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Application of the Doehlert design for the defluoridation of industrial wastewater by adsorption onto natural clay

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ABSTRACT

Following the increased demand for water in addition to water resources' strain, treatments of polluted water allow its reutilization after getting rid of all the impurities. In this work, the defluoridation of industrial wastewater by adsorption on natural clay by applying the Doehlert design was investigated. The optimized factors were the mass of clay chosen in the range 2–6 g, the concentration of fluoride ions which varies from 2,000 to 4,000 mg L^{-1}, the pH of the medium opted in the range 2–9 and the contact time is taken varying between 20 and 40 min. The experimental response was fluoride levels in used water were considerably reduced. The elsewhere cited factors influenced the performance of the wastewater defluoridation and the quality of the rejected water after application of the Doehlert design. Herein, it is possible to determine the optimum conditions for the treatment of industrial water discharge by natural clay. The application of these conditions on a sample of industrial wastewater discharge treated with this clay gave rise to a remarkable defluoridation rate of around 99.6% which corresponded to a fluoride concentration value reduced from 4,320 mg L^{-1} contained in the wastewater to the standard value of 11.2 mg L^{-1} contained in the treated one.

Keywords: Industrial wastewater; Adsorption; Natural clay; Defluoridation; Doehlert design

1. Introduction

During the last decades, the water demand has become too pressing and countries are in an almost total water shortage. Therefore, the galloped demography and industrial development consume huge amounts of water which resulted in a gap between availability and demand [1–4]. These facts requires water saving by finding ways to depollute the quantities of water discharged by industry. The supply and the treatment of water today represent the first item of environmental expenditure for industrialists. The scarcity of pure drinking water has forced producers to diversify their sources of soil supply. Groundwater is considered an important source of supply for small towns. In some cases, groundwater is not directly suitable for human consumption due to certain concentrations of ions exceeding drinking water quality standards, such as fluoride [5]. Industrial water discharges resulting from the extraction or transformation processes of raw materials in the manufacture of industrial products or goods consumers. Their quantity and quality vary depending on the used process. They often have a wide spectrum of chemical pollutants: solid or dissolved compounds, organic

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and mineral materials, metals, hydrocarbons, solvents, polymers, oils, fats, and salts, at various levels of toxicity. This great diversity requires a specific approach for each type of effluent [6]. Therefore, it is urgent to think and propose a new strategy to control and adapt the hydraulic system of our countries with a view to sustainability. It is not only a question of being aware of the risks but also of the possible solutions and setting standards of the economy for sustainable exploitation [7,8]. The research was then directed towards treatment processes using natural materials, such as agricultural materials (agricultural waste, activated carbon, etc.), activated alumina, certain macromolecular resins, and especially clays because of their availability and their low costs [9,10]. Clays are particularly remarkable nanoparticles due to their reactivity; their nanometric size and their sheet structure offering a large specific surface with respect to adsorption give them a crucial role in the retention of a large number of pollutants of natural or anthropogenic origin. The study of their reactivity is a major issue in environmental sciences, with significant repercussions, both on the fundamental level and applied in particular in the management and protection of water resources. The adsorption process is one of the most practical methods of treating industrial wastewater [11]. In addition, a wide range of adsorbent materials has been developed in recent years to improve adsorption performance [12]. This process does not require much energy compared to electrochemical processes, which can lead to the formation of free radicals and even more toxic intermediates than the initial compound [13]. It is well suited to the specific elimination of fluorine with a controlled medium pH. Extensive studies on the use of local adsorbents in low incoming countries could lower costs significantly and make the process more attractive. One of the processes employed for optimization of wastewater defluoridation is the plans' experience points proposed by David H. Doehlert in 1970 which uniformly fill the experimental space [14]. These plans also allow the easy introduction of new factors. The only precaution to be taken is to keep the factors not studied at a constant value (level 0) during the study of the active factors. All the points of the Doehlert design are on a circle of unit radius (in reduced centered magnitudes). The domain defined by the Doehlert design is a spherical domain, a circle in two-dimensional space, a sphere in three-dimensional space, and a hypersphere in more than three-dimensional space [14]. If the desired results are not in the domain of study, we can extend this domain in the direction where we are most likely to find the desired solution. Therefore in the present study, industrial wastewater from an aluminum fluoride manufactory highly charged with fluoride ions were treated by local natural clay was investigated by application of the Doehlert plane design.

2. Material and methods

2.1. Characteristics of the adsorbent

The used adsorbent is natural clay whose chemical composition was determined by X-ray fluorescence spectrometry (X-ray fluorescence spectrometer, Philips Brand and Model PW2400 equipped with a 3Wh power tube, Netherlands). The phase identification of the employed clay was established using X-ray diffraction (PrO-Analytical, Netherlands) and Fourier-transform infrared spectroscopy (Perkin Elmer GX 2000, USA). As indicated by the values given in Table 1, the chemical composition of the natural clay indicated that it contains almost 20% calcium carbonate favoring the adsorption of fluoride ions and their precipitation into CaF_2. Therefore, the treatment of rejection with this clay may lead to high abatement rates.

The X-ray diffraction (XRD) of the sieved raw clay powder is illustrated in Fig. 1. Its indexation indicates the presence of two intense peaks; the first one corresponds to the phases of calcite ($CaCO_3$), quartz (SiO_2), illite [$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$], kaolinite ($Al_2Si_2O_5(OH)_4$) and vermiculite [$(Mg,Al)_3(Si,Al)_4O_{10}(OH)_2,4H_2O$], respectively. Indeed, these phases are detected separately or as a mixture between them.

Table 1
Chemical composition of the natural clay used as adsorbent (content %)

Parameters	Values
CaO	11.80
SiO_2	44.83
Al_2O_3	15.32
Fe_2O_3	5.56
SO_3	0.93
K_2O	1.11
Na_2O	0.25
Cl	77.00
MgO	2.04
MnO	0.00
P_2O_5	0.00
TiO_2	0.03
ZnO	0.01
$CaCO_3$	19.9
LSF	7.60
TOT	81.90

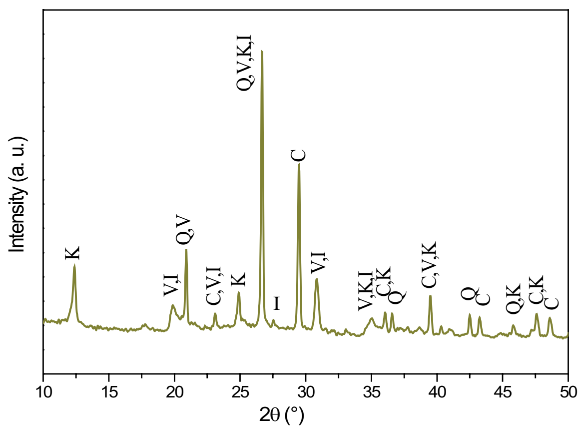

Fig. 1. XRD diffractogram of raw clay (C: Calcite, Q: Quartz, K: Kaolinite, V: Vermiculite, I: Illite).

Fig. 2 shows the Fourier-transform infrared spectroscopy (FTIR) analysis of the clay. The absorption band located at 3,700; 3,621.26; 1,630.70 and 686.56 cm^{-1} respectively, are characteristic of the O–H bond of the hydroxyl groups simultaneously contained in kaolinite, illite and vermiculite [15,16]. The bands located at 1,431 and 872.6 cm^{-1} are both attributed to the CO_3 groups existing in calcium carbonate $CaCO_3$ [17,18]. Finally, the bands centered around 778.4 and 1,003.8 cm^{-1} correspond to the vibrations of the Si–O and Si–O–Al bonds characteristic of quartz and kaolinite, respectively [19,20]. Thus, the infrared spectroscopy, the XRD and X-ray fluorescence results are in good agreement and all of them indicated the phase composition of the clay formed of quartz, kaolinite, vermiculite and illite.

2.2. Physico-chemical analysis of the wastewater

The wastewater originates from the aluminum fluoride manufactory. The pH and the conductivity of the water were measured using a pH meter (HANNA Instruments, HI 3220, ICF Gabès, Tunisia) and a conductometer (HANNA Instruments, HI 2300, ICF Gabès, Tunisia), respectively. The Nephelometric Turbidity Unit (NTU) was measured by a turbidimeter (Turbiquant Model 3000T, ICF Gabès, Tunisia). The chemical composition of the rejected wastewater was obtained using an ion chromatography device (Ion chromatography device, Model 850 Professional IC, Metrohm, ISSTE Gabes, Tunisia). The content of fluoride ions contained in the water discharge was determined by a potentiometer using a PF4-L specific F^--selective electrode. The measured values of the previously cited parameters for raw water discharge are gathered in Table 2. The primordial preliminary deductions are that the water discharge is highly charged with fluoride ions attaining concentrations of 4,320 mg L^{-1} whether the pH is highly acidic.

2.3. Wastewater treatment: experimental protocol

Once the used clay was characterized, it was used for wastewater treatment. Hence, a preselected mass of clay was weighed and then added to 250 mL of condensate whose pH has been adjusted to the required value and stirred for 30 min. Before the end of contact time, the stirring is stopped and the mixture is allowed to settle for 5 min. After that, the mixture is filtered using filter paper of 0.45 µm pores' diameter and the filtrate is stored in an airtight in a plastic bottle while the obtained residue was dried in an oven at a temperature of 80°C for 24 h. Finally, the concentration of fluoride ions contained in the filtrate and the fluorine reduction rate was measured. The experimental response studied during this treatment of industrial water rejection is the fluorine abatement rate (in %), symbolized by Y:

$$Y = \frac{\left[F^-\right]_0 - \left[F^-\right]_i}{\left[F^-\right]_0} \times 100 \tag{1}$$

$[F^-]_0$ is the concentration of fluorine in the condensate sample before treatment and $[F^-]_i$ is the concentration of fluorine in the condensate sample after treatment with clay.

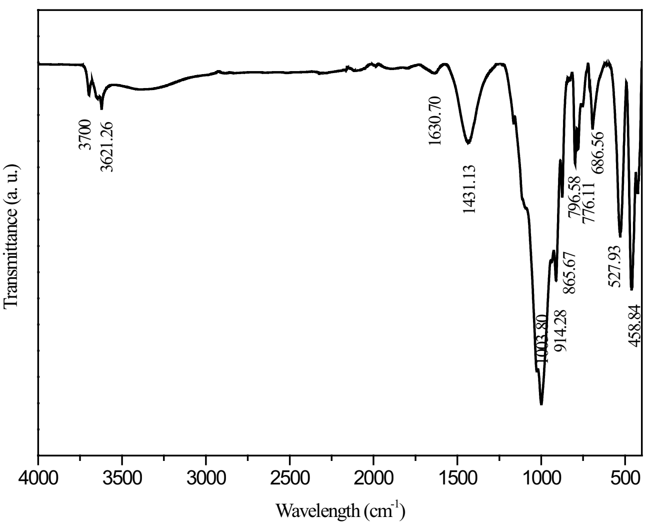

Fig. 2. FTIR spectrum of the natural clay.

3. Results and discussion

3.1. Methodology

For the treatment condition optimization of an industrial water discharge with natural clays, the methodology of experimental research was adopted [21]. The experimental designs represent an interesting alternation minimizing the difficulty of obtaining optimal conditions. Indeed, this tool allows modeling the responses of a system using empirical polynomials of postulated order. This technique also has the advantage of structuring the experimental campaign, in order to minimize the number of tests to be carried out [22]. Doehlert's design using the NemrodW software, version 2000 was thus chosen because it allows the use of an order 2 polynomial model [23]. The easy transformation in the space of the variables while keeping most of the tests

Table 2
Physico-chemical characteristics of the wastewater discharge

Parameters	Values
F^-, mg L^{-1}	4,320
HCO_3^-, mg L^{-1}	3.6
Cl^-, mg L^{-1}	129,831.4
Br^-, mg L^{-1}	6
SO_4^{2-}, mg L^{-1}	1,762.3
Na^+, mg L^{-1}	73,683.5
K^+, mg L^{-1}	227.4
Ca^{2+}, mg L^{-1}	249
Mg^{2+}, mg L^{-1}	776.2
Salinity, g L^{-1}	209
Suspended matter, %	0.3
Turbidity, NTU	550
Conductivity, mS cm^{-1}	2,500
pH	2

already carried out. There was also, the addition of more variables, while still retaining the tests already carried out.

The coefficients of the polynomial are calculated using the test results and a multi-linear regression. To calculate the coefficients of the empirical model, the experimental designs are based on a linear multi-regression. It is therefore, necessary, to integrate the variance of the coefficients in the model because these can have a very significant influence on the parameters of the distribution of the model and therefore on the final probability.

3.2. Selected factors

The preliminary tests and the bibliographic search were necessary to precise the factors which can influence the reduction rate of fluorine during the treatment of industrial water rejection by the clay.

Thus, the factors likely to influence the rate of fluoride reduction are:

- U_1: mass of clay (g);
- U_2: concentration of fluoride ions in industrial water discharge (mg L^{-1});
- U_3: pH of the medium;
- U_4: contact time (min).

The following factors were also set:

- Temperature: 25°C;
- Rejection volume: 250 mL.

3.3. Experimental area and proposed mathematical model

The experimental area studied in this work is defined in Table 3.

For this study, the polynomial retained will be of order 2 (coefficient b_{ii}), with an interaction between the variables (coefficients b_{ij}, with $i \neq j$).

The model used to relate the experimental response to the factors studied is:

$$\begin{aligned} Y = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 \\ & + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \\ & + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \\ & + b_{14}X_1X_4 + b_{24}X_2X_4 + b_{34}X_3X_4 \end{aligned} \quad (2)$$

where b_0: value of the response at the center of the domain; b_i: main effects of each factor; b_{ii}: deviation from linearity and b_{ij}: interactions between factors.

The transformation of a natural variable (U_{ij}) into a coded variable (X_{ij}) is obtained by the relation [24]:

$$X_{ij} = \frac{U_{ij} - U_j^0}{\Delta U_{ij}} \quad (3)$$

where X_{ij}: value of the coded variable j for experiment i; U_{ij}: value of the natural variable j for experiment i; U_j: value of the natural variable j at the center of the experimental domain, corresponding to $X_j = 0$ for experiment i and ΔU_{ij}: no variation of the natural variable j, corresponding to a variation of the coded variable j equal to +1.

To determine the coefficients of the mathematical model equation, we use the method of least squares [25], according to the formula:

$$B_i = \left(X'X\right)^{-1} X'Y \quad (4)$$

where B_i: vector for estimating coefficients; ($X'X$): information matrix; $(X'X)^{-1}$: dispersion matrix; X': matrix transposed from the model matrix and Y: vector of experimental results.

3.4. Experimentation plan

We used the uniform networks of the Doehlert design [23], to determine the coefficients of the model. Thus, we will carry out 23 experiments from Table 4.

3.5. Experimental results and interpretation

The various tests of the experimental plan were carried out for the treatment of industrial water discharge by clay and the results obtained are collated in Table 5. After presenting the results of the tests relating to the treatment of industrial water discharge by each of the clays, we proceed to the interpretation of the different results, to the determination of the optimal conditions as well as their applications to a real sample of the industrial water discharge from the fluorine industry.

3.5.1. Mathematical model

After carrying out the various tests, the equation of the mathematical model relating to the answer Y is:

$$\begin{aligned} Y = {} & 18.93 + 4.36X_1 + 1.86X_2 - 49.73X_3 + 0.35X_4 \\ & - 3.43X_1^2 - 12.47X_2^2 + 51.55X_3^2 - 1.30X_4^2 \\ & + 7.56X_1X_2 - 8.86X_1X_3 - 2.66X_2X_3 - 4.90X_1X_4 \\ & + 6.15X_2X_4 + 3.00X_3X_4 \end{aligned} \quad (5)$$

Table 3
Factors and experimental area

Factors	Unit	Low level	Domain center	High level
Mass of clay	g	2	4	6
$[F^-]$	mg L^{-1}	2,000	3,000	4,000
Medium pH	–	2	5.5	9
Contact time	min	20	30	40

Table 4
Experimentation plan

Exp. No.	Factors			
	U_1	U_2	U_3	U_4
1	6.0	3,000.0	5.5	30.0
2	2.0	3,000.0	5.5	30.0
3	5.0	4,000.0	5.5	30.0
4	3.0	2,000.0	5.5	30.0
5	5.0	2,000.0	5.5	30.0
6	3.0	4,000.0	5.5	30.0
7	5.0	3,333.4	9.0	30.0
8	3.0	2,666.6	2.0	30.0
9	5.0	2,666.6	2.0	30.0
10	4.0	3,666.7	2.0	30.0
11	3.0	3,333.4	9.0	30.0
12	4.0	2,333.3	9.0	30.0
13	5.0	3,333.4	6.4	40.0
14	3.0	2,666.6	4.6	20.0
15	5.0	2,666.6	4.6	20.0
16	4.0	3,666.7	4.6	20.0
17	4.0	3,000.0	8.1	20.0
18	3.0	3,333.4	6.4	40.0
19	4.0	2,333.3	6.4	40.0
20	4.0	3,000.0	2.9	40.0
21	4.0	3,000.0	5.5	30.0
22	4.0	3,000.0	5.5	30.0
23	4.0	3,000.0	5.5	30.0

Table 5
Experimentation plan and experimental results

Exp. No.	Factors				Response
	U_1	U_2	U_3	U_4	Y
1	6.0	3,000.0	5.5	30.0	24.0
2	2.0	3,000.0	5.5	30.0	7.0
3	5.0	4,000.0	5.5	30.0	10.5
4	3.0	2,000.0	5.5	30.0	13.5
5	5.0	2,000.0	5.5	30.0	5.2
6	3.0	4,000.0	5.5	30.0	5.7
7	5.0	3,333.4	9.0	30.0	7.0
8	3.0	2,666.6	2.0	30.0	89.5
9	5.0	2,666.6	2.0	30.0	95.6
10	4.0	3,666.7	2.0	30.0	99.4
11	3.0	3,333.4	9.0	30.0	11.0
12	4.0	2,333.3	9.0	30.0	1.4
13	5.0	3,333.4	6.4	40.0	15.7
14	3.0	2,666.6	4.6	20.0	21.0
15	5.0	2,666.6	4.6	20.0	30.0
16	4.0	3,666.7	4.6	20.0	22.2
17	4.0	3,000.0	8.1	20.0	16.0
18	3.0	3,333.4	6.4	40.0	13.7
19	4.0	2,333.3	6.4	40.0	6.0
20	4.0	3,000.0	2.9	40.0	56.0
21	4.0	3,000.0	5.5	30.0	23.0
22	4.0	3,000.0	5.5	30.0	19.4
23	4.0	3,000.0	5.5	30.0	14.4

3.5.2. Study of the factors effects

To highlight the effect of each chosen factor, as well as that of their interactions, we present in Fig. 3, the diagram of the effects of the factors chosen on the rate of reduction of fluoride. This diagram shows that the mass of clay has a positive influence on the rate of abatement and the pH of the medium negatively influences the response. Thus, to increase the rate of abatement of fluoride, it is necessary to increase the mass of clay and decrease the pH of the medium. The other factors chosen have almost no significant effect on the experimental response. Consequently, to improve the rate of abatement of fluorine, it is necessary to decrease the pH of the medium and the concentration of fluorine and to increase the mass of clay.

3.5.3. Graphical analysis of the effects according to Pareto

The graphical analysis of the effects according to the Pareto method [26] was made in order to highlight the percentage of contribution of each term of the model for the explanation of the response variation. It is a visualization, analysis and decision-making aid. It allows making a choice and to concentrate the action around the problem to be treated as a priority. It is used for measurable, quantitative data. It is a column chart, outlining and ranking, in decreasing order of importance, the causes of a problem. The height of the columns is then proportional to the importance of each cause. So the priorities for action are quickly visualized. These percentages of effects have been calculated according to the formula:

$$P_i = \frac{\left(CV_i \cdot b_i\right)^2}{\sum\left(CV_i \cdot b_i\right)^2} \times 100 \tag{6}$$

where P_i: percentage of effect due to each factor compared to the total effect of the factors, all normalized to 100 and CV_i: covariance and b_i: coefficients of the model determined from the matrix. The graphical analysis of the effects of the factors chosen during this Pareto study is shown in Fig. 4. It can be seen that the pH of the medium has the largest percentage of effects which is 44.68%, therefore it has a significant contribution to the variation due to the fluorine abatement rate. In the contrary, the contact time has no contribution. Besides, the other factors and their interactions contribute to the low variation. Therefore, to improve the response, it is mainly necessary to lower the pH of the medium. This condition constitutes a very important advantage since the industrial water discharge treated has a fairly acidic pH (pH = 2).

3.5.4. Study of response surfaces and isoresponse curves

The response surfaces present the variations of the experimental response as a function of two factors, the other being

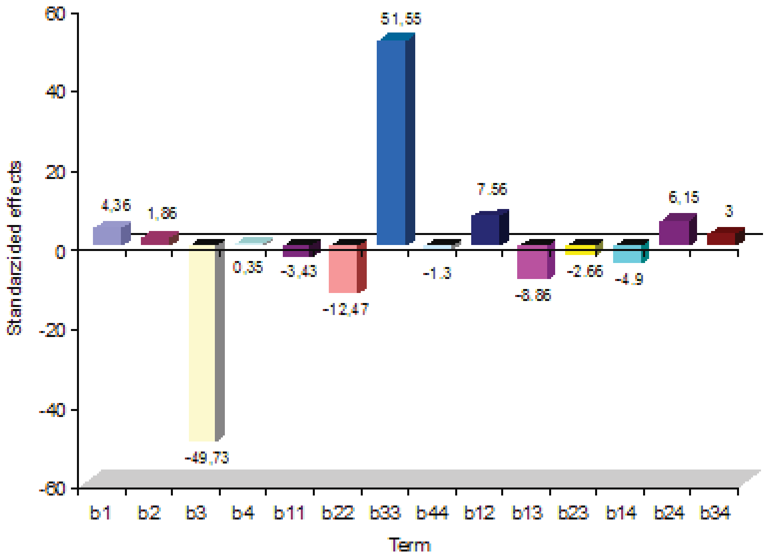

Fig. 3. Bar graphs of the model coefficients.

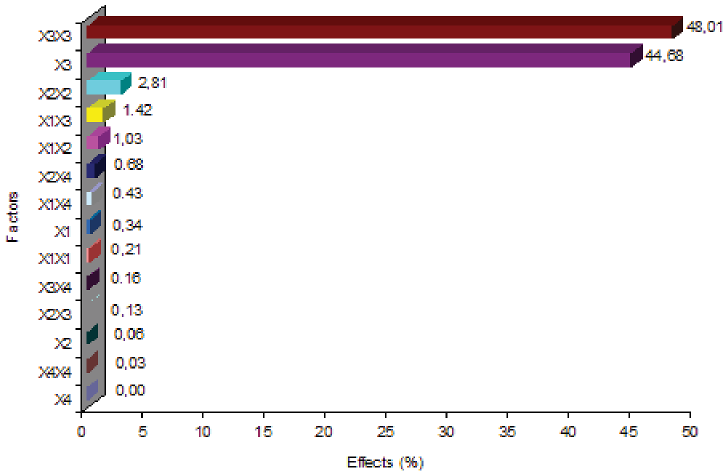

Fig. 4. Pareto graphical analysis of the effects.

fixed [14]. The projection of the surface-response diagram is convenient for visualizing the region of the maximum with the contour lines. Once the values predicted by the model in the form of isoresponse curves, the effect of factors on the rate of fluoride reduction from this diagram might be analyzed [14]. The graphical representation of the pre-established model in the variable space allows obtaining the isoresponse curves. Hence the response according to the different synthesis parameters was visualized. Their analysis highlights the influence of the factors on the response and also allows for determining the optimal region [14]. Herein the different representations of response surfaces and isoresponse curves are gathered in Fig. 5.

The analysis of the following different figures allows pronouncing that to increase the fluorine abatement rate it is necessary to increase the mass of clay and decrease the medium pH. In fact, for low pH values and adequate mass of clay, the fluoride rate reduction can reach percentages greater than 99.0%. Moreover, for basic pH values and whatever the values taken by the other factors, the fluoride rate reduction is very low. In conclusion, an increase in the clay mass, a decrease in the fluorine concentration in a sufficiently acidic medium and whatever the contact time allows predict fairly high fluorine rate abatement.

3.5.5. Optimal conditions and application

The interpretation of the factor effects diagram and the isoresponse curves, as well as the graphical analysis of the factors effects according to Pareto, enabled us to retain the optimal conditions given in Table 6.

The application of these conditions to an industrial water discharge sample allows obtaining a fluoride reduction rate of 99.6% ($[F^-]$ after treatment is 11.2 mg L^{-1}). The pH of the medium and the conductivity measured are 5 and 54 mS cm^{-1}, respectively. These results are in agreement

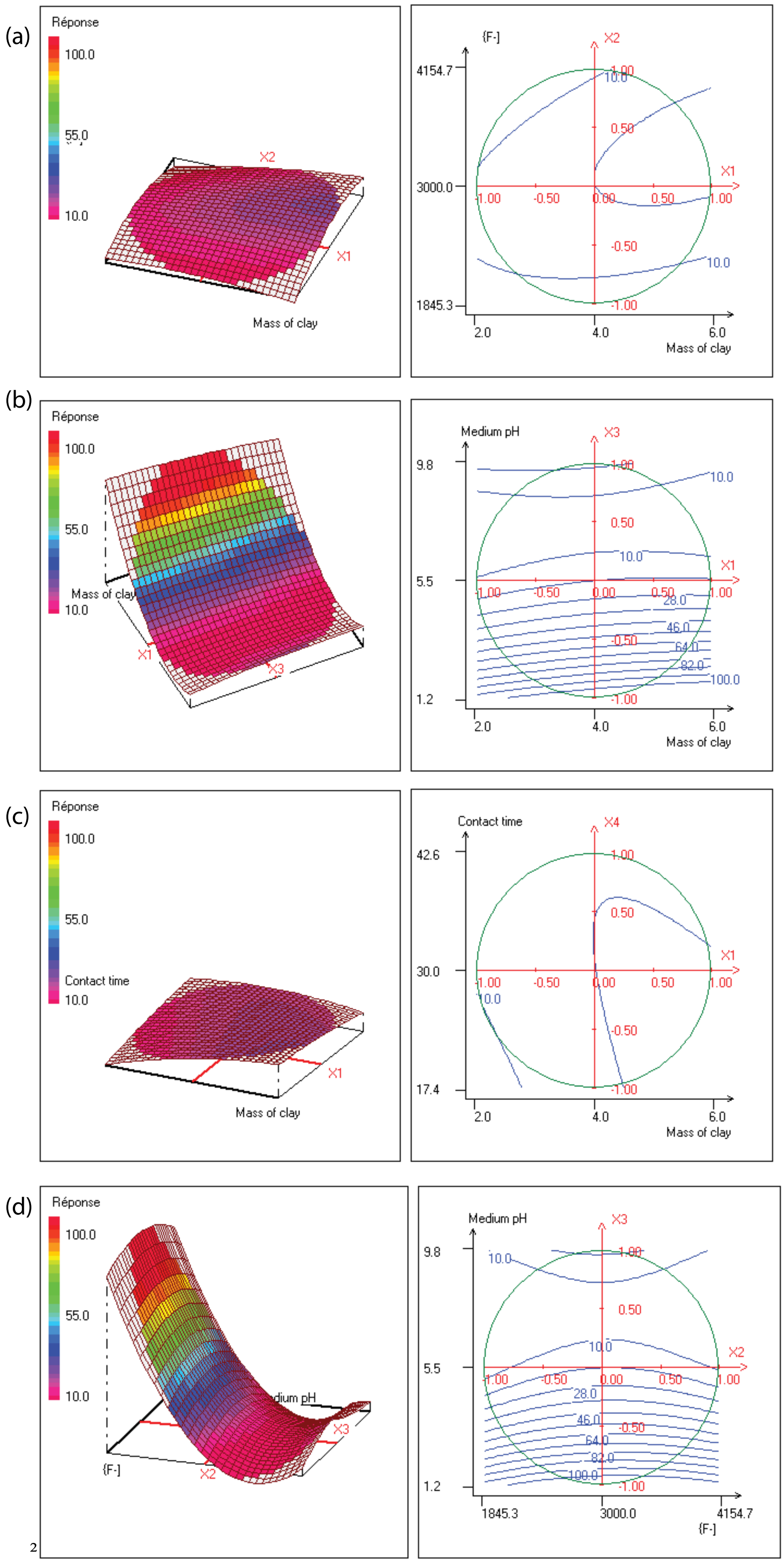

Fig. 5. (Continued)

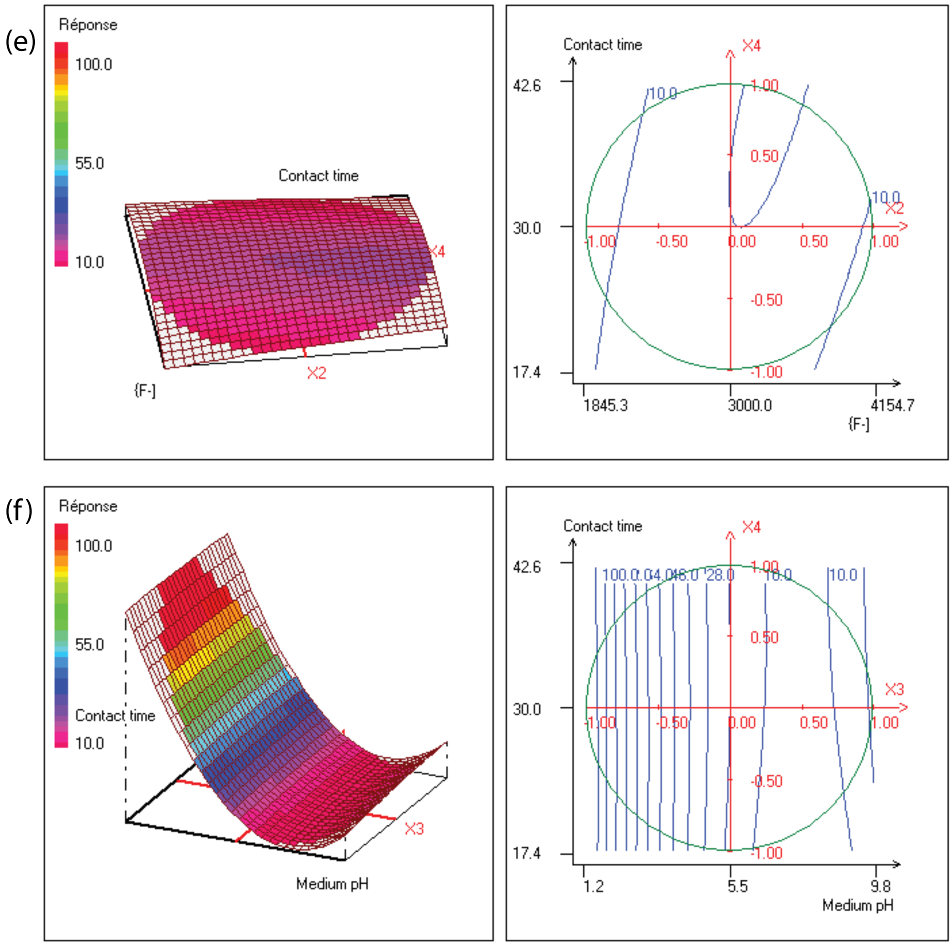

Fig. 5. (a) 2D evolution of the fluorine abatement rate: clay mass, [F⁻] (Fixed factors: pH = 5.5 and contact time = 30.0 min). (b) 2D evolution of the fluorine abatement rate: clay mass, pH (Fixed factors: [F⁻] = 3,000.0 mg L⁻¹ and contact time = 30.0 min). (c) 2D evolution of the fluorine abatement rate: clay mass, time of contact (Fixed factors: [F⁻] = 3,000.0 mg L⁻¹ and pH = 5.5). (d) 2D evolution of the fluorine abatement rate: [F⁻], pH (Fixed factors: clay mass = 4.0 g and contact time = 30.0 min). (e) 2D evolution of the fluorine abatement rate: [F⁻], contact time (Fixed factors: clay mass = 4.0 g and pH = 5.5). (f) 2D reduction of fluorine rate: pH, contact time (Fixed factors: clay mass = 4.0 g and [F⁻] = 3,000.0 mg L⁻¹).

Table 6
Retained optimal conditions

Factors	Values
Mass of clay, g	6
[F⁻], mg L⁻¹	2,800
Medium pH	2
Contact time, min	30
Medium temperature, °C	25
Raw release volume, mL	250

with the bibliographic data [27–29]. Therefore, it is found that the conductivity of the solution has decreased and the pH of the medium has greatly increased. Thus, this treatment has reduced the fluoride ions content in the raw discharge considerably. This was confirmed by the XRD and FTIR spectra depicted in Figs. 6 and 7. The residue obtained after treatment of the condensate with clay showed that the

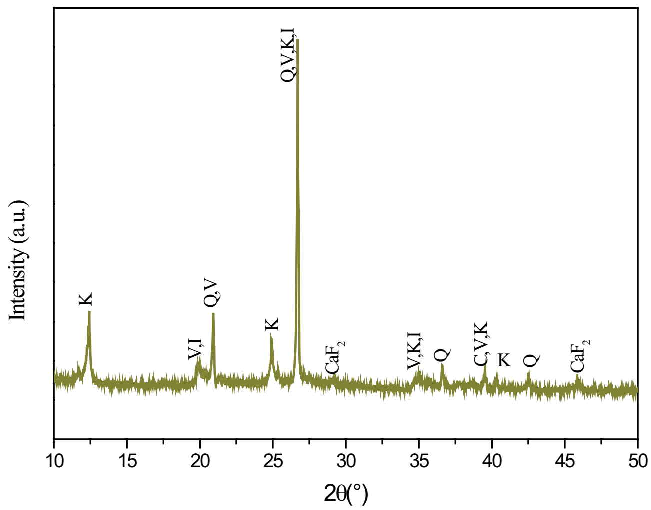

Fig. 6. XRD spectrum of the residue obtained after treatment of the condensate with clay.

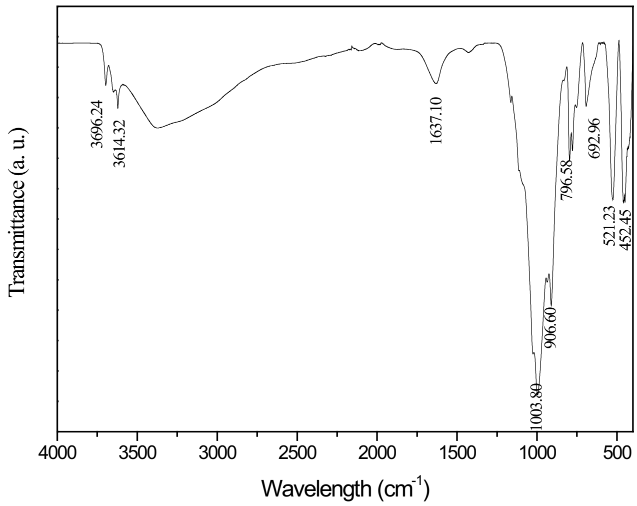

Fig. 7. FTIR spectrum of the residue obtained after treatment of the condensate with clay.

calcite peaks disappeared whereas those of CaF_2 appeared and carbonates bands of calcite disappeared in the infrared spectrum. The measurements of the pH before and after the treated industrial water discharge by clay show that it decreases with an increasing amount of adsorbent. Thus, the average acidity leads to the formation of aluminum-fluoro complexes [30]. In this case, increased acidity allows releasing aluminum and silicate ions and the resulting clay contains fluorine salts. The content of fluoride ions has decreased significantly, and this decrease can be explained by the attack of clay components, such as silica ions during treatment [30,31]. Similarly, the elimination of fluoride ions may also depend on the level of calcium and magnesium contained in the clay which allows the retention of fluoride on clay during the treatment process of rejected industrial wastewater [22]. In fact, the reduction in fluorine is mainly due to its precipitation as CaF_2 [30]. For better reuse of these industrial wastewaters, the pH was increased by keeping the reduction rates of fluorine at an acceptable level, following the application of the Doehlert design.

4. Conclusion

This work represents a contribution to the study of defluoridation of industrial wastewater from aluminum fluoride factory by adsorption on natural clay. The determination of the optimal conditions for treating industrial wastewater discharge was established using the Doehlert design method. Thus, the study of the effects of different factors, the study of the effects of the graphical factors and the study of the iso-response curves allow determining the optimal conditions for the wastewater treatment by natural clay. The optimal conditions were: mass of clay (6 g); concentration of fluoride ions in the discharge (2,800 mg L^{-1}); pH of the medium: 2; contact time: 30 min; medium temperature: 25°C and treated wastewater volume: 250 mL. The application of these optimal conditions to an industrial wastewater sample led to a fluorine abatement rate of 99.6%. After the treatment, the fluoride concentration belongs to standard values (11.2 mg L^{-1}). Thus the use of natural clay a material cheap and available with adjusted conditions allow the elimination of higher content of fluoride in wastewater.

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Declaration of competing interest

The authors declare that they have no competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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