

## Activated alumina as adsorbent for fluoride and nitrate ions removal from synthesized photovoltaic cells manufacturing effluents

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### ABSTRACT

Considerable volumes of ultrapure water and chemicals are necessary during photovoltaic cells manufacturing, consequently a large amount of wastewater needs to be treated. The present study investigates the activated alumina for fluoride and nitrate ions contaminate adsorptions. Analyses of experimental data were done in order to understand the adsorption phenomena in which pollutants forms intermediates molecules by reacting onto the adsorbent surface, that intermediates reaction can be expressed by Langmuir and Freundlich's adsorption isotherms models. While both ions were found to be adsorbed following the Langmuir model, the nitrates' elimination was found to be more so consistent with the Freundlich model. A significant nitrate ions removal percentage (near to 67%), and an adsorption capacity more than 1.8 mg/g were attained; while for the fluoride ions removal an additional treatment is necessary since a lower removal percentage was obtained with an adsorption capacity of 0.2 mg/g, and using a longer treatment time; also the concentration of fluoride ions in the treated solutions are higher than that recommended by World Health Organization. These results can be used to improve the pollutants removal recoveries at continuous mode and at a large scale. When one considers an additional suitable treatment, the obtained treated ultrapure water can be envisaged to be recycled into the process. Furthermore, from a techno-economic point of view, the cost of the photovoltaic cells production should decrease considerably, since ultrapure water is expensive and its consumption is high in this industry.

*Keywords:* Fluoride; Nitrate; Wastewater treatment; Adsorption; Activated alumina

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### 1. Introduction

The last two decades have witnessed an exponentially growing interest in renewable energy production systems, and the Intergovernmental Panel on Climate Change (IPCC) in Switzerland in 2023 is but one example among many undertaken actions that express the importance of developing a suitable industry based on green energy [1].

Photovoltaic (PV) energy conversion system industry is a leader in this regard, albeit not totally green, and a vigilant consideration of potential environmental risks linked to PV manufacturing remain necessary [2]. Indeed, in semiconductor and PV manufacturing plants, a large quantity of hydrofluoric acid (HF) is currently used for wafer etching and quartz-cleaning operations. It has been found that acid fluoride-containing wastewater contributes to 40%

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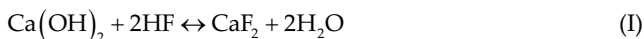
of hazardous waste produced from that manufacturer. Fluoride concentrations, up to 3,500 mg/L, are found in this type of wastewater considerable volumes of water, ultrapure water (UPW) and chemicals are necessary during PV cells manufacturing [3–7], that eventually find their way as contaminated wastewaters. These must then comply with the norms and proper regulations in order to maintain a friendly environment and good public health. The dominant pollutants in these effluents are  $F^-$  and  $NO_3^-$  ions, derived from an extensive use of HF and nitric acid ( $HNO_3$ ) during the silicon wafers production step.

The release of such discharges into the environment represents an important warning [8–15].  $F^-$  ions in acceptable concentrations in drinking water is vital for human health, especially for children below 8 y old. However, beyond a threshold, it usually produces adverse effects on body metabolism and leads to dental and skeletal fluorosis, lesions of endocrine glands, thyroid and liver [12,16–20]. Due to its high toxicity, industrial wastewater containing  $F^-$  ions is severely controlled. The current discharge standards for wastewater containing  $F^-$  ions vary according to different countries; Algeria and Taiwan recommend 15 mg/L.

The second most common pollutant is the  $NO_3^-$  ion which also exhibit harmful effects on human health (Methaemoglobinemia and other diseases) [21–23], as well as on the ecosystem (eutrophication phenomena). Besides infant mortality, high concentrations of  $NO_3^-$  in wastewater and drinking water were correlated with stomach cancer, central nervous system defect, birth defects and hypertension [19,24].

Several recent studies reported that activated alumina (AA) can be used as adsorbent to remove  $F^-$ ,  $NO_3^-$ , and other pollutant ions from wastewaters [25–27]. Since the wastewaters and the contaminated UPW resulted from PV industry contains  $F^-$  and  $NO_3^-$  ions at high concentrations [7,10,22,28], the direct discharge of such solutions may represent a huge threat for the environment.

Real wastewaters from the Semiconductor Research Center for Energy (Algiers, Algeria) were formed during the etching of silicon wafers with a mixture of hydrofluoric acid, nitric acid and acetic acid, followed by several rinsing operations with ultrapure water, until the neutrality of the rinsing water was reached [28]. Most commonly, fluoride ions are removed by forming calcium fluoride ( $CaF_2$ ) after adding lime. Neutralization can be described according to the following reaction:



It has been found that the wastewater treated according to the precipitation process still contains high concentration of dissolved fluoride. Usually, the concentration of fluoride in the treated wastewater can reach 20–100 mg/L. Consequently, another decontamination process must be performed after calcium precipitation to remove residual fluoride, typically the concentrations of nitrate and fluoride anions were of 88.2 and 40.6 mg/L, respectively [7,28]. As  $F^-$  and  $NO_3^-$  ions originated from two sources; expended acids baths and waste rinse ultrapure water, in this study 30 mg/L for fluoride and 50 mg/L for nitrates as initial concentrations were used in order to simulate the three last rinsing steps using exclusively ultrapure water, consequently

the pollutants initial concentrations of both pollutants are less than that mentioned above. For the adsorption phenomena study, Langmuir and Freundlich isotherms approximation were applied to understand the adsorption mechanism of pollutants, which are the most applied approximation for the initial adsorption study and defining the best adsorption models because of their simplicity and ability to quantify the distribution of functional sites of adsorbent. Langmuir-type adsorption is a monolayer (surface) adsorption, which implies that a large surface area will result in a higher adsorption capacity; and Freundlich-type adsorption is considered a multilayer adsorption process.

In this study we wish to report herein our contribution to the solution of the wastewaters from the PV factory problem, through the use of AA as adsorbent. Indeed, we found that the polluting  $F^-$  and  $NO_3^-$  ions could be removed efficiently from mimicked PV manufacturing wastewaters through adsorption on AA.

## 2. Materials and methods

### 2.1. Materials

Prepared solutions mimicking the PV cells rinsing wastewaters were used for the study of the experimental parameters that affect the performances of the fluoride and nitrate ions removal by adsorption on AA. For the adsorption procedure, tests were performed in 1 L beakers. Stirring was carried out using a Jar Test Apparatus (DAIHAN SCIENTIFIC WISE STIR JTM6C, South Korea). The AA was purchased from MERCK (USA), with surface area of 250 m<sup>2</sup>/g and a granulometry varying from 0.063 to 0.200 mm.  $NaNO_3$  and NaF were analytical grade and were purchased from Biochem Chemopharma (Montreal, Quebec) and Sigma-Aldrich (USA), respectively. For the samples analysis, an ionometer (HANNA HI 4222, USA), and a specific electrode for each ion (nitrate half-cell electrode: HI 4013, and fluoride combined electrode: 9655C) were used.

### 2.2. Methods

The batch tests were carried out at ambient temperature (20°C–25°C) using synthetic solutions prepared by dissolving separately  $NaNO_3$  and NaF in deionized water. For the adsorption experimental tests, in which a desired amount of the adsorbent was mixed with the above-prepared solution at a fixed pH (that was adjusted by adding few drops of an acid or basic solutions at 0.1 N), samples were taken periodically from an on-going stirring and analyzed by potentiometry using an ionometer (HANNA HI 4222), a specific electrode for nitrate ion (nitrate half-cell electrode: HI 4013) and interfering suppressant ionic strength adjuster (ISISA) solution, whenever nitrate ions analysis was involved. The residual fluoride concentration in each sample was determined using the ion selective electrode (fluoride combined electrode: 9655C) and total ionic strength adjustment buffer (TISAB) solution.

#### 2.2.1. Adsorption isotherms

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. Two adsorption

isotherms (1) and (2) were used to fit the equilibrium data namely, Langmuir and Freundlich. Their applicability was validated through the correlation coefficients ( $R^2$ ).

The Langmuir equation can be linearized by Eq. (1):

$$\frac{1}{Q_e} = \left( \frac{1}{K_1 \times Q_m} \right) \left( \frac{1}{C_e} \right) + \frac{1}{Q_m} \quad (1)$$

where  $C_e$  represents the equilibrium concentration in liquid phase, mg/L,  $Q_m$  represents the monolayer adsorption capacity, mg/g,  $K_1$  the Langmuir constant related to the free adsorption energy, L/mg.

The Freundlich equation can be linearized by Eq. (2):

$$\ln Q_e = \ln K_f + \left( \frac{1}{n} \right) \ln C_e \quad (2)$$

where  $K_f$  represents the Freundlich constant indicative of the adsorption capacity of the adsorbent, mg/g,  $1/n$  indicates the intensity of the adsorption.

### 3. Results and discussion

The linear plot of Langmuir isotherm for  $F^-$  ions adsorption shows that, the model correlated well with experimental data with a regression coefficient  $R^2$  value of 0.974, as well for the linear plot of Freundlich isotherm with an  $R^2$  value of 0.938.

From the experimental data, it can be concluded that the  $F^-$  ions adsorption mechanism onto AA can be determined using Langmuir and Freundlich's adsorption isotherm equation. Both isotherms show well-fitted experimental data with coefficients of determination of  $R^2 > 0.9$ , suggesting that both approximations are suitable for describing the adsorption mechanism. Langmuir equation provided an excellent mathematical approximation to describe the adsorption equilibrium, where the plot fitted the experimental data with  $R^2 = 0.974$ , which suggested the monolayer adsorption, while Freundlich plot has a lower regression coefficient of 0.938. However, the intrinsic parameters of Langmuir isotherm have negative values (Table 1) of  $K_1$  and  $Q_m$ ; that negative values are possibly due to an ineffective functional site at the adsorbent surface to bind  $F^-$  ions using a high value of adsorbent mass. Consequently, adsorption reaches the saturation point; therefore adsorption is suitable for the heterogeneous sites with non-uniform distribution of energy level. These present results are in accordance with that mentioned by similar studies [29,30] from other references.

The linear plot of Langmuir isotherm for  $NO_3^-$  ions adsorption onto AA and the calculated parameters along with regression coefficient  $R^2$  value approaching to one

( $R^2 > 0.9$ ), clearly suggest that Langmuir isotherm follows a good relation of  $NO_3^-$  ions adsorption onto AA. The linear plot of Freundlich equation for  $NO_3^-$  ions adsorption has also an  $R^2$  value approaching to one, evidently advice that Freundlich isotherm model fit well with the  $NO_3^-$  ions adsorption onto AA. From the intrinsic parameters it can be concluded that both models can be representative of the  $NO_3^-$  ions adsorption since there is a good mathematical approximations for both cases with  $R^2$  values approaching to one, while Freundlich equation is more suitable to describe the adsorption mechanism, where the linearized plot gives positive values of  $K_f$  and  $n$  (Table 2), although the Freundlich isotherm model was found best fitting with the experimental data as its expresses higher  $R^2$  value ( $0.992 > 0.957$ ); also the calculated values of ' $n$ ' that shows the intensity between adsorbate and adsorbent, prove that the adsorption of nitrate ions onto AA is favorable as its value is higher than 1.

Maximum adsorption capacity ( $Q_m$ ) for complete monolayer coverage was found to be 5.790 mg/g for the nitrate ions adsorption onto AA, interestingly enough, consideration of  $Q_m$  values strongly suggest that the nitrate ions are more favorable toward adsorption than the fluoride ions, (5.790 mg/g for nitrates vs. -1.368 mg/g for fluorides), in which the maximum adsorption capacity is negative.

From a review paper [29] that some research found that  $F^-$  ions adsorption can be expressed by Langmuir isotherm model and others find that  $F^-$  ions adsorption can be expressed by Freundlich isotherm model, this difference might be due to the AA having different characteristics and the different conditions in which experiments were done.

#### 3.1. Effect of the (initial concentration/adsorbent quantity) ratio

The effects of the  $R$  ratio (the initial concentration of the pollutants (mg/L)/adsorbent quantity (g/L)), that is a mass ratio expressed by (mg/g), on the  $F^-$  ions removal were studied at a neutral pH. The results are given in Fig. 1. The tests confirmed that fluoride ions elimination depends on AA quantity.

Fig. 1 shows the results obtained for the  $R$  ratio values of 2 mg/g and less for an initial fluoride concentration of 30 mg/L at the contact time of 30 min. Similarly to other research studies [26,31], by decreasing the  $R$  value that correspond to the increase of AA quantity, the adsorption capacity decrease, it seems that an equilibrium is reached from 10 min, in which no further removal at the AA dosage corresponding of an  $R$  ratio value less than 2 mg/g occurred, that is possibly due to that more active sites of adsorbent remained unsaturated during the fluoride adsorption process.

The effects of the initial concentration/adsorbent quantity ratio ( $R$ ) on the  $NO_3^-$  ions removal at a neutral pH are shown in Fig. 2. The tests confirmed that their elimination depends strongly on the AA quantity.

Table 1  
Langmuir's parameters

Ions	$Q_m$ (mg/g)	$K_1$ (L/mg)	$R^2$
Fluoride	-1.368	-0.612	0.974
Nitrate	5.790	0.007	0.957

Table 2  
Freundlich's parameters

Ions	$K_f$ (mg/g)	$n$	$R^2$
Fluoride	1.965	0.691	0.939
Nitrate	0.183	1.899	0.992

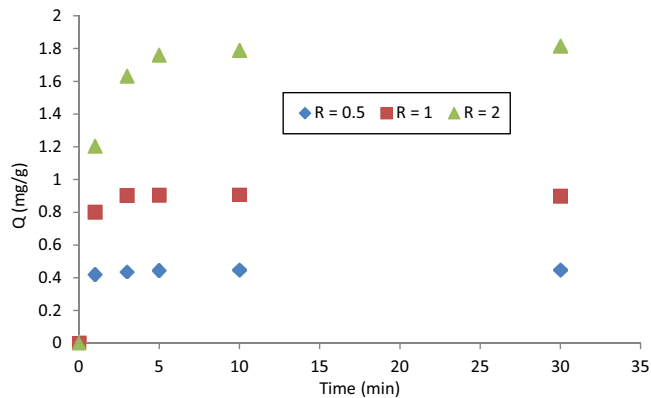


Fig. 1. Fluoride ions removal efficiency for different (initial concentrations/adsorbent quantities)  $R$  ratio (mg/g) ( $C_0 = 30$  mg/L;  $\text{pH} = 7 \pm 0.2$ ).

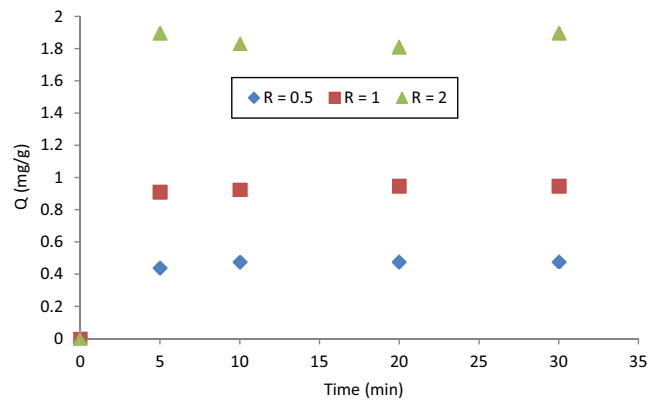


Fig. 2. Nitrate ions removal efficiency for different (initial concentrations/adsorbent quantities)  $R$  ratio (mg/g) ( $C_0 = 30$  mg/L;  $\text{pH} = 7 \pm 0.2$ ).

Fig. 2 shows the results obtained for the  $R$  ratio values of 2 mg/g and less for an initial nitrate concentration of 30 mg/L at the contact time of 30 min. By decreasing the  $R$  value that corresponds to the increase of the adsorbent quantity, the adsorption capacity decrease. These results are in the same trend to that of other research works [26,31], in which it seems that an equilibrium is reached from 5 min, no further removal at the AA dosage corresponding of an  $R$  ratio value less than 2 mg/g is possible, that is probably due to that more active sites of adsorbent persisted unsaturated during the reaction of the nitrate adsorption.

### 3.2. Effect of the initial pH

The pH is a controlling factor for any kind of pollutants adsorption processes from an aqueous solution. The surface properties of adsorbents, the ionic state of functional groups and the pollutants species all depend on pH. In this present experiment tests, the desired pH values were obtained by adding few drops of acid or basic HCl or NaOH solutions at 0.1 N to the initial solution. The initial fluoride ions concentration of 30 mg/L and an AA amount of 30 g/500 mL were used. The results are presented in Fig. 3, indicating that

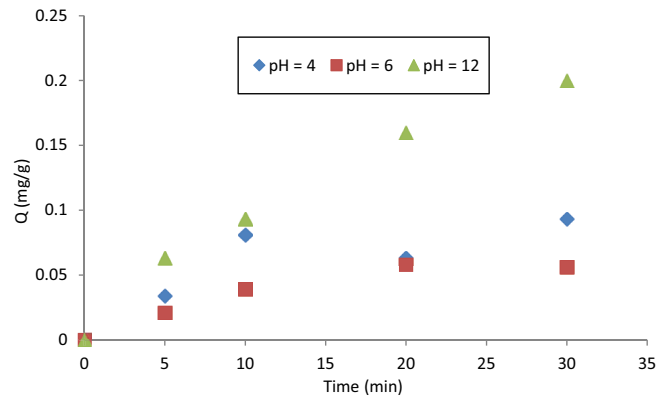


Fig. 3. Fluoride ions removal efficiency at different pH ( $T^\circ = 21^\circ\text{C} \pm 3^\circ\text{C}$ ).

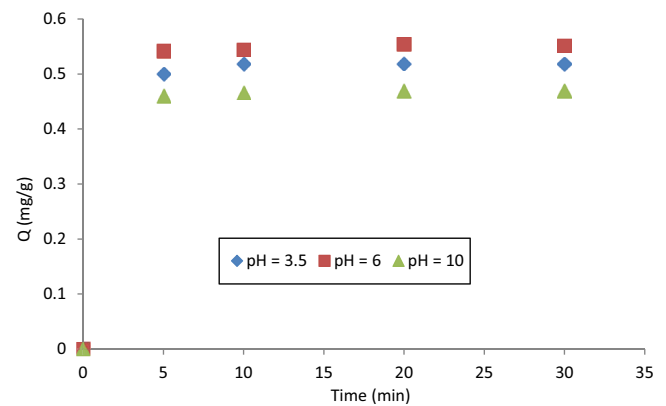


Fig. 4. Nitrate ions removal efficiency at different pH ( $T^\circ = 21^\circ\text{C} \pm 3^\circ\text{C}$ ).

removal was best using a basic medium corresponding an initial pH value of 12.

It seems that the presence of the  $\text{OH}^-$  ions increase the fixation of the  $\text{F}^-$  ions on the adsorbent surface. One possible explanation is the fact that in general, ions with smaller intrinsic crystal radius have higher hydration numbers. Since the crystal ionic radius of  $\text{F}^-$  is 0.116 nm and is smaller than 0.152 nm, that of the  $\text{OH}^-$  ion; there is more electric charge diffusion for the ion with larger crystal ionic radius, [19,20,23]. Since  $\text{F}^-$  ions is less charged than  $\text{OH}^-$  ions, and the adsorbent surface is possibly charged negatively, then the repulsions phenomena between the  $\text{F}^-$  ions and the adsorbent surface will be less than in the case of the  $\text{OH}^-$  ions and the AA surface, this might be favorable for the fluoride ions to be fixed on the adsorbent surface.

The effect of the pH on the nitrates ion adsorption on AA was studied using various pH values comprised in the interval from 3 to 10. The desired pH values were obtained by adding few drops of solutions of  $\text{H}_2\text{SO}_4$  or NaOH at 0.1 N. An initial nitrate concentration of 50 mg/L and an AA amount of 30 g/500 mL were used. Results are presented in Fig. 4.

The removal efficiency decreased while in basic medium. Such may be due to a possible removal competition between the hydroxide ions ( $\text{OH}^-$ ) and the nitrate ions ( $\text{NO}_3^-$ ), which

Table 3

Experimental parameters of the F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions eliminations by adsorption on activated alumina

Ions	Initial concentration (mg/L)	pH	Removal percentage (%)	Final concentration (mg/L)	WHO authorized value in wastewater (mg/L)	Treatment time (min)	Recommendations
Fluoride	30	12	36.60	19.02	15	40	An additional treatment is needed
Nitrate	50	6	66.44	16.78	50	10	This treatment is sufficient

can be interpreted by the repulsion phenomena between the nitrate ions and the AA surface that might be negatively charged in the basic medium. Indeed, one can deduce that the nitrate removal rate at basic pH was the lowest, and the acid and neutral one were in the same order. The results are in accordance with others research works [26], in which a best removal percentage was obtained for a slightly acidic medium with a pH value near to 6, also there is no significant removal percentage increase after 10 min of treatment time, then this time can be applied in this treatment under these experimental conditions.

These results are interesting enough, which correspond to all tests at batch mode, that guide and give us an idea of the expected results range for an application, in which a study at a continuous mode is necessary and after a results optimization, tests at pilot scale should be done in order to envisage an industrial application; particularly when a suitable additional treatment is considered in the case of F<sup>-</sup> ions elimination, and after achieving higher removal percentage, the treated UPW can be recycled into the process, this reaching the zero discharge concept.

A synthesis of the various tested conditions led us to define the suggested conditions for the removal of both ions. Those are reported in Table 3, along with some recommendations.

#### 4. Conclusions, recommendations and future perspectives

The obtained results from this research work, hence suggesting an interesting alternative to the current process which is more expensive and is not fully environmentally friendly, indeed this study allowed understanding how the F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions, that are the main pollutants in the solar cells rinsing wastewater, can be removed by adsorption process using AA as adsorbent.

Significant F<sup>-</sup> ions removals (near to 40%) were obtained after 40 min of treatment period for an initial concentration of 30 mg/L in a basic medium, in which a suitable additional treatment is recommended for increasing the removal percentage. In the case of the NO<sub>3</sub><sup>-</sup> ions removal, using a slightly acid medium, a higher percentage removal was obtained that was near to 70% after 10 min only, for an initial concentration of 50 mg/L; remaining pollutant concentration in the treated solutions were found to be way below the amount recommended by the World Health Organization (WHO).

For future investigations, a study for certain experimental parameters, such as variation of initial concentration of both ions, lower addition of adsorbent mass corresponding of different values or R ratio at a slightly acid medium for

NO<sub>3</sub><sup>-</sup> removal, and at a basic medium of pH ≥ 12 for F<sup>-</sup> ions removal, and the influence of the presence of the co-pollutants ions should be done; also other isotherm approximations should be applied for understanding the adsorption mechanisms by studying these different parameters. The obtained results can be considered to further optimize both pollutants removal recovery process at batch mode, continuous mode, and tests at pilot scale should be done in order to envisage an industrial application.

From a techno-economic point of view, in fact the recycling the treated ultrapure water in the process will decrease considerably the price of the photovoltaic cells manufacturing, since the UPW cost is expensive and its consumption in this industry as well as for the semiconductor industry is very high.

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#### Compliance with ethical standards

#### Conflict of interest

The authors find no conflict of interest in this work.

#### References

- <https://www.ipccc.ch/2023/03/20/press-release-ar6-synthesis-report/>
- N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, N. Mameri, Study on the treatment of photovoltaic wastewater using electrocoagulation: fluoride removal with aluminium electrodes-characteristics of products, *J. Hazard. Mater.*, 169 (2009) 65–69.
- Y.S. Tsoo, J.M. Gee, P. Menna, D.S. Strebkov, A. Pinov, V. Zadde, Environmentally Benign Silicon Solar Cell Manufacturing, Presented at the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, 6–10 July, 1998.
- N. Drouiche, N. Ghaffour, H. Lounici, M. Mameri, Electrocoagulation of chemical mechanical polishing wastewater, *Desalination*, 214 (2007) 31–37.
- <http://engineeredenvironment.tumblr.com/post/30464844411/water-use-in-the-semiconductor-manufacturing>
- <http://www.wmconlon.com/wp-content/uploads/papers/Semicon.pdf>
- S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, Development of an integrated electrocoagulation–flotation for semiconductor wastewater treatment, *Desal. Water Treat.*, 55 (2015) 1422–1432.

- [8] <https://www.envirochemie.com/en/news-events/news/sustainable-water-technology-for-photovoltaic-module-production/>
- [9] <https://www.bluetechresearch.com/tools/web-briefings/ultrapure-water-technologies>
- [10] N. Drouiche, F. Djouadi-Belkada, T. Ouslimane, A. Kefai, J. Fathi, E. Ahmetovic, Photovoltaic solar cells industry wastewater treatment, *Desal. Water Treat.*, 51 (2013) 5965–5973.
- [11] A. Cheikh, H. Grib, N. Drouiche, N. Abdi, H. Lounici, N. Mameri, Water denitrification by a hybrid process combining a new bioreactor and conventional electro dialysis, *Chem. Eng. Process. Process Intensif.*, 63 (2013) 1–6.
- [12] <https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/water-quality/guidelines-canadian-drinking-water-quality-summary-table.html>
- [13] D. Căilean, C. Teodosiu, I. Volf, B. Ciobanu, Occurrence and Associated Risk of Nitrates/Nitrites in the Ground Waters from the North-Eastern Part of Romania, L.I. Simeonov, M.A. Hassanien, Eds., *Exposure and Risk Assessment of Chemical Pollution – Contemporary Methodology*, NATO Science for Peace and Security Series C: Environmental Security, Springer, Dordrecht, 2009. [https://doi.org/10.1007/978-90-481-2335-3\\_29](https://doi.org/10.1007/978-90-481-2335-3_29)
- [14] V.W. Chen, R.R. Abu-Elyazeed, D.E. Zavala, Risk factors of gastric precancerous lesions in a high-risk Colombian population. II. Nitrate and nitrite, *Nutr. Cancer*, 13 (1990) 67–72.
- [15] D. Forman, Are nitrates a significant risk factor in human cancer?, *Cancer Surveys*, 8 (1989) 443–458.
- [16] C.Y. Hu, S.L.S. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, *Water Res.*, 37 (2003) 4513–4523.
- [17] O. Barbier, L. Arreola-Mendoza, L.M. Del Razo, Molecular mechanisms of fluoride toxicity, *Chem. Biol. Interact.*, 188 (2010) 319–333.
- [18] M. Pontié, C.K. Diawara, A. Lhassani, J.-C. Schrotter, Traitement des eaux destinées à la consommation humaine [Treatment of water intended for human consumption], *Fluor et Environnement [Fluor Environ.]*, 301–302 (2006) 106–112.
- [19] S.S. Waghmare, T. Anfir, Fluoride removal from water by various techniques: review, *Int. J. Innovative Sci. Eng. Technol.*, 2 (2015) 560–571.
- [20] E. Ergun, A. Tor, Y. Cengeloglu, I. Kocak, Electro dialytic removal of fluoride from water: effects of process parameters and accompanying anions, *Sep. Purif. Technol.*, 64 (2008) 147–153.
- [21] F. Djouadi Belkada, Nitrates Adsorption Assays as a First Treatment Step for the Synthetic Photovoltaic Factory Effluents, Presented at the 1st International Conference on Materials for Energy and Environmental Engineering, ICM3E'14, Algiers, Algeria, 23–25 November, 2014.
- [22] F. Djouadi Belkada, O. Kitous, N. Drouiche, S. Aoudj, O. Bouchelaghem, N. Abdi, H. Grib, N. Mameri, Electro dialysis for fluoride and nitrate removal from synthesized photovoltaic industry wastewater, *Sep. Purif. Technol.*, 204 (2018) 108–115.
- [23] L. Banasiak, A.I. Schäfer, Removal of boron, fluoride and nitrate in electro dialysis in the presence of organic matter, *J. Membr. Sci.*, 334 (2009) 101–109.
- [24] N. Abbas, F. Deeba, M. Irfan, M.T. Butt, N. Jamil, R.A. Khan, Treatability study of arsenic, fluoride and nitrate from drinking water by adsorption process, *J. Chem. Soc. Pak.*, 36 (2014) 1–4.
- [25] K. Rakesh, S. Prabhakar, K.A. Abhay, K.S. Rakesh, Equilibrium sorption of fluoride on the activated alumina in aqueous solution, *Desal. Water Treat.*, 197 (2020) 224–236.
- [26] S. Ramalingam, A. Subramania, Effective removal of nitrates from the drinking water by chemical and electrochemical methods, *Eng. Sci.*, 15 (2021) 80–88.
- [27] G. Yujia, Y. Kun, F. Jinxiang, W. Juliang, Q. Weiyi, Manganese modified activated alumina through impregnation for enhanced adsorption capacity of fluoride ions, *Water*, 14 (2022) 1–15.
- [28] H. Tounsi, T. Chaabane, K. Omine, V. Sivasankar, H. Sano, M. Hecini, A. Darchen, Electrocoagulation in the dual application on the simultaneous removal of fluoride and nitrate anions through respective adsorption/reduction processes and modeling of continuous process, *J. Water Process Eng.*, 46 (2022) 1–13.
- [29] S.S. Madhu, S.A. Jai. Recent advances in defluoridation of water using alumina-based adsorbents: a review, *Int. J. Res. Eng. Sci.*, 11 (2023) 113–121.
- [30] D.S. Perwitasari, Y.A.Y. Pracesa, M.A. Pangestu, P.S. Tola, Langmuir and Freundlich isotherm approximation on adsorption mechanism of chrome waste by using tofu dregs, *Nusantara Sci. Technol. Proc.*, (2021) 106–112.
- [31] F. Gorzin, M.M.B.R. Abadi, Adsorption of Cr(VI) from aqueous solution by adsorbent prepared from paper mill sludge: kinetics and thermodynamics studies, *Adsorpt. Sci. Technol.*, 36 (2018) 149–169.