

Article

# Zero-Liquid Discharge Treatment of Wastewater from a Fertilizer Factory

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Received: 10 December 2019; Accepted: 1 January 2020; Published: 3 January 2020



**Abstract:** This article describes the improvement of wastewater treatment in a fertilizer plant located in Central Italy (municipality of Vasto). In this facility, water is used for the removal of dust and fluorinated gases from the air. The resulting wastewater contains fluorides and phosphates in hazardous forms. Its treatment ordinarily does not result in a Zero-Liquid Discharge (ZLD) process. To achieve this purpose, several reagents were tested, focusing on the correlation linking pH, type of reagent and the effect on the separation of fluorides and phosphates from the wastewater. It was eventually found, and explained with a model, that hydrated lime at pH = 12 was so effective as a precipitating agent that phosphate and fluoride separation reached a value of 99.9%, thus allowing for reuse of the water in the plant process. Furthermore, phosphates and fluorides precipitated in a non-hazardous form, so that the material could also be recycled. In synthesis, wastewater treatment of the fertilizer plant was upgraded so that it became a ZLD process coupled with the recovery and recycling of fluorides and phosphates.

**Keywords:** fluoride; phosphates; separation; ZLD; fertilizer; wastewater

## 1. Introduction

The raw materials for the production of phosphate fertilizers, phosphoric acid, and elemental phosphorus are natural phosphate ores like apatite and phosphorite. The main component of these phosphorus double salts is tricalcium phosphate, whose raw chemical formula is  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaX}$ , where  $X = \text{F}^-$ ,  $\text{OH}^-$ , and  $\text{Cl}^-$ . Apart from this, such raw materials can also contain  $\text{CaCO}_3$  (7%–13%wt),  $\text{SiO}_2$  (1%–8%),  $\text{CaSO}_4$  (1%–5%),  $\text{CaF}_2$  (4%–8%),  $\text{Al}_2\text{O}_3$  (1%–1.5%),  $\text{Fe}_2\text{O}_3$  (0.5%–1%),  $\text{MgO}$  (0.3%–0.6%). In the manufacturing process of phosphate fertilizers, raw material containing phosphorus in the form of  $\text{Ca}_3(\text{PO}_4)_2$ , which is an insoluble and poorly available form for plants, is chemically treated by sulfuric acid to obtain a product with a high concentration of  $\text{P}_2\text{O}_5$ , which can be easily absorbed by plants.

During acidulation of phosphate rock to produce phosphoric acid or superphosphates, fluoride is released as hydrofluoric acid HF, which in turn reacts with silica forming the volatile gas silicon tetrafluoride  $\text{SiF}_4$  and hydro-soluble hexafluorosilicic acid  $\text{H}_2\text{SiF}_6$ . Both of these are partially carried along in the wastewaters coming from the operations of gaseous waste scrubbing and phosphogypsum transportation performed during the processing of phosphate rock [1]. Wastewater from the industrial production of phosphate fertilizers is generated in a relatively small quantity. However, it contains very fine suspended solids and a high concentration of hazardous substances (phosphoric acid  $\text{H}_3\text{PO}_4$ ,

hydrofluoric acid HF, and hexafluorosilicic acid  $H_2SiF_6$ ) which make purification treatments difficult. Chemical precipitation can be suggested as the most adopted method. But, in turn, the complex chemical structure of sediments makes it un-economical to re-use them in any form. As a result, the fertilizer industry discharges wastewater into the environment, including several thousand tons of fluorides per year and even more phosphates.

Methods of recovering silica from waste hexafluorosilicic acid from the fertilizer industry for applications such as chromatography and reinforcing material for rubber and plastics have been reported [1,2].

Fluorides and phosphates can be removed from wastewater using several treatments, such as biological and physical-chemical methods. Methods of removal include precipitation [3], microfiltration [4], electrocoagulation [5], reverse osmosis (RO), nanofiltration (NF) [6], selective separation [7] and fluoride removal in a fluidized bed reactor [8].

For example, hexafluorosilicic acid can be neutralized with sodium hydroxide or sodium carbonate, with the resulting precipitation of sodium fluorosilicate. Sodium chloride can also be used as a precipitating agent for the same purpose.

It is used as a fluoridation agent for drinking water, insecticide, production of high purity silicon tetrafluoride and the production of enamels for china and porcelain products [9].

Furthermore, phosphorous and fluorides can be recycled as raw materials in either agricultural or industrial applications. For instance, calcium fluoride and calcium phosphate-based by-products can be used in several industrial sectors, such as ceramic manufacturing and phosphate fertilizer industries [10].

In most chemical treatments, phosphorus can be removed by precipitation with a metal salt, e.g., iron, aluminum and calcium salts [11]. In wastewater with high fluoride content, the most commonly adopted method is precipitation under calcium fluoride form ( $CaF_2$ ), using different calcium salts ( $CaCl_2$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ , and hydrated lime  $Ca(OH)_2$ ) as precipitants [12–14].

However, precipitation by the use of metal salts and lime results in the formation of a large quantity of sludge which is difficult to treat for the extraction of valuable components [15,16].

The overall research was designed to study a neutralization/precipitation-based process using NaCl, KOH, NaOH and hydrated lime as precipitating agents in the treatment of wastewater from the fertilizer industry containing phosphate and fluoride ions, the latter in the HF and  $H_2SiF_6$  forms in a wide range of pH, from 1.5 up to 12.

Sodium chloride was chosen as a reagent for the neutralization of hexafluorosilicic acid with the formation of non-hazardous sodium fluoride and sodium fluorosilicate. Fluoride precipitation in calcium fluoride form ( $CaF_2$ ) caused by hydrated lime was chosen as it is the most commonly adopted method. Potassium and sodium hydroxide were chosen as an alternative to hydrated lime in order to decrease the volume of the precipitated solids.

Due to the high odor intensity of the studied wastewater, special attention was paid to its removal after treatment.

This experimental study resulted in the discovery of the optimal reagent and parameters of a process that made the conversion of phosphate and fluoride into non-hazardous materials in a Zero-Liquid Discharge (ZLD) process.

## 2. Materials and Methods

### 2.1. Chemicals and Solutions

The experiments were carried out using real wastewater collected from the Puccioni S.p.a fertilizer plant (Vasto, Italy).

Hydrated lime (calcium hydroxide 10% wt/vol), sodium hydroxide 10% wt/vol, potassium hydroxide 10% wt/vol, sodium chloride 10% wt/vol and epichlorohydrin-dimethylamine (EPI-DMA) were used for the precipitation tests.

For all the fluoride-containing solutions, only polypropylene (PP) vessels were used for sample preparation and storage.

## 2.2. Analytical Methods

The analysis of phosphates and fluorides contained in acid mixtures is rather difficult from the analytical point of view, and this has already been the subject of some recent works [17]. For instance, in the case of phosphate industry effluents, the presence of the poly-acid  $H_3PO_4$  next to  $H_2SiF_6$  and HF makes the mixture even more complex from an analytical point of view [18]. Hexafluorosilicic acid  $H_2SiF_6$  has a complex and widely unresolved speciation [19]. Consequently, the analysis of  $H_2SiF_6$  containing an acid mixture is usually considered as a complicated case. In the present work, the exact concentration of each acid solution was initially determined by potentiometric titration of acid mixtures.

Titration was performed by using an HF resistant glass electrode (Metrohm-60, 421.100). The titrant was a  $9.53 \cdot 10^{-2}$  mol/L NaOH solution.

An X-ray fluorescence (XRF) spectrophotometer (Spectro XEPOS 2000) and a fast sequential atomic absorption spectrometer (AAS, Varian AA240FS) were used to perform the chemical analyses of the wastewater and the precipitate from wastewater.

Both Fourier-transform infrared spectroscopy (FTIR, Impact 410 Nicolet spectrophotometer, SpectraLab, Alexandria, VA, USA) and X-ray diffraction (XRD, X'Pert PRO diffractometer, Panalytical, Malvern, UK) were used to characterize the obtained precipitates.

All the quantitative analyses were carried out three times, and the results in the figures and tables are expressed as average values.

The analysis of the wastewater odor intensity was determined by using a sensory method in which 10 raters were asked to judge the odor. Odor intensity was evaluated by following the odor panel presented in Table 1, where the intensity level changes from 6 (extremely strong) to 0 (not perceptible).

**Table 1.** Odor intensity categories [20].

Odor Strength	Intensity Level
Extremely strong	6
Very strong	5
Strong	4
Distinct	3
Weak	2
Very weak	1
Not perceptible	0

## 2.3. Flocculation Experiments

The flocculation experiments were carried out in a jacketed stirred tank reactor. The time and speed for mixing were set with an automatic controller.

The flocculation behavior of wastewater was investigated for cationic flocculant, EPI-DMA, in concentrations ranging from 1 to 20 mg/L. To finely set the dosage of the EPI-DMA (initial viscosity equal to 3200 mPa·s) in the experiments, the flocculant was provided using 10% wt solution in distilled water.

The flocculation experiments were conducted to determine the effect of the EPI-DMA dosage on the separation efficiency (measured by the total suspended solids (TSS) content of the residual liquor) and the relevant effect on  $K^+$  and  $Cl^-$  dissolution.

Subsequently, the precipitate was filtered by a vacuum pump (XX1004700, Millipore, Milano, Italy) and the solution was stored for XRF and AAS analyses. Filter cakes were dried at 105 °C for 24 h and prepared for the XRD, XRF and FTIR analysis.

#### 2.4. Precipitation Tests

During the precipitation stage, the reagents were gradually added under constant stirring until reaching the desired pH. The mixture was stirred further for 2h to ensure precipitation equilibrium. Precipitation tests were performed in a pH range of 1.5–12, at room temperature ( $25 \pm 2$  °C).

Precipitation tests in the pH range of pH 1.5–2 were performed with sodium chloride and in the pH range of pH 2–12 with metal hydroxides.

The final pH was measured and the precipitate separated from the slurry by vacuum filtration, washed three times with demineralized water and then dried at 105 °C overnight. For each considered pH, the obtained filtrate was analyzed for determining the residual  $\text{PO}_4^{3-}$ ,  $\text{SiF}_6^{2-}$ ,  $\text{F}^-$  ions content.

The pH after precipitation tests with metal hydroxides was adjusted to 2.0 before starting titration, by adding HCl to the wastewater.

The amount of precipitated fluoride or phosphate ions was expressed in term of removal efficiency calculated as follows,

$$\text{Removal (\%)} = \frac{C_0 - C_P}{C_0} \cdot 100 \quad (1)$$

where  $C_0$  is the initial concentration and  $C_P$  is the concentration after precipitation (mg/L).

### 3. Results and Discussion

In this section, a quick overview of the main results achieved during the experimental campaign is given. After the characterization of two different wastewater samples, the effect of the flocculant was reported, hence the results obtained after the addition of NaCl and KOH or NaOH were discussed, together with the analysis of the chemistry and the precipitation mechanisms of fluorides and phosphates caused by lime. In the end, a process flow-sheet was proposed to recycle all the water recovered from the fertilizer manufacturing plant.

#### 3.1. Characterization of the Wastewater

The experiments were performed on two samples of wastewater, taken on two different days after a scrubber treatment, containing both soluble and insoluble phosphates and fluorides.

The composition of the liquid and solid phase of the wastewater resulting from the scrubber varies considerably depending on the kind of raw material (phosphates) used for the fertilizer production. Tables 2 and 3 show the results of the analysis carried out with XRF.

**Table 2.** Semi-quantitative analysis of the solid and liquid phase of the wastewater.

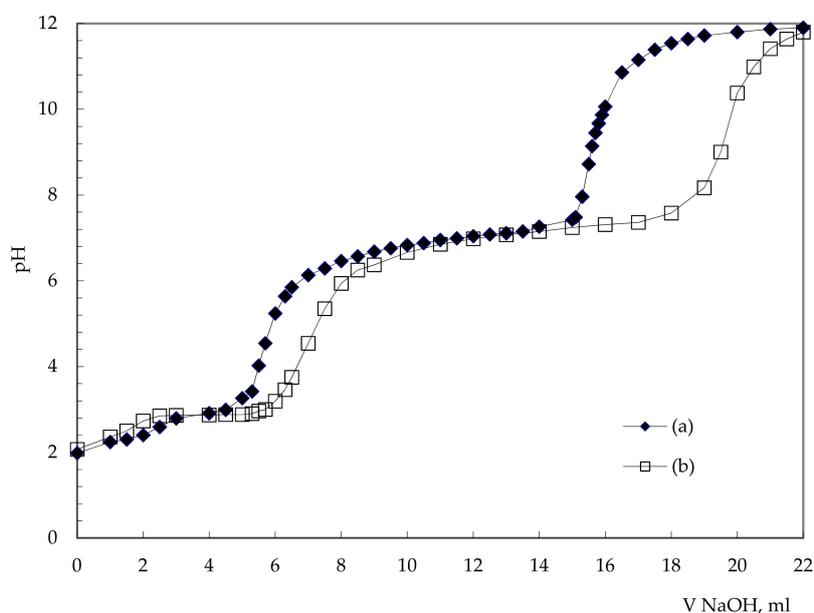
Wastewater Sample	Concentration (%wt)						
	Al	Si	Ca	Fe	S	Cl	P
Solid Phase							
I	0.12	86.72	8.28	0.31	0.64	0.27	3.54
II	0.35	84.01	8.08	1.21	0.34	0.15	5.55
Liquid Phase							
I	0.056	1.733	0.430	0.005	0.033	0.207	0.346
II	0.600	2.179	1.525	0.011	0.495	0.279	0.834

**Table 3.** Semi-quantitative analysis of the raw materials.

Raw Material	Concentration (%wt)						
	Al	Si	Ca	Fe	S	Cl	P
Morocco	0.28	2.66	25.5	0.44	0.25	0.01	6.73
Senegal	0.96	1.45	24.44	1.28	0.14	0.004	9.63

The suspended solids contained in the wastewater were composed of the raw materials used for the production of the phosphate fertilizers after decomposition by acid, in particular CaO, P<sub>2</sub>O<sub>5</sub>, CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. Soluble impurities were composed of PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup>, and SiF<sub>6</sub><sup>2-</sup> ions.

The exact concentrations of PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup>, and SiF<sub>6</sub><sup>2-</sup> in the wastewater were determined by potentiometric titrations. Three separated equivalence points can be clearly recognized from the potentiometric titration curves (Figure 1) and can be related to the reactions listed in Table 4.



**Figure 1.** Potentiometric titration curves with  $9.53 \cdot 10^{-2}$  mol/L NaOH in 15 mL of wastewater: (a) n°1; (b) n°2.

**Table 4.** Equilibrium equations of the E-pH diagram.

pKa [21]	pH	Equilibrium Equations	P-F-Si-H <sub>2</sub> O System	
			pH	Equivalence Point
1.7	3.5	$H_2SiF_6 \leftrightarrow SiF_6^{2-} + 2 H^+$	2.4	first
2.1	4.6	$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$		
3.1	7.0	$HF \leftrightarrow H^+ + F^-$	4.3	second
3.9	8.6	$SiF_6^{2-} + 2 H_2O \leftrightarrow 6 F^- + 4 H^+ + SiO_2$		
7.4	9.6	$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$		

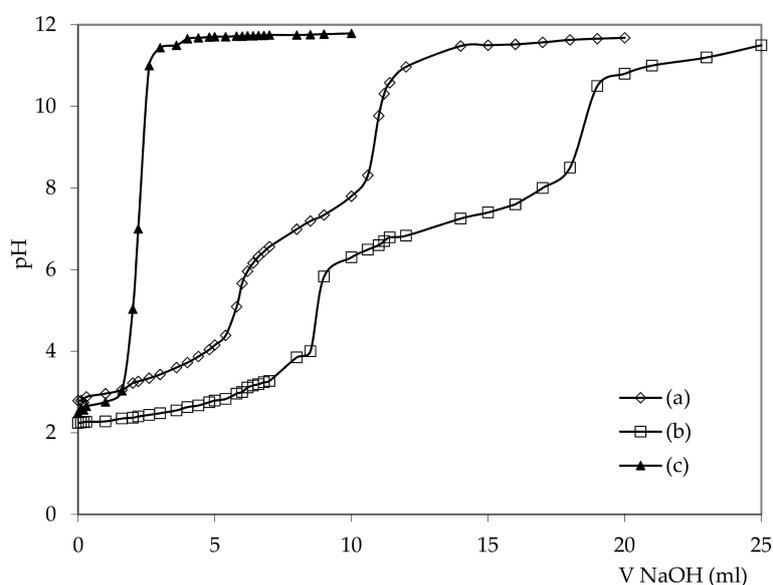
The concentrations of phosphates and fluorides in the wastewater were calculated and listed in Table 5, based on titration data (Figure 1).

**Table 5.** Chemical composition of the wastewater.

Wastewater Sample	pH	Concentration (g/L)		
		PO <sub>4</sub> <sup>3-</sup>	SiF <sub>6</sub> <sup>2-</sup>	F <sup>-</sup>
Sample I	1.86	59.88	6.96	1.68
Sample II	1.97	76.83	13.76	0.58

Table 2 shows the elemental composition of the wastewater and its precipitate according to the XRF measurements. The concentrations of PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup> and SiF<sub>6</sub><sup>2-</sup> in the wastewater shown in Table 5 are calculated on the basis of the titration curves. Table 5 shows in which form the fluorine compounds are present in wastewater. The authors measured fluoride under the HF form and the fluoride silicate complex.

To cross-check the reliability of the above table, three model solutions were prepared with 78.6 g/L of  $\text{PO}_4^{3-}$  and 4.8 g/L of  $\text{F}^-$ . The relevant titration curves were plotted (Figure 2). The recalculated concentration values were 76.8 g/L of  $\text{PO}_4^{3-}$  and 4.5 g/L of  $\text{F}^-$ .

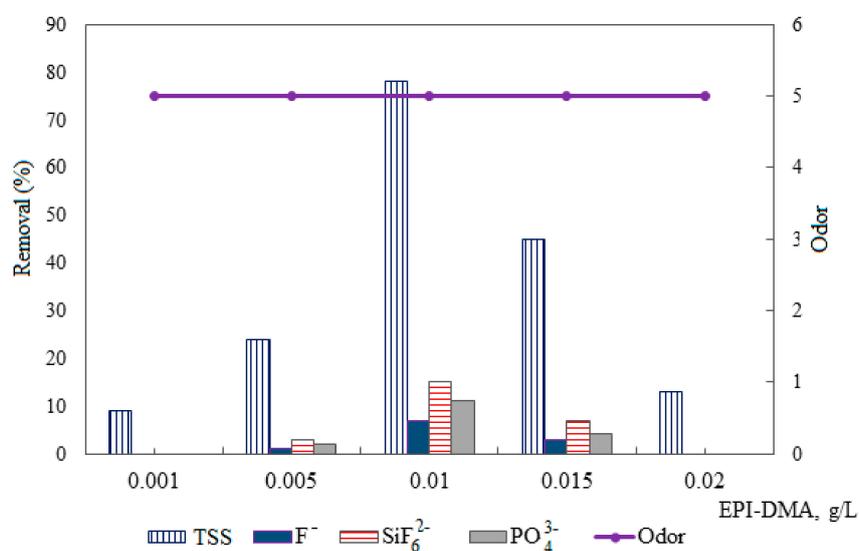


**Figure 2.** Potentiometric titration curves of model solutions containing: (a)  $\text{H}_3\text{PO}_4$  and HF mixture, (b)  $\text{H}_3\text{PO}_4$  and (c) HF.

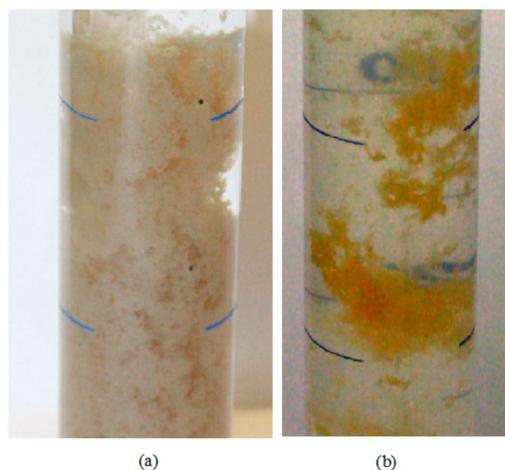
### 3.2. Wastewater Treatment

#### 3.2.1. Effect of Flocculant

The studied wastewater contains suspended and nanosized solids that originated from the particles of the raw material. The flocculation of the suspension was studied at pH 1.8 (sample I) and 1.9 (sample II). The effect of EPI-DMA dosage on the TSS, fluorides, phosphates, and odor is shown in Figure 3. The flocculation rate increased with the increase of the EPI-DMA concentration; it reached a maximum and then decreased. According to the results of the experiments, the flocculant was helpful in forming flocks (Figure 4) and furthering fast sedimentation, but did not show good efficiency in phosphate, fluoride or odor removal.



**Figure 3.** Effect of epichlorohydrin-dimethylamine (EPI-DMA) dosage on contaminant removal.



**Figure 4.** Flocculation effect of EPI-DMA (0.01 g/L): (a) Sample I; (b) Sample II.

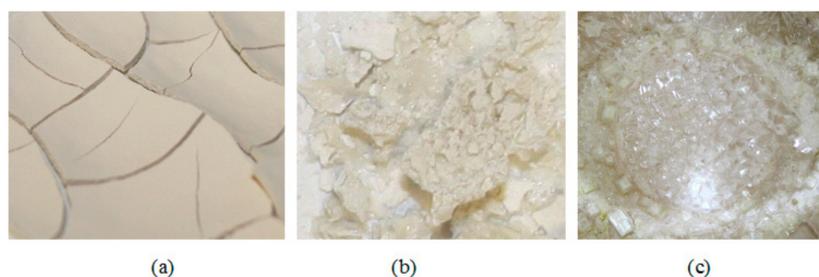
### 3.2.2. Effect of Sodium Salt

As said above, sodium chloride was chosen as a reagent for the neutralization of hexafluorosilicic acid with the formation of sodium fluorosilicate (Table 6). The use of sodium chloride or sodium hydroxide leads to the formation of coarser sodium hexafluorosilicate and precipitation of amorphous silica, which plays the role of active centers for deposition of phosphate and fluoride ions. Different amounts of NaCl were added to the wastewater sample in order to reach the desired pH value. It was found that, along with a decrease in the pH value from 1.7 to 1.5, the removal efficiency of  $\text{SiF}_6^{2-}$  increased from 41% up to 74% and then decreased (Figure 4a). The precipitation of  $\text{SiF}_6^{2-}$  contained in wastewater by the addition of sodium chloride relies on the formation of sodium fluorosilicate at pH 1.7–1.5 and its dissolving at pH <1.5.

**Table 6.** Fluoride, phosphate and fluorosilicate precipitate formation at different pH levels.

pH	P-F-Si-Na(K)-H <sub>2</sub> O System	P-F-Si-(Na-Cl)-Ca-H <sub>2</sub> O System
2–1.5	-	$\text{H}_2\text{SiF}_6 + 2 \text{NaCl} \rightarrow \text{Na}_2\text{SiF}_6\downarrow + 2 \text{HCl}$
2–6	$\text{H}_2\text{SiF}_6 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SiF}_6\downarrow + 2 \text{H}_2\text{O}$ $\text{H}_3\text{PO}_4 + \text{NaOH} \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$ $\text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O}$	$2 \text{H}_3\text{PO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2 \text{H}_2\text{O}$ $\text{H}_2\text{SiF}_6 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSiF}_6\downarrow + 2 \text{H}_2\text{O}$ $2 \text{HF} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaF}_2\downarrow + 2 \text{H}_2\text{O}$
6–9	$\text{H}_2\text{SiF}_6 + 6 \text{NaOH} \rightarrow 6 \text{NaF} + \text{SiO}_2 \cdot n\text{H}_2\text{O}\downarrow$ $\text{H}_3\text{PO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + 2 \text{H}_2\text{O}$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2 \text{CaHPO}_4\downarrow + 2 \text{H}_2\text{O}$ $\text{CaSiF}_6 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaF}_2\downarrow + \text{SiO}_2 \cdot n\text{H}_2\text{O}\downarrow$
9–12	$\text{SiO}_2 \cdot n\text{H}_2\text{O} + 4 \text{NaOH} \rightarrow \text{Na}_4\text{SiOH} + (n+2)\text{H}_2\text{O}$	$2 \text{CaHPO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2\downarrow + 2 \text{H}_2\text{O}$

NaCl as a precipitating agent was not effective for phosphates, fluorides or odor removal. According to the XRF results, residual concentration of  $\text{Cl}^-$  ions in the wastewater after precipitation increased from 23.8 g/L at pH 1.7 up to 182.2 g/L at pH 1.5. The precipitate after the addition of NaCl has a crystalline structure for the following reasons: at pH = 1.7 this is due to the formation of rough sodium hexafluorosilicate crystals (Figure 5b), and at pH = 1.5 it is because of excess NaCl concentration (Figure 5c).

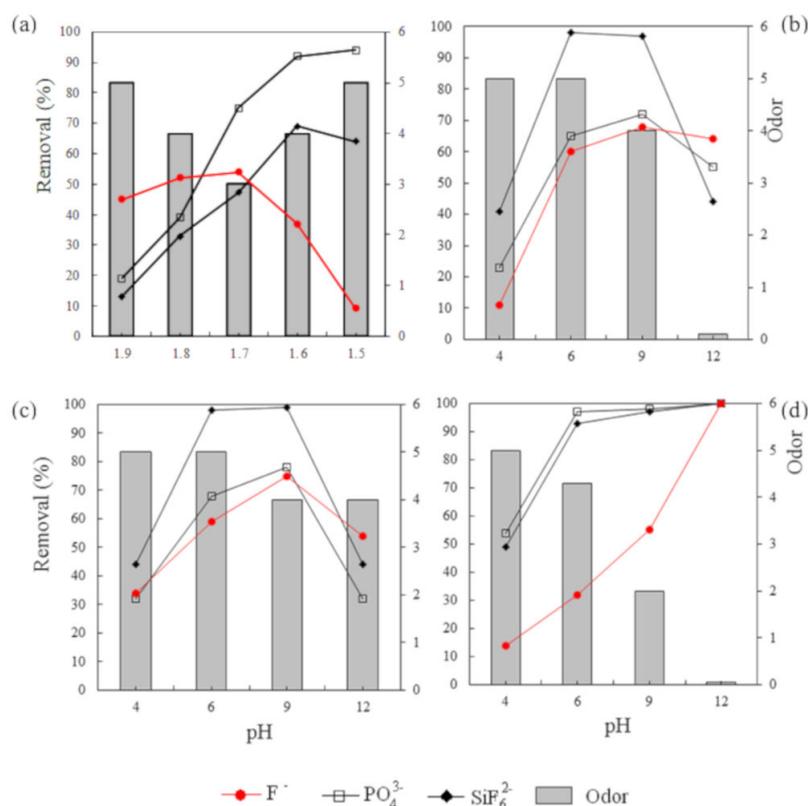


**Figure 5.** Wastewater sediment (a) before treatment (pH = 2) and after precipitation with NaCl (b) pH = 1.7, (c) pH = 1.5.

### 3.2.3. Effect of Metal Hydroxides

The efficiency of fluoride and phosphate removal obtained after the precipitation with K, Na and Ca hydroxides was studied in the pH range 4–12.

It was found that KOH and NaOH as precipitation agents did not make a considerable difference in the removal efficiency of  $\text{PO}_4^{3-}$  and  $\text{F}^-$  ions. The recovery of  $\text{SiF}_6^{2-}$  ions reached a maximum at pH 6–9 and then decreased with further increases in the pH (Figure 6). Residual concentration of Si (measured with the AAS) after precipitation with NaOH and KOH at pH >9 increased from 0.24 g/L (pH = 9) to 4.13 g/L (pH = 12) and from 0.09 g/L (pH = 9) to 1.75 g/L (pH = 12), respectively.



**Figure 6.** Effect of pH on treatment efficiency of wastewater with different reagents: (a) sodium chloride 10% (wt/vol); (b) sodium hydroxide 10% (wt/vol); (c) potassium hydroxide 10% (wt/vol); (d) calcium hydroxide 10% (wt/vol).

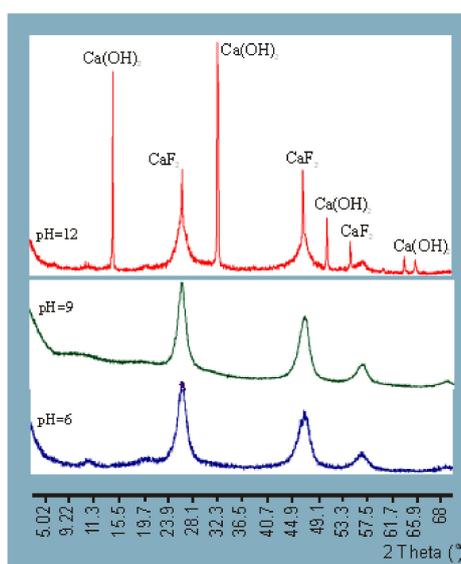
The decrease in odor intensity after precipitation with NaOH can be explained by a reaction between HF and NaOH that results in the formation of odorless NaF. By contrast, precipitation with KOH does not abate odor, as the resulting substance is KF. In fact, at pH 12, after precipitation with NaOH odor intensity was 0 (not perceptible), whereas after precipitation with KOH odor intensity was 4 (strong odor).



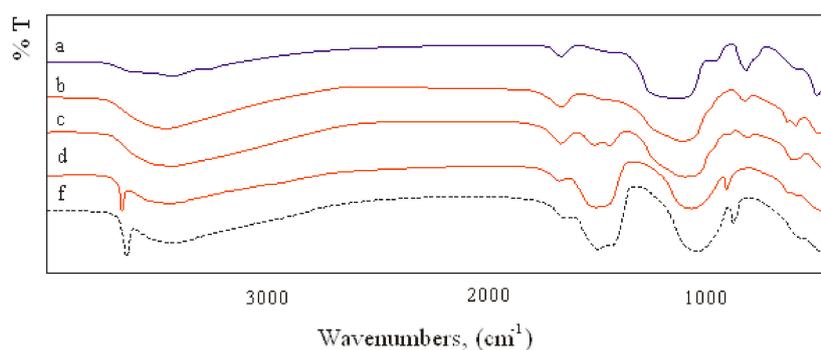
XRD and IR analyses were performed on samples of wastewater (II) before and after precipitation with lime at different pH values.

The results suggest that fluoride and phosphate removal by hydrated lime is a combination of chemical adsorption on the surfaces of lime particles, ion exchange of  $F^-$  with  $OH^-$  and some direct precipitation. Higher values of pH most likely result in the formation of negatively charged OH-groups on the surface of the particles. This leads to an enhancement of the sorptive capacity of  $Ca^{2+}$  ions, thus creating favorable conditions for the formation and deposition of calcium-silicate complexes. In simplified form, the following reactions can be written (Table 6).

The XRD patterns (Figure 8) showed characteristic Bragg peaks of  $CaF_2$  after precipitation at pH 9 and both of  $CaF_2$  and  $Ca(OH)_2$  at pH 12, with the latter as a result of its excess in the precipitation process. The obtained IR spectrum (Figure 9) was characteristic of  $SiO_2 \cdot nH_2O$  (match 95.27%) at pH 6 and  $Ca(OH)_2$  (match 98.75%) at pH 12.



**Figure 8.** X-ray diffraction (XRD) patterns of the precipitates obtained by the  $Ca(OH)_2$  treatment of wastewater (II) at different pH levels.



**Figure 9.** Infrared (IR) spectrum of the precipitate obtained by the  $Ca(OH)_2$  treatment of wastewater (II) at different pH levels: (a) before treatment; after treatment (b) at pH = 6, (c) pH = 9, (d) pH = 12, and (f)  $Ca(OH)_2$ .

As can be inferred from Figure 6a, the addition of NaCl up to pH 1.7 led to the formation of  $Na_2SiF_6$  and also caused a decrease in odor intensity, resulting in the removal of  $F^-$  and  $PO_4^{3-}$ .

The composition of the wastewater after precipitation with  $Ca(OH)_2$  at different pH values is given in Table 7. No more elements were detected at a concentration greater than 0.01%wt.

**Table 7.** Semi-quantitative analysis of the solid and liquid phase of wastewater after treatment with  $\text{Ca}(\text{OH})_2$  at different pH values.

pH	Concentration (%wt)						
	Al	Si	Ca	Fe	S	Cl	P
Solid Phase							
6	0.23	16.22	75.77	0.30	0.016	0.58	6.86
9	0.23	16.22	74.88	0.26	0.033	0.72	7.62
12	0.21	8.67	86.14	0.19	0.028	0.43	4.36
Liquid Phase							
6	0.01	0.027	0.03	0.002	0.001	0.189	0.0009
9	0.02	0.019	0.04	0.001	0.047	0.046	0.0002
12	0.10	0.004	0.04	0.001	0.001	0.044	0.0001

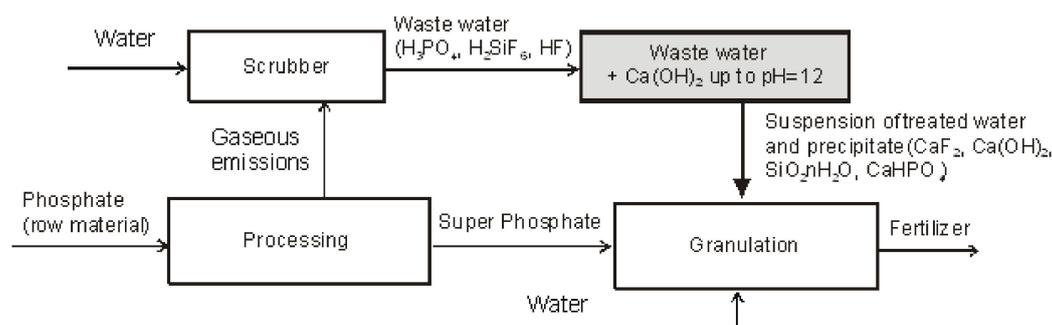
#### 4. Conclusions

This work investigated possible ways to treat wastewater from a fertilizer plant containing  $\text{H}_3\text{PO}_4$  and fluoride ions, which were present in both “free” (HF) and combined form ( $\text{H}_2\text{SiF}_6$ ).

As illustrated, several different reagents were tested to figure out the reaction mechanisms. In the end, hydrated lime was found to be the most effective reagent, as in its presence dangerous  $\text{PO}_4^{3-}$ ,  $\text{SiF}_6^{2-}$ ,  $\text{F}^-$  ions would convert into their insoluble calcium-based salts. It was also found that process efficiency is highly depending on the fine-tuning of pH.

Finally, it was found that as the resulting suspension is not hazardous, it can be recycled in the plant process for the granulation stage of fertilizer production, thus achieving ZLD conditions for the wastewater treatment.

The main and final finding of the research was therefore that the use of  $\text{Ca}(\text{OH})_2$  as a precipitating reagent, at pH 12, results in the possibility of recycling the wastewater without further filtration steps (Figure 10). This is due to the conversion into non-hazardous solid forms of 99.9% of the formerly hazardous and soluble phosphates and fluorides.

**Figure 10.** Flowchart of the process.

**Author Contributions:** Conceptualization, F.V.; methodology, S.B.Z.; validation, I.P.; investigation, S.B.Z.; data curation, I.D.M.; writing—original draft preparation, S.B.Z.; XRD analyses, G.T.; writing—review and editing, F.F.; visualization, I.D.M.; supervision, F.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sector.

**Acknowledgments:** The authors are very grateful to Fabiola Ferrante and Marcello Centofanti for their helpful collaboration given for the XRF and AAS analyses.

**Conflicts of Interest:** The authors declare no conflict of interest.

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