential to retain  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  [17], which would be an additional aid to control the eventual pollution episodes due to these elements.

Further future research could focus on alternatives to solve wheat straw's low efficacy regarding Cr(VI) and As(V) immobilization. In this way, the utilization of complementary bio-sorbents would be interesting. Specifically, pine bark could be used to retain Cr(VI) [26,27], whereas mussel shell could be used to facilitate As(V) retention [28]. Some studies have also dealt with the retention of pollutants on wheat straw, although under conditions different from those of the present work. These studies, collectively, have used carbonized wheat straw to remove up to 99.9% Cr(VI) at pH 1 [43], used neuro-fuzzy techniques to predict the removal capacity of Cu(II) and Cr(VI) from aqueous solutions by wheat straw [44], investigated Ni(II) and Zn(II) bio-sorption potential of sulfuric-acid-treated wheat straw by means of column experiments [45], reviewed the efficacy of wheat straw as a bio-sorbent for As removal (finding up to  $3.8 \text{ mg}\cdot\text{g}^{-1}$  in modified straw) [46], and reviewed the bio-sorption of heavy metals on wheat-straw-based materials [47], finding up to 87.8% Cr(VI) removal at pH 2, and up to  $12.0 \text{ mg}\cdot\text{g}^{-1}$  Ni removal at pH 5. This means that other alternatives to the use of complementary bio-sorbents could be taken into account in order to increase pollutants removal, when working conditions can be safe and effectively changed in this way. Future works should also focus on used (as sorbent) wheat straw management. Finally, additional future research is needed to reach a deeper understanding of the sorption mechanism taking place on wheat straw, as previously carried out in other studies performed by different authors, whose focuses have included iron oxide nanoparticles [48], biochar [49], flower powder [50], biomass [51], microbial bio-sorbents [52], and various other bio-sorbents [53,54].

## 4. Conclusions

In this work, where batch-type experiments were used to study As(V), Cr(VI),  $\text{F}^-$ , and  $\text{Ni}^{2+}$  sorption/desorption on/from wheat straw,  $\text{Ni}^{2+}$  showed notable sorption (60.7% and 67.5% when 3 and  $6 \text{ mmol L}^{-1}$  Ni were added); it was rather high for  $\text{F}^-$  (from 52.3% to 93.4%), rather low for Cr(VI) (maximum of 36.9%), and almost non-existent for As(V). The satisfactory fitting of Cr, F, and Ni data to the Freundlich model suggests multilayer-type adsorption on wheat straw for these elements. The lowest desorption corresponded to Ni, whereas it was high for F. The results of this research could aid to program the appropriate use of wheat straw as a bio-sorbent, especially in cases where

Ni and/or F concentrations are too high. It could be also relevant in agricultural soils where straw is recycled, or in soils suffering from forest fires and exposure to high erosion risks, where straw mulching is frequently applied, and when peaks of runoff pollution take place. At the laboratory scale, different aspects could be subjects of further research that focuses on wheat straw used as a bio-sorbent, such as the competitive sorption of anions, or even the effects of the simultaneous presence of both anions and cations, as well as the effects of changing environmental conditions such as temperature, pH, ionic strength, and incubation time.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4441/9/9/690/s1](http://www.mdpi.com/2073-4441/9/9/690/s1). Table S1: Results of the chemical characterization of the wheat straw used. Average values for 3 replicates, with coefficients of variation always <5%); Figure S1: Infrared spectrum of wheat straw.

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