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# Fluoride pollutants removal from industrial wastewater

G. El Diwani, Sh. K. Amin\* , N. K. Attia and S. I. Hawash

## Abstract

**Background:** The main object of the present study is the industrial wastewater effluent treatment resulting from a solar cell manufacturing process, which is a Joint Egyptian Chinese Renewable Energy laboratory, in Sohag Governorate. Fluoric and hydrochloric acids are the main pollutants causing a pH of 1 to 3. The effluent is neutralized by the addition of both potassium hydroxide and calcium hydroxide to permit the precipitation of the resulting sparingly soluble calcium fluoride. The chlorides are partially precipitated as calcium chloride, and the further addition of hydrated aluminum sulfate is used to precipitate the remaining extra chloride as an insoluble complex to reach the allowable chloride concentration in the treated effluent. Set of experiments at bench and pilot scales were run to achieve the optimum conditions for defluorination and dichlorination taking into consideration not exceeding the allowable ranges of pollutants as soluble salts in the final effluent.

**Results:** Experimental results showed that the performance of a pilot scale was satisfactory in fluorides, chlorides, and dissolved solids by 97.64, 78.85, and 79.4% removal, respectively. Based on these results a full-scale industrial treatment unit was designed for construction and operation as a treatment unit for industrial wastewater contaminated with fluorides as main pollutant.

**Conclusions:** The recommended treatment procedure succeeded in the removal of fluorides and chlorides as main contaminants in the effluent which permit the use of treated water in the irrigation of non-edible plants, according to Egyptian Code No. (501/2015).

**Keywords:** Defluorination, Fluoride separation, Chemical precipitation, Fluorine recovery

## Background

In natural water resources like rivers, lakes, wells, etc., fluorides occur up to 5 mg/L (Industry News 2017). The presence of fluorides in drinking water with right amount protects the teeth from decay and reduces the risk of cavities, but exposure to excess fluorides results in hyperactivity, muscle disorders and brain impairment (Kumar et al. 2019).

Industrial wastewater usually contains different chemicals that may have effects on defluorination process (Shen et al. 2003). Due to fluoride toxicity, industrial

wastewater contaminated with fluoride is severely regulated. For example, China established discharge standard of 5 mg/L in some Chinese cities (Liu et al. 1983) and in some jurisdictions this limit must not exceed 2 mg/L (Saltworks Technologies Inc., 2019). But according to WHO fluorides contents must not exceed 0.5 to 1 mg/L (Khatibikamala et al. 2010).

Various high-tech products like quartz glass, precious metal recovery, and semiconductors need fluorides as necessary chemical in processing. So industrial effluents of the above industries contain many fluorides or hydrofluoric acid as main pollutants (Saha 1993; Wan et al. 2021).

Excess of fluorides in water causes adverse effects on human health such as lipid metabolism disorder, myeloclerosis, disorder of the central nervous, dental and

\*Correspondence: dr.shereenkamel@hotmail.com; sheren51078@yahoo.com

Chemical Engineering and Pilot Plant Department, Engineering and Renewable Energy Research Institute, National Research Centre (NRC), 33 El Bohouth St. (Former El Tahrir St.), Dokki, P.O. Box 12622, Giza, Egypt

skeletal fluorosis, and other diseases caused by the intake of fluoride (Wang et al. 2021). Thus, fluorides as contaminants in discharged industrial wastewater must be within safety limit, or otherwise it would be harmful to the environment (Industry News 2017).

Wastewater from fertilizer industry contains fluorides and phosphates as hazardous contaminants, and to achieve a zero-liquid discharge (ZLD) process, several reagents were tested. Using hydrated lime as effective precipitating agent resulted in phosphate and fluoride separation reaching 99.9% which can be recovered and recycled (Zueva et al. 2020).

Fluorides and phosphates can be separated from wastewater by two methods. Firstly, phosphates are precipitated with calcium in the presence of aluminum at pH 3. Secondly, fluorides were separated at pH 8 in the form of insoluble  $\text{CaF}_2$  (Grzmil and Wronkowski 2006).

Managing industrial wastewater treatment especially fluoride removal is practiced via ion-exchange and/or reverse osmosis and adsorption for drinking water. These technologies are suitable only for low concentration of fluorides due to their high cost (Waghmare and Arfin 2015).

For much higher fluoride concentrations associated with wastewater from microelectronics industry, coagulation and precipitation of calcium fluoride is another option to remove fluoride from industrial wastewater to meet discharge requirements (Chang and Liu 2007). Ceramic membrane filtration system is a new modular, intelligent, and automated chemical precipitation option to eliminate the challenges of chemical overdosing (Saltworks Technologies Inc., 2019).

Precipitation, coagulation, and solids separation are the main traditional methods for fluorides removal. In precipitation process, large quantities of chemicals are added which leads to fluoride precipitate formation and the process produces certain amounts of sludge daily. On the other hand, in coagulation method, wastewater is treated with calcium hydroxide for controlling pH, and formed calcium fluoride precipitate can be removed by solid separation process (Industry News 2017). Ion exchange, reverse osmosis, and adsorption processes are used for drinking water applications and for final fluoride polishing (Saltworks Technologies Inc., 2019). Combination of electrofloatation and electrocoagulation processes is successfully used in treating wastewater containing fluorides (Khatibikamala et al. 2010). Also, 94.5% removal of total fluorides was achieved successfully from wastewater containing fluorides by precipitation and then adsorption onto hydroxyapatite (Melidis 2015).

Some investigators explored simultaneous effect of chemical precipitation and electrocoagulation in wastewater defluorination; then, they studied the optimization

and statistical modeling of the process (Jadhaio et al. 2019). In electrochemical treatment of wastewater containing fluorides, it was found that anions and cations affect the removal process because anions had a negative effect on the removal process (Drouiche et al. 2008). Moreover, it was found that one liter of wastewater consumed 0.976 gm of iron and cost calculations revealed that in case of iron electrodes, the operating cost of treating 1 L of wastewater was approximately 0.059 USD (Drouiche et al. 2008).

The main objective of this investigation is to design, construct, and operate an efficient and low-cost industrial unit for treatment of wastewater containing fluorides, to be used in the irrigation of non-edible plants, according to Egyptian Code No. (501/2015) (ECP 501 , 2015).

## Methods

### Chemicals and solutions

#### *Industrial wastewater*

The experiments were carried out using real industrial wastewater, resulting from the solar cell manufacturing process, which was collected from the Joint National Egyptian—Chinese Renewable Energy laboratory, South Upper Egypt Region Development Center, Al-Qaraman Island—Sohag Governorate.

The industrial wastewater to be treated is generated from two units: texturing unit and silica glass removal unit. The acidic polluted water with hydrofluoric acid (HF) and hydrochloric acid (HCl) is collected and mixed together in one tank, while the alkaline polluted water with potassium hydroxide (KOH) is collected in another tank. The acidic and alkaline industrial wastewater are mixed together in a larger final tank, and it is transported, disposed, and buried in designated landfills in Alexandria Governorate, under the supervision and approval of the Ministry of Environment. The amount of industrial wastewater produced is 15 cubic meters/month.

After well mixing, the raw industrial wastewater is subjected to complete chemical analyses to determine the elements and its limit according to Egyptian Code No. (501/2015) (ECP 501 , 2015).

#### *Potassium hydroxide (KOH)*

Pellets of pure grade, with molecular weight 56.11 and maximum assay 85%, were obtained from BDH Company.

#### *Quick lime (CaO)*

This is mainly calcium oxide (CaO) with insignificant impurities, which is collected from local quarries in Egypt. It is freshly prepared by calcination of limestone at 900 °C for 4-h soaking time using calibrated laboratory

furnace SH Scientific, made in Korea, Model SH-FU-11MH, in Chemical Engineering and Pilot Plant Department, National Research Centre.

#### Experimental apparatus

##### *Calibrated electronic digital balance*

Chyo, Japan, Model JS110, maximum weight 110 g, capable of weighing to an accuracy of  $\pm 0.0001$  g.

##### *Calibrated pH meter*

Jenway, Model 3510.

##### *Magnetic stirrer*

TORRY PINES Scientific, with standard rod magnet.

##### *Laboratory volumetric glassware*

Grade (A or B).

##### *Sampling bottles*

Dark polypropylene bottles were used for fluorides containing solutions in preparation, handling, and storage for analyses.

##### *Analytical procedure*

Complete chemical analysis for both raw and treated industrial wastewaters was performed in the Analysis and Consultation Unit—Domain of Evaluation and Remediation of Hazards Wastes—National Research Centre—Egypt.

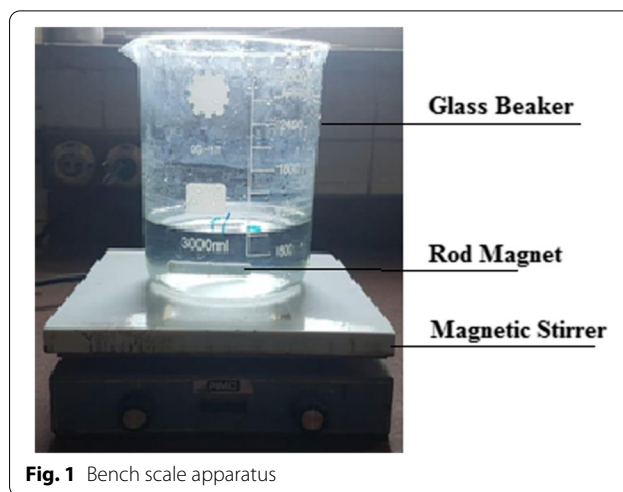
The precipitate was characterized for its chemical composition using XRF, AXIOS, PANalytical 2005, Wavelength Dispersive (WD-XRF) Sequential Spectrometer, at Analysis and Consultation Unit—Preparation and Chemical analysis by X-ray Fluorescence (XRF) Lab.—National Research Centre—Egypt.

##### *Experimental setup*

The treatment process of industrial wastewater contaminated with fluorides and chlorides was conducted on both bench (1 L) and pilot scales (about 30 L), at Chemical Engineering and Pilot Plant Department. It is achieved by the addition of alkali solution to neutralize both fluoric and hydrochloric acids to achieve the optimum dose so that pH reaches 6.5–8.5.

The bench scale experiments were done using a bench scale apparatus, which consists mainly of a magnetic stirrer with rod magnet, a glass beaker grade (A) for containing treated solution, and four-digit electronic balance, as shown in Fig. 1.

The pilot scale experiment was carried out in a locally fabricated stainless-steel reactor equipped with a paddle stirrer, heating, or cooling coil and provided with a feeder



**Fig. 1** Bench scale apparatus

tank about 10-L volume for addition of chemicals, as illustrated in Fig. 2.

##### *Experimental technique*

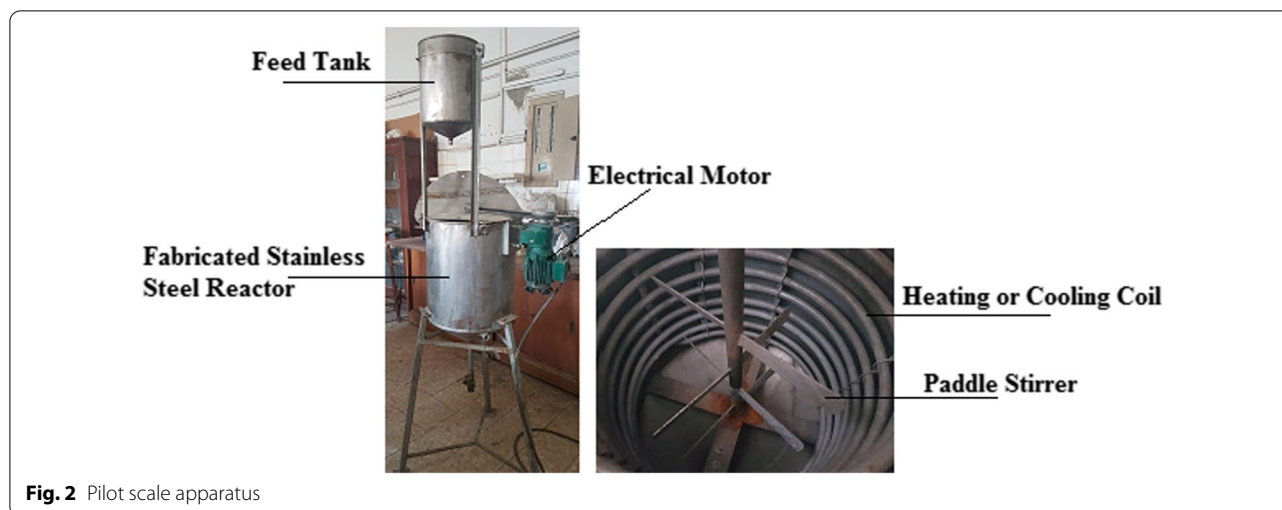
- A certain volume of industrial wastewater was filtered and then mixed well with known amount of alkali (KOH or CaO) for certain time; then, the solution was allowed to precipitate.
- After complete precipitation, solid liquid separation was performed by filtration and then the filtrate was subjected to complete chemical analysis, and the results were compared with the Egyptian Code No. (501/2015) (ECP 501, 2015).
- Results obtained from pilot scale treatment aid in the design of the proposed unit for industrial wastewater treatment.

##### *Bench scale treatment*

*Treatment using (KOH)* Due to the very low pH of the wastewater, the treatment process starts by neutralization of the filtered wastewater by adding 1 N (KOH) solution gradually with continuous stirring about 1 h at ambient temperature, till reaching pH from 6.5 to 7.5. Then, the treated wastewater was subjected to chemical analysis.

*Treatment using quick lime (CaO)* In this step, freshly calcined quick lime (CaO) is used for the neutralization process, which is added as a saturated solution (1 g of CaO/840 ml of water) to the effluent at room temperature, while stirring at about 60 rpm for 1 h, to reach pH (6.5–8.5).

In case of the addition of solid CaO as powder gradually with vigorous stirring (300 rpm) for 1 h, till pH



**Fig. 2** Pilot scale apparatus

reached 8. Turbid solution was obtained and required more than 3 h for settling at the solid phase. After that, the supernatant layer was filtered and analyzed.

**Treatment using both (KOH) and (CaO)** Treatment was started by using  $\text{Ca}(\text{OH})_2$  solution till pH 3; then, a certain weight of CaO powder was added and stirred well till pH = 7.5. After filtration, pH of filtrate was adjusted to 7 by adding (KOH) in solid state. The solution was then left to settle then filtered, and the filtrate was analyzed.

#### **Pilot scale treatment**

In this section, after quick overview, the best results achieved from bench scale experiments were applied on pilot scale.

Raw wastewater (20 L) was stirred with  $\text{Ca}(\text{OH})_2$  solution (16 L) for 20 min at room temperature. Calculated amount of hydrated aluminum sulfate (alum) is added to precipitate the excess chlorides in the solution, then a calculated weight of KOH was added till pH 7.5.

Total solution volume (~36 L) was left to precipitate for one hour. The upper layer about 25 L was clear, and the lower layer about 11 L was a turbid solution. Both upper and lower layers (treated wastewater) were filtered, mixed, and then analyzed.

#### **Results**

In this section, main results obtained from experimental procedure are presented.

#### **Industrial wastewater characterization**

Table 1 shows the complete chemical analysis of the raw wastewater. It was found that: the main pollutants that exceed the permissible limits, according to the Egyptian Code No. (501/2015) (ECP 501, 2015) related to

irrigation of non-edible plants are: the pH, chlorides, fluorides, bicarbonates, and dissolved solids.

The effect of neutralization and treatment processes with different types of alkalis was reported taking into consideration the chemical analysis results of the treated samples.

#### **Bench scale neutralization**

##### **Results of (KOH) neutralization**

After adding about 130 ml of 1 N (KOH) solution to the raw wastewater, the pH reached 6.5–7.5, but chemical analysis of treated wastewater showed an elevation of the dissolved solids to 13,000 mg/L, suspended solids to 113.8 mg/L, and fluorides content was still over the permissible range.

##### **Results of (CaO) neutralization**

The results obtained using  $\text{Ca}(\text{OH})_2$  saturated solution in the treatment process were: pH 7.5, total dissolved solids 4500 mg/L, chlorides 1600 mg/L, fluorides 280 mg/L, and total suspended solids 10.2 mg/L.

On the other hand, the results obtained when adding quick lime as powder in two steps, firstly addition of 3.5 gm gradually with continuous stirring, then let the mixture to settle for half an hour, then filter and measure filtrate pH which was found to be 5.5. To the filtrate, add another 0.1 gm of powder lime, and after vigorous mixing, settling, and filtration, the final filtrate was analyzed.

The results were pH 7, total dissolved solids 2885 mg/L, chlorides 1760 mg/L, fluorides 2.17 mg/L, and total suspended solids = 4.17 mg/L.

#### **Using both (KOH) and (CaO) in neutralization process**

Table 2 shows the analysis results for the final treated water by using both of (KOH) and (CaO).

**Table 1** Complete chemical analysis of industrial wastewater

| Element to be analyzed                       | Results       | Units       | Accepted limits according to Egyptian Code No. (501/2015) maximum limit |
|--|---------------|-------------|---|
| <i>Physical parameters:</i>                  |               |             |   |
| pH   | <b>1</b>      | –           | <b>8.5</b>  |
| Color  | Colorless     | mg/l Pt Co  | Colorless   |
| <i>Physicochemical parameters:</i>           |               |             |   |
| Chloride [Cl <sup>-</sup> ]                  | <b>1574.4</b> | <b>mg/l</b> | <b>400</b>  |
| Sulfate [SO <sub>4</sub> <sup>2-</sup> ]     | 74.47         | mg/l        | 500   |
| Bicarbonate [HCO <sub>3</sub> <sup>-</sup> ] | <b>1125</b>   | <b>mg/l</b> | <b>400</b>  |
| Sodium absorption rate [SAR]                 | 4.3           | mg/l        | 9   |
| Sodium [Na <sup>+</sup> ]                    | 170.85        | mg/l        | 230   |
| Potassium [K <sup>+</sup> ]                  | 220           | mg/l        | –   |
| Magnesium [Mg <sup>++</sup> ]                | 30.629        | mg/l        | 100   |
| Calcium [Ca <sup>++</sup> ]                  | 69.89         | mg/l        | 230   |
| Fluoride [F <sup>-</sup> ]                   | <b>528.17</b> | <b>mg/l</b> | <b>15</b>   |
| Phosphate [PO <sub>4</sub> <sup>+++</sup> ]  | –             | mg/l        | 30  |
| Lithium [Li]                                 | –             | mg/l        | 2.5   |
| Phenol                                       | –             | mg/l        | 0.002   |
| Total dissolved solids [TDS]                 | <b>12,000</b> | <b>mg/l</b> | <b>3000</b>   |
| Total suspended solids [TSS]                 | 1.2           | mg/l        | < 30  |
| Biochemical oxygen demand [BOD]              | 12            | mg/l        | < 400   |
| Aluminum [Al <sup>+++</sup> ]                | 13.7          | mg/l        | 20  |
| Arsenic [As <sup>+++</sup> ]                 | < 0.001       | mg/l        | 2   |
| Beryllium [Be <sup>++</sup> ]                | 0.4           | mg/l        | 0.5   |
| Copper [Cu <sup>++</sup> ]                   | 0.06          | mg/l        | 5   |
| Iron [Fe <sup>++</sup> ]                     | 2.6           | mg/l        | 20  |
| Manganese [Mn <sup>++</sup> ]                | 0.17          | mg/l        | 10  |
| Nickel [Ni <sup>++</sup> ]                   | 0.04          | mg/l        | 2   |
| Lead [Pb <sup>++</sup> ]                     | 0.6           | mg/l        | 10  |
| Selenium [Se]                                | < 0.001       | mg/l        | 0.02  |
| Cadmium [Cd]                                 | < 0.001       | mg/l        | 0.01  |
| Zinc [Zn <sup>++</sup> ]                     | 0.57          | mg/l        | 10  |
| Chromium [Cr]                                | 0.09          | mg/l        | 1   |
| Mercury [Hg]                                 | < 0.001       | mg/l        | 0.002   |
| Vanadium [V]                                 | < 0.001       | mg/l        | 1   |
| Cobalt [Co]                                  | < 0.001       | mg/l        | 5   |
| Boron [B]                                    | 1.28          | mg/l        | 2   |
| Molybdenum [Mo]                              | < 0.001       | mg/l        | 0.01  |

Bold are indicates the high levels of pollutants

Table 3 presents the chemical composition of the precipitate using XRF technique.

#### Pilot scale neutralization

Table 4 shows the complete chemical analysis of the treated wastewater at pilot scale, followed by second-stage treatment for residual chloride removal.

#### Design and construction of industrial scale treatment unit

Based on experimental results of pilot scale, treatment industrial unit of 15 m<sup>3</sup> capacity was designed as illustrated in Fig. 3. It consists of:

- 50-L capacity, vertical cylindrical chemical-resistant tank (material of construction is stainless steel 316), with a variable speed mixer.



**Table 2** The chemical analysis of treated wastewater

| Element to be analyzed                       | Results    | Units       | Accepted limits according to Egyptian Code No. (501/2015) maximum limit |
|--|------------|-------------|---|
| pH   | 7          | –           | 8.5   |
| <b>Chloride [Cl<sup>-</sup>]</b>             | <b>470</b> | <b>mg/l</b> | <b>400</b>  |
| Bicarbonate [HCO <sub>3</sub> <sup>-</sup> ] | 35         | mg/l        | 400   |
| Potassium [K <sup>+</sup> ]                  | 26         | mg/l        | –   |
| Calcium [Ca <sup>++</sup> ]                  | 24         | mg/l        | 230   |
| Fluoride [F <sup>-</sup> ]                   | 0.5        | mg/l        | 15  |
| Total dissolved solids [TDS]                 | 2285       | mg/l        | 3000  |

Bold are indicates the high levels of pollutants

**Table 3** XRF results of the precipitate

| Main constituents                             | (wt.%) |
|---|--------|
| SiO <sub>2</sub>                              | 2.91   |
| Al <sub>2</sub> O <sub>3</sub>                | 0.96   |
| Fe <sub>2</sub> O <sub>3</sub> <sup>tot</sup> | 0.56   |
| TiO <sub>2</sub>                              | 0.04   |
| MgO   | 1.55   |
| MnO   | 0.006  |
| CaO   | 49.10  |
| Na <sub>2</sub> O                             | 0.61   |
| K <sub>2</sub> O                              | 4.09   |
| P <sub>2</sub> O <sub>5</sub>                 | 0.14   |
| SO <sub>3</sub>                               | 0.08   |
| F   | 39.56  |
| Cl  | 0.09   |
| NiO   | 0.004  |
| ZnO   | 0.018  |
| SrO   | 0.278  |
| As <sub>2</sub> O <sub>3</sub>                | 0.003  |
| Total   | 99.999 |

- 350-L capacity, vertical cylindrical—chemical-resistant—cone-shaped bottom reactor (material of construction is stainless steel 316), with both of: a variable speed stirrer and a feeder for material entry and product exit.
- Suitable chemical-resistant water pumps.
- Single cartridge filter housing with filter unit.

## Discussion

### Bench scale neutralization

#### KOH neutralization

Using KOH in the neutralization process increases dissolved solids content due to the formation of potassium fluoride, which is highly soluble in water at room

temperature, which leads to increase in fluorides content. So, according to the above findings, KOH is not recommended to be used alone in the treatment process.

#### CaO neutralization

Using CaO as solution in the neutralization process does not reduce both of total dissolved solids, chlorides, and fluorides contents in treated water down to the permissible limits in the Egyptian Code No. (501/2015) (ECP 501, 2015), so it is not recommended.

Adding quick lime as powder in two steps resulted in both total dissolved solids and fluorides contents within the law permissible limits, while only chlorides content is high.

#### Using both (KOH) and (CaO) in neutralization process

In this case, all pollutants were within the acceptable limits of the Egyptian Code No. (501/2015) (ECP 501, 2015), except chlorides content which was slightly above the permissible limit (470 instead of 400).

XRF technique illustrates that the CaO and F were the main constituents (88.7%) in the precipitate, which revealed that the fluoride contaminants were decreased in the treated wastewater.

There are many processes for chlorides removal, for example by reacting chlorine extractant with H<sup>+</sup> and Cl<sup>-</sup> and then separating chlorides from wastewater by complex extraction (Yiwen et al. 2018); however, this method is suitable for wastewater with high chlorine concentration (15,485 mg/L) which can be extracted for recycling and reuse (Yiwen et al. 2018).

Some investigators exhibited high percentage removal efficiencies for chloride (80.70% ± 2.01%) and fluoride ions (93.18% ± 1.67%) from real wastewater samples by absorption using eggshells (Stevens and Batlokwa 2018).

Also, previous studies revealed that removal of excess chlorides can be achieved by chemical precipitation of insoluble Friedel’s salt using calcium and

**Table 4** The chemical analysis of treated industrial wastewater

| Element to be analyzed                           | Results      | Units       | Accepted limits according to Egyptian Code No. (501/2015) maximum limit |
|--|--------------|-------------|---|
| <i>Physical parameters:</i>                      |              |             |   |
| <b>pH</b>  | <b>6.85</b>  | ---         | <b>8.5</b>  |
| Color  | Colorless    | mg/l Pt Co  | Colorless   |
| <i>Physicochemical parameters:</i>               |              |             |   |
| <b>Chloride [Cl<sup>-</sup>]</b>                 | <b>333</b>   | <b>mg/l</b> | <b>400</b>  |
| Sulfate [SO <sub>4</sub> <sup>2-</sup> ]         | 85           | mg/l        | 500   |
| <b>Bicarbonate [HCO<sub>3</sub><sup>-</sup>]</b> | <b>61</b>    | <b>mg/l</b> | <b>400</b>  |
| Sodium absorption rate [SAR]                     | 4.3          | mg/l        | 9   |
| Sodium [Na <sup>+</sup> ]                        | 163          | mg/l        | 230   |
| <b>Potassium [K<sup>+</sup>]</b>                 | <b>75</b>    | <b>mg/l</b> | –   |
| Magnesium [Mg <sup>++</sup> ]                    | 30           | mg/l        | 100   |
| <b>Calcium [Ca<sup>++</sup>]</b>                 | <b>215.8</b> | <b>mg/l</b> | <b>230</b>  |
| <b>Fluoride [F<sup>-</sup>]</b>                  | <b>12.46</b> | <b>mg/l</b> | <b>15</b>   |
| Phosphate [PO <sub>4</sub> <sup>+++</sup> ]      | –            | mg/l        | 30  |
| Lithium [Li]                                     | –            | mg/l        | 2.5   |
| Phenol   | –            | mg/l        | 0.002   |
| <b>Total dissolved solids [TDS]</b>              | <b>2472</b>  | <b>mg/l</b> | <b>3000</b>   |
| <b>Total suspended solids [TSS]</b>              | <b>2.2</b>   | <b>mg/l</b> | <b>&lt; 30</b>  |
| Biochemical oxygen demand [BOD]                  | 13           | mg/l        | < 400   |
| Aluminum [Al <sup>+++</sup> ]                    | 15.3         | mg/l        | 20  |
| Arsenic [As <sup>+++</sup> ]                     | < 0.001      | mg/l        | 2   |
| Beryllium [Be <sup>++</sup> ]                    | 0.3          | mg/l        | 0.5   |
| Copper [Cu <sup>++</sup> ]                       | 0.12         | mg/l        | 5   |
| Iron [Fe <sup>++</sup> ]                         | 1.9          | mg/l        | 20  |
| Manganese [Mn <sup>++</sup> ]                    | 0.27         | mg/l        | 10  |
| Nickel [Ni <sup>++</sup> ]                       | 0.06         | mg/l        | 2   |
| Lead [Pb <sup>++</sup> ]                         | 0.49         | mg/l        | 10  |
| Selenium [Se]                                    | < 0.001      | mg/l        | 0.02  |
| Cadmium [Cd]                                     | < 0.001      | mg/l        | 0.01  |
| Zinc [Zn <sup>++</sup> ]                         | 0.38         | mg/l        | 10  |
| Chromium [Cr]                                    | 0.11         | mg/l        | 1   |
| Mercury [Hg]                                     | < 0.001      | mg/l        | 0.002   |
| Vanadium [V]                                     | < 0.001      | mg/l        | 1   |
| Cobalt [Co]                                      | < 0.001      | mg/l        | 5   |
| Boron [B]  | 1.31         | mg/l        | 2   |
| Molybdenum [Mo]                                  | < 0.001      | mg/l        | 0.01  |

Bold are indicates the high levels of pollutants

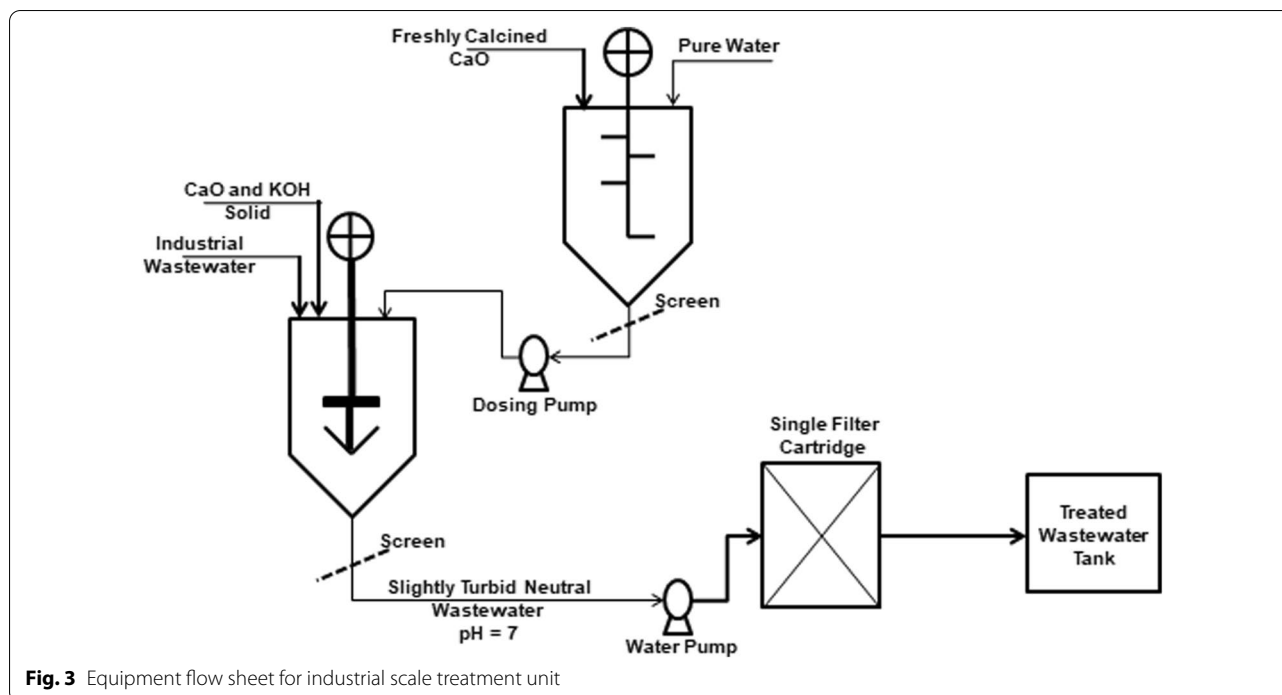
aluminum compounds mainly calcium hydroxide and sodium aluminates as reagents (Wang et al. 2018), which is applied in the actual study to minimize chloride in the solution.

In the last decades, new treatment processes were found, which are less in energy consumption and environmentally friendly than conventional methods. These methods include nanofiltration (NF)

membranes (Hao et al. 2020) and ceramic membranes (Amin et al. 2016, 2018, 2020; Abdallah et al. 2018).

#### Pilot scale neutralization

Fluorides, chlorides, pH, and total dissolved solids are acceptable to be used in the irrigation of non-edible plants, according to the Egyptian Code No. (501/2015) (ECP 501, 2015) after proposed pilot experimental scheme.



### Preliminary cost evaluation

In this study the essential chemicals used for fluorides removal from industrial wastewater are: commercial quick lime or CaO (60 \$/t) from Egyptian local market and KOH cost (from 850 \$ to 1000 \$/ton) (Inner Mongolia Pulis Chemical Co. Ltd, China, 2021), which is much more expensive. Even though fluoride removal from aqueous solutions has been broadly studied, but only few investigations about the cost were found (Jadhao et al. 2019). Elazhar et al. (2009) stated that operating cost was 0.212 \$/m<sup>3</sup> for fluoride removal from 2.32 to 1 mg/L, while Lahnid et al. (Lahnid et al. 2008) mentioned that treatment of 1 m<sup>3</sup> of wastewater costed 0.154 \$.

In this paper operating cost is about 0.159 \$/m<sup>3</sup> for fluoride removal from more than 500 mg/L to about 2 mg/L which is lower than the limits of published costs regarding the fluoride's removal in previous work (Inner Mongolia Pulis Chemical Co. Ltd, China, 2021; Elazhar et al. 2009).

It is recommended to conduct more detailed techno-economic study to assure more precise cost for fluorides removal from industrial wastewater.

### Conclusions

From this investigation, it is concluded that:

- The proposed treatment procedure succeeded in treatment of fluorides, chlorides, bicarbonates, and total dissolved solids, as main pollutants.
- Quick lime is more efficient than potassium hydroxide in treatment of wastewater contaminated by fluorides.
- The recommended treatment procedure succeeded in the removal of required value of fluorides as contaminant.
- Preliminary economic evaluation revealed that operating cost for 1 m<sup>3</sup> of industrial wastewater treatment is about 0.159 \$.

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### Author contributions

G.E.D. conceived the presented idea and developed the theory and performed the design of the experiments. Sh.K.A. performed the experimental work, the computations, and wrote the manuscript. N.K.A. performed the analysis and the experimental work. S.I.H. conceived of the presented idea and developed the theory, performed the design of the experiments, the experimental work, the computations, and wrote the manuscript. All authors discussed the results and contributed to the final manuscript.

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waste water to permit its use in irrigation of unfruitful tree forests, according to Egyptian Code No. (501/2015).

#### Availability of data and materials

Not applicable.

#### Declarations

#### Ethics approval and consent to participate

Not applicable.

#### Consent for publication

Not applicable.

#### Competing interests

The authors declare that they have no competing interests.

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