Optimization studies for industrial wastewater defluoridation by adsorption: application of a design of experiments

Mohamedou BA[1], Abdessalem EZZEDDINE[2]

[1]Department of Chemistry, Faculty of Sciences of Gabes, University of Gabes, Erriadh City, 6072 Zrig, Gabes, Tunisia.
Email: mohamadou.samba@gmail.com
[2]Department of Chemical-Process Engineering, National School of Engineering of Gabes, University of Gabes, Omar Ibn Elkhattab Street, 6072 Zrig, Gabes, Tunisia
Email: abdessalem.ezzeddine@enig.rnu.tn

***Abstract*— *This paper aims to examine the treatment of aluminum fluoride-manufacturing wastewaters (AFMW) by adsorption on Tunisian natural clay using a two-level full factorial design. For this sake, three operating parameters supposed to affect the removal efficiency were chosen: dose of adsorbent, concentration of fluoride ions, and pH of the medium. Factors that influence the fluoride removal efficiency were evaluated statistically by using factorial plots. Diagram of the effects was used to check the significance of the effect on percentage removal. The statistical analysis allowed verifying that the dose of adsorbent and pH have an influence on the fluoride elimination. Treatment of a strongly acidic (pH ~ 2) and fluoride-rich AFMW (F=26,000 mg/L) by adsorption on natural clay was used to determine the optimum conditions. The application of this method has led to an important decrease in fluorine content (> 98%).*

Keywords*—Adsorption, Aluminum fluoride-manufacturing, Design of Experiment, Fluoride, Industrial wastewater, Natural clay.

I. INTRODUCTION

The importance of water in the human economy is growing and the supply of good quality water is becoming increasingly difficult, both because of the increase in population and living standards, as accelerated development of modern industrial techniques. The scarcity of surface drinking water forced growers to diversify supply sources, drawing increasingly further into the ground. Ground water is considered an important source for the supply of small towns. In some cases, groundwater is not directly suitable for human consumption because of certain ion concentrations exceeding the standards for the quality of drinking water, such as fluorides [1]. Industrial liquid wastes are the most significant sources of pollution to the environment. They have become a factor of pollution that should be taken into consideration for the ecosystem balance. So, it becomes clearly important to fight against this type of pollution and to take severe measures by introducing perseverant laws against untreated discharges to protect our environment.

The main sources of emissions of fluorides are presumably related to the production of phosphoric acid and phosphate fertilizers, as well as aluminum metallurgy. The fluoride ingestion by humans may be one of the main causes of acute or chronic poisoning. Thus, chronic fluoride exposure primarily affects the digestive and skeletal systems [2].

Like most industries, especially fluorine chemical industries encounter operational problems upon their water discharges (AFMW). So it is necessary to find a solution which is consistent with the requirements of releases into the environment according to recommended standards.

In this context, the use of the methodology of experimental research to optimize industrial liquid waste processing conditions would be of special importance [3]. Given the difficulty of obtaining the optimum conditions, design of experiments represent an interesting alternative. Indeed, this tool allows to model the responses of a system using empirical polynomials priori postulated order. This technique also has the advantage of structuring the experimental companion to reduce the number of tests to be performed [3].

Extraction processes or processing raw materials for the manufacture of industrial products or consumer goods are the key sources of industrial liquid discharges. Their quantity and quality vary depending on the process used by industrial sector. They often exhibit a broad spectrum of chemical polluting compounds in solid or dissolved organic and inorganic materials, metals, hydrocarbons, solvents, polymers, oils, fats or salts with varying levels of toxicity. This requires a specific approach for each type of waste [4].

The adsorption process on clay is very suitable for specific removal of fluoride in order to control the pH of the medium. Extensive studies of the use of local adsorbents in developing countries could significantly reduce costs and make the process more attractive. Current adsorbent materials have a short life and the difficulties of their regeneration limit the possibility of large-scale use. Examples of materials used in water treatment include the following adsorbents: activated alumina, activated carbon, ion exchange resins, silica gel, diatomaceous earth, molecular sieves, activated silica and metal oxides. A certain number of authors [5-7] have demonstrated the ability to remove fluoride by adsorption on different clays. The structure of the clay used may allow the determination of the load on its surface and the type of exchange that can occur with ions in solution [5]. Generally, the more the clay surface is positively charged, the better the adsorption performance (the adsorption capacity is strongly dependent on pH). Meenakshi and al. [8, 9] studied water defluoridation with kaolinite in a batch system. The adsorption of fluoride ions on the clay was carried out in the pH range 3-11. The adsorption isotherms on clay obey the types of Langmuir and Freundlich in a concentration range from 2 to 10 mg/L. Analysis of this clay showed that Al_2O_3 (36.98%) and SiO_2 (47.05%) were the major constituents. The specific surface was 15.11 m^2/g. This quality of clay removes the fluoride ions from drinking water. The thermodynamic study of clay on fluoride system showed that the adsorption is endothermic. Several fluorine analytical techniques in water were used [10, 11].

In this work, we used potentiometry with a specific fluoride electrode. A specific electrode is an electrode which is sensitive only to changes in concentration of a given chemical species. In practice, the electrode can also be sensitive to a lesser extent to other species. In the case of fluoride ion, the specific electrode is a solid electrode membrane formed by a crystal of lanthanum trifluoride doped with europium. In this method, first a calibration is made of the electrode using known concentration solutions of the species. It is important that the ionic composition of the solutions is similar so as to obtain the same ionic strength. This is achieved in part by adding a buffer electrolyte of higher concentrations that does not interfere with the measuring electrode. These electrolytes are known as total ionic strength adjustment buffers (TISAB).

II. MATERIALS AND METHODS

For characterization of the AFMW, we used:

- pH meter type Hanna pH 213 (Microprocessor pH Meter).
- Conductivity, Metrohm 856.
- Spectrophotometer UV-Vis, type T-60.
- Potentiometer to a specific electrode for fluoride ions, Metrohm 781 pH/Ion meter equipped with an ion selective electrode (Metrohm 6.0502.150) and the reference electrode Ag/AgCl (Metrohm 6.0726.100).

One advantage of this method compared to the others is the absence of interference between the fluoride ions and the other ions (OH^-, Cl^-, SO_4^{2-}, Cu^{2+}, Cr^{3+}, ...) which may exist in natural water, using a buffer solution. A calibration curve is however necessary to evaluate the concentration of an experimental sample. The fluoride electrode is highly selective. Indeed, it allows the measurement of F- of 10^{-1} to 10^{-6} mol/L.

Because of its reactivity, the fluoride ion can be complexed by several elements, such as Al^{3+}, Fe^{3+}, Cu^{2+}, Cr^{3+}, which may alter the results of the assay. To avoid the interference of these ions, a TISAB buffer solution is added to the sample before analysis.

The TISAB solution will fix the pH and prevent interference with the OH^- ions; F^- releases the complexed and maintains a constant and high ionic strength.

Is performed for each standard solution measurement of potential. All potential readings are taken after stabilization of the potential of the electrode. Note that it is better to do the measurements on the standard solutions in order of increasing concentrations, to avoid memory phenomena of the electrode, and the risks of solution pollution.

2.1 Reagents

In the experiments, analytical grade chemicals were used. They include: sodium hydroxide (NaOH), sodium fluoride (NaF), silver chloride (AgCl), silver nitrate ($AgNO_3$), sodium chloride (NaCl), cyclohexane diamino-tetra-acetic acid (CDTA) and hydrochloric acid (HCl).

2.2 Preparation of TISAB

To 58 g of NaCl in 500 mL distilled water was added 5 g of CDTA and the mixture is stirred to dissolution. Then, 57 mL of acetic acid were added; the electrode rinsed in the solution; and NaOH is added to pH = 5.5; Diluted to 1000 mL and phenolphthalein or methyl orange is added.

The adsorbent used is natural clay whose chemical composition is collected in Table 1.

It is found that this clay is calcium and oxides predominating its structure are SiO_2, Al_2O_3 and CaO.

TABLE 1
CHEMICAL COMPOSITION (IN WT %) OF THE CLAY USED IN THE EXPERIMENT.

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SO_3
42.67	13.66	10.56	8.46	2.2	0.82	0.01
Na_2O	**P_2O_5**	**TiO_2**	**ZnO**	**LOI***	**Total**	
0.51	0.13	0.66	0.01	20.09	99.78	

*** Loss on ignition at 975 °C**

Characterization of crude AFMW give the results summarized in Table 2.

Note that the AFMW is charged fluoride, sulfate, phosphate and calcium.

TABLE 2
COMPOSITION OF A REPRESENTATIVE SAMPLE OF AFMW.

pH	Conductivity (mS/cm)	SO_4^{2-} (mg/L)	SiO_2 (mg/L)	F^- (mg/L)	PO_4^{3-} (mg/L)	Ca^{2+} (°F)	Mg^{2+} (°F)
2.30	296.40	416.00	62.66	590.59	234.00	499.20	39.52

The goal is to defluoridate a fluoride-rich industrial waste water. For this purpose, it is desired to remove the maximum amount of fluorine using clay as an adsorbent.
For each test, we proceed as follows:

- set the amount of clay needed in a liter of AFMW and stir for 2 hours and filter the resulting solution ;
- a test sample of 10 g of the filtered solution and add phenolphthalein ;
- neutralizing the sample with sodium hydroxide (1M) until the appearance of the pale pink color and add 200 mL of distilled water ;
- heating the solution for one hour on sand to boiling point and add 100 mL of TISAB ;
- adjusting the volume of distilled water to 500 mL;

Measuring the equilibrium potential of the solution and determining the concentration of fluoride ions remaining in the AFMW.

III. RESULTS AND DISCUSSION

To search for optimum conditions, it is useful to use the methodology of experimental research [12]. Thus, the experiments design imperatively require to be established by the experimenter a causal relationship between the "factors", which are assumed as the parameters influencing the behavior of the analytical protocol and "answers" that characterize the result of the trial [13]. These plans reflect the experiences transposition in the real experimental field of "experimental matrix". The latter is a mathematical object that represents, in coded form, the set of experiments to be performed [14]. Understanding the design experience method is thus based on two key concepts, the experimental space and the mathematical modeling of the studied variables.

In this work we used for optimization the defluoridation conditions of an industrial liquid discharge, the full factorial design to study the effects and interactions of factors and Doehlert plan for the study of surfaces - answers.

3.1 Selected Factors and experimental response

Factors that influence the experimental response are:

U_1: adsorbent dose (g) ;
U_2: Fluorine concentration (mg/L);
U_3: pH.

The fixed factors are:
AFMW volume : 1 L ;
contact time : 1 h 30 min.

The experimental response (Y) in question, expressed in percentage, is the fluorine reduction rate which is given by the following formula:

$$R\% = 100\ \frac{(C_0 - C_i)}{C_0}$$

C_0 : concentration of fluoride in the pre-treatment rejection sample;

C_i : concentration of fluoride in the rejection of sample after treatment with the adsorbent.

3.2 Passage of a natural variable to a variable coded

Transforming a natural variable (U_{ij}) in an encoded variable (X_{ij}) is obtained by the equation below [15]:

$$X_{ij} = \frac{U_{ij} - U_j^0}{\Delta U_{ij}}$$

X_{ij}: value of the coded variable d for experience i ; U_{ij} : value of natural variable i for the experience j ; $U_j°$: value of natural variable j at the center of the experimental range corresponding to $X_j = 0$ for experience i ; ΔU_{ij} : no variation of the natural variable j, corresponding to a change of the encoded variable j equal to +1.

3.3 Determination of the model coefficients

To determine the coefficients of the equation of the mathematical model, we use the least squares method [16], according to the formula :

$$B_i = (X'X)^{-1} X'R$$

Bi: estimating the coefficients vector ; (X'X) : information matrix;

$(X'X)^{-1}$: dispersion matrix;

X': transposed matrix of the matrix of the model;

R: Vector experimental results.

In the general case, the values of the model coefficients are calculated independently of each other. Each ratio was also calculated by taking the sum of the responses, each being multiplied by the sign of the column corresponding to this coefficient divided by the number of trials.

3.4 Graphical analysis of effects

Analysis of the effects was made in order to identify the contribution percentage of each term in the model for the explanation of the variation of the response. It is a visualization tool, analysis and help in decision making. It allows choosing and focusing the action to treat the key problem. So the priorities for action are quickly displayed [3]. Unlike coefficients bi and bij, the Pi percentage of influence is a relative value which allows for a comparison of the influence of factors on the response, but does not allow highlighting the significance of each factor. The effects diagram presented with P values (percentage) is known as the "Pareto’s chart of effects".

3.5 Full factorial Plan

In order to determine the optimum conditions for defluorinating liquid industrial waste, we used the full factorial design which allows studying the effects of factors on the experimental response chosen [17].

A full factorial design is a two-level design study by factor and the mathematical model used is a first degree model with or without interactions in relation to each factor. This is the most commonly used plan because it allows the screening of factors and sometimes leads to simple but sufficient models [15].

3.5.1 Domain and experimental mathematical model proposed

Following a preliminary study of the factors that may affect defluorination of liquid industrial waste, we were able to define the experimental field. This area is summarized in Table 3.

TABLE 3
THE 2^3 FACTORIAL DESIGN FOR FLUORIDE ADSORPTION ONTO CLAY.

Variables	Factors	Minimum Value (-1)	Maximum Value(+1)
U_1	Adsorbent dose (g)	0.5	4
U_2	[F-] (mg/L)	500	2003
U_3	pH	2	11

A mathematical model of first degree polynomial type is postulated in which all levels of all factors are combined. Thus, the model used to link the response to experimental factors studied is :

$$\%R = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{123} X_1 X_2 X_3$$

Where %R represents the experimental response, b_0 : value of the response centrally in the park ; b_i : main effect of each factor taken separately ; b_{ij} : effect of two -way interactions ; b_{123} : 3-way interactions.

Table 4 summarizes the matrix of experiences.

TABLE 4
MATRIX OF EXPERIMENTS.

		Factors	
Experiment	**X_1**	**X_2**	**X_3**
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
Level (-1)	0.5	500	2
Level (+1)	4.0	2003	11

The experimental matrix includes the experimental matrix, to which are added two lines to clarify the meaning of the levels. After completing the 8 experiments on the experimental design, the results obtained in this study are gathered in Table 5.

TABLE 5
MATRIX OF EXPERIENCE AND EXPERIMENTAL RESULTS.

		Factors		Response
Experiment	**X_1**	**X_2**	**X_3**	**R(%)**
1	-1	-1	-1	95.19
2	+1	-1	-1	97.34
3	-1	+1	-1	97.14
4	+1	+1	-1	96.66
5	-1	-1	+1	97.72
6	+1	-1	+1	97.98
7	-1	+1	+1	96.09
8	+1	+1	+1	97.71

3.5.2 Mathematical model obtained

After calculating the coefficients of the mathematical model, the model equation with respect to the response is :

$$R = 96.979 + 0.444\,X_1 - 0.079\,X_2 + 0.396\,X_3 - 0.159\,X_1 X_2 + 0.026\,X_1 X_3 - 0.396\,X_2 X_3 + 0.449\,X_1 X_2 X_3$$

3.5.3 Study of factor effects

In Figure 1 is shown the diagram of the effects of factors selected on the abatement rates fluorine. This diagram shows that most factors have a positive influence on the abatement rates fluorine; especially the mass of adsorbent and pH that have the most significant effect on the reduction of fluoride levels. So the mass of adsorbent and pH have a positive influence on the abatement rates fluorine. On the contrary, the concentration of fluoride ions has a little negative effect. The 3-way interactions (adsorbent dose - concentration of fluoride ions - pH) have the largest positive effect compared to 2-way interactions (adsorbent dose - pH) that have a significant positive effect.

Furthermore, interactions concentration of fluoride ions - pH negatively affect levels of the abatement rates fluorine and adsorbent dose - concentration of fluoride ions interactions have a more or less negative effect on defluorination. Therefore to improve the rate of the abatement rates fluorine, decrease the concentration of fluoride ions must be decreased, whereas the pH and the amount of adsorbent should be increased.

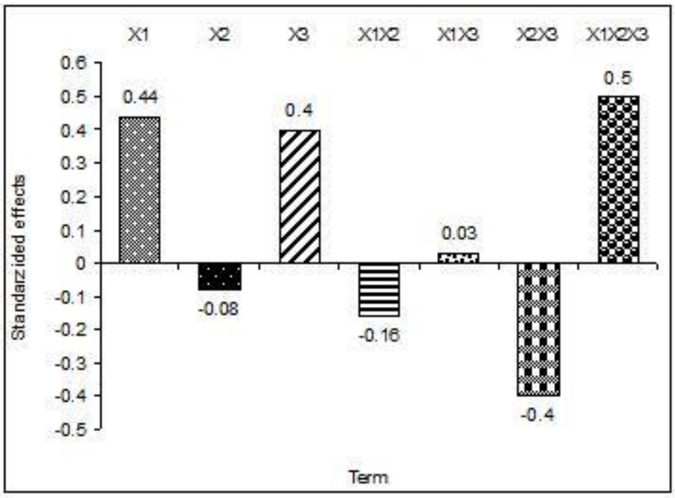

FIG. 1: DIAGRAM OF THE EFFECTS OF FACTORS ON THE REDUCTION OF FLUORIDE LEVELS.

Thus, the optimum conditions adopted are:

Adsorbent dose : 4 g ;

Concentration of fluoride ions : 500 mg/L ;

pH = 11 ;

AFMW volume : 1 L ;

Contact time : 1 h30 min.

Under these conditions, industrial liquid waste samples were treated and these characteristics and composition are summarized in Table 6.

TABLE 6
COMPOSITION OF THE AFMW AFTER TREATMENT.

pH	Conductivity (mS/cm)	SO_4^{2-} (mg/L)	SiO_2 (mg/L)	F- (mg/L)	PO_4^{3-} (mg/L)	Ca^{2+} (°F)	Mg^{2+} (°F)
9.90	3.19	35.00	2.60	10.77	76.00	0.00	4.67

The contents of SiO_2, PO_4^{3-} and SO_4^{2-} can be explained by the presence of these elements in the clay used in the treatment of rejection.

The conductivity of the solution decreased as a result of treatment of the condensate by the clay. For instance, the removal of fluorine ions influences the value of the conductivity of the solution.

We also measured the pH before and after the clay treatment. The results show that the pH decreases with the increase in the amount of adsorbent. Thus, the mid acidity leads to the formation of alumino-fluoro complexes [18]. In this case, an increased acidity promotes the release of aluminum ions and silicate clay, resulting in the formation of fluorine salts as shown in the reactions. The fluoride ion content decreased to a significant extent. This decrease is shown by the attack from the components of the clay, such as silica (SiO_2) with fluoride ions during the treatment according to the reaction [18] :

$Al_2Si_2O_3(OH)_4 + 6\ H^+ \leftrightarrows 2Al_3^+ + 2\ H_4SiO_4 + H_2O$

$Al^{3+} + n\ F^- \leftrightarrows AlF_3^{-n}$

$SiO_2 + 6\ HF \leftrightarrows H_2SiF_6 + 2\ H_2O$

Similarly, removal of the fluorine may also depend on the presence of significant levels of calcium and magnesium that promote retention of fluorine on the clay during naturally fluorinated water process through a bridging effect [6]. In fact, the reduction of fluoride is due to its precipitation as CaF_2 [19].

For better reuse of these industrial liquid waste waters, the pH was lowered by keeping the the abatement rates fluorine to an acceptable level. For this, the approach of Doehlert (study of surface patterns - response variation fluorine abatement rates) was applied to the optimization of processing conditions of an industrial liquid discharge.

3.6 Doehlert plan

The goal is the defluoridation of a fluoride-rich industrial liquid waste. For this purpose, it is desirable to remove the maximum amount of fluorine using clay as an adsorbent. With this in mind, we apply the Doehlert plan for the study of surfaces - response curves to obtain the optimum conditions for rejection defluorination [3]. Experience points of the plans proposed by David H. Doehlert in 1970 fill uniformly the experimental space [3]. These plans also allow easy introduction of new factors. New experiences will complement the first and no experience will be lost. The only precaution to take is to maintain non studied factors at a constant value (level 0) for the study of active factors. All points of the plan are Doehlert on a unit circle (centered in reduced quantities). The area defined by the planes of Doehlert is a spherical domain, a circle in a two-dimensional space, a sphere in a three-dimensional space, a hypersphere in a space with more than three dimensions [3]. If the desired results are not in the field of study, we can extend this area in the direction where we most likely to find the desired solution.

3.6.1 Domain and experimental mathematical model proposed

We also kept the same experimental field by specifying the area of the center and not the variation of each factor.

TABLE 7
FACTORS AND EXPERIMENTAL FIELD.

Variables	Factors	Area center	Variation step
U_1	Adsorbent dose (g)	2.25	1.75
U_2	[F-] (mg/L)	1251.5	751.5
U_3	pH	6.5	4.5

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

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

$$R = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3$$

b_0: value of the response centrally in the park; b_i: main effects of each factor; b_{ii}: deviation from linearity; b_{ij}: interactions between factors.

3.6.2 Matrix for calculation of model coefficients

In this work, the coefficients of the mathematical model were determined. For this, we performed 15 experiments in Table 8.

TABLE 8
EXPERIMENTAL MATRIX

		Factors	
Experiment	**U_1 (g)**	**U_2 (mg/L)**	**U_3**
1	4.00	1251.5	6.5
2	0.50	1251.5	6.5
3	3.13	1902.3	6.5
4	1.38	600.7	6.5
5	3.13	600.7	6.5
6	1.38	1902.3	6.5
7	3.13	1468.5	10.2
8	1.38	1034.5	2.8
9	3.13	1034.5	2.8
10	2.25	1685.4	2.8
11	1.38	1468.5	10.2
12	2.25	817.6	10.2
13	2.25	1251.5	6.5
14	2.25	1251.5	6.5
15	2.25	1251.5	6.5

After carrying out the 15 experiments on the experimental design, the results obtained in this study in are depicted in Table 9.

TABLE 9
EXPERIMENTAL DESIGN AND RESULTS.

		Factors		Response
Experiment	U_1	U_2	U_3	R (%)
1	4.00	1251.5	6.5	98.15
2	0.50	1251.5	6.5	97.85
3	3.13	1902.3	6.5	97.07
4	1.38	600.7	6.5	98.43
5	3.13	600.7	6.5	98.05
6	1.38	1902.3	6.5	97.77
7	3.13	1468.5	10.2	97.87
8	1.38	1034.5	2.8	97.93
9	3.13	1034.5	2.8	97.84
10	2.25	1685.4	2.8	97.85
11	1.38	1468.5	10.2	98.17
12	2.25	817.6	10.2	98.18
13	2.25	1251.5	6.5	97.89
14	2.25	1251.5	6.5	97.71
15	2.25	1251.5	6.5	98.31

3.6.3 Mathematical model obtained

After calculating the coefficients of the model, the equation relating the response factors is:

$$R = 97.97 - 0.109\,X_1 - 0.383\,X_2 + 0.122\,X_3 + 0.030\,X_1^2 - 0.197\,X_2^2 + 0.047\,X_3^2 \\ - 0.185\,X_1 X_2 - 0.063\,X_1 X_3 - 0.169\,X_2 X_3$$

3.6.4 Study of response surface curves

Answer surfaces have variations in experimental response based only on two factors at a time, other factors being fixed. Figure 2 shows the surface pattern - response variation of the abatement rates fluorine in the map : adsorbent mass - the concentration of fluoride ions at a pH set at 6.5.

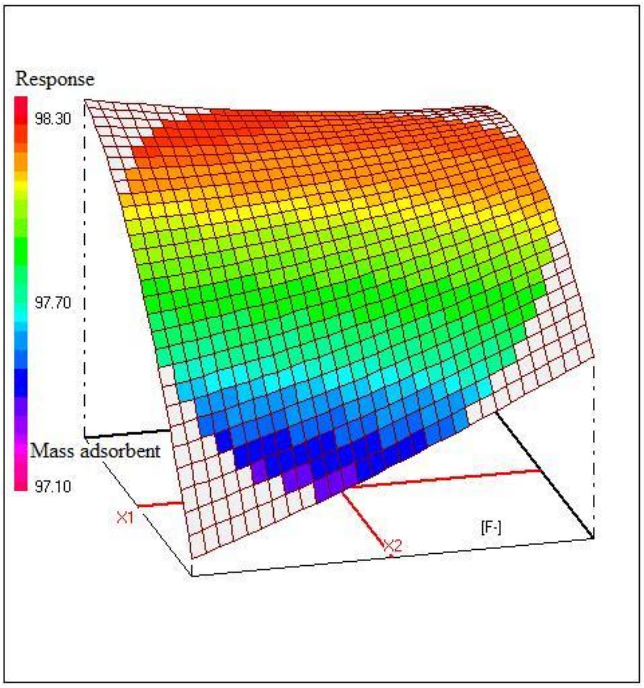

FIG. 2 : SURFACE CHART - RESPONSE VARIATION OF THE ABATEMENT RATES FLUORINE

in the plan : adsorbent dose- [F$^-$] . Fixed factor: pH = 6.5.

It can be seen from Figure 2 that the response reaches a maximum, but this type of graphs is difficult to operate. The projection of the surface pattern - previous response (top view) is convenient to visualize the maximum area with contour lines. By putting the values predicted by the model as isoresponse curves, the effect of factors on the abatement rates fluorine can be analyzed from this diagram. The graphical representation of the design template in the variables of space provides the isoresponse curves. They allow visualizing the response as a function of different parameters. The analysis shows the influence of factors on the response and also determines the optimal region.

3.6.5 Study of curves isoresponse

Figure 3 shows the diagram of isoresponse curves of the variation of the abatement rates fluorine in the adsorbent mass map - [F] for a pH set at 6.5. By analyzing the diagram, we note that obtaining a significant reduction in the rate depends fluorine of a low concentration of fluoride ions and a large mass of adsorbent. Indeed, for an experimental field of fluoride ion concentrations between 491.7 and 1251.5 mg/L and an experimental area of the adsorbent dose between 2.25 and 4.02 g, the answer can reach the value of 98.1 %.

On the other hand, when the concentration of fluoride ions increases for a dose range of fixed adsorbent, we observe a decrease in the defluorination. Therefore, increasing the concentration of fluoride ions inhibits the positive effect of the mass of adsorbent on the response. The diagram of isoresponse curves shown in Figure 3 reveal the existence of an optimal region which corresponds to a response of 98.05 %.

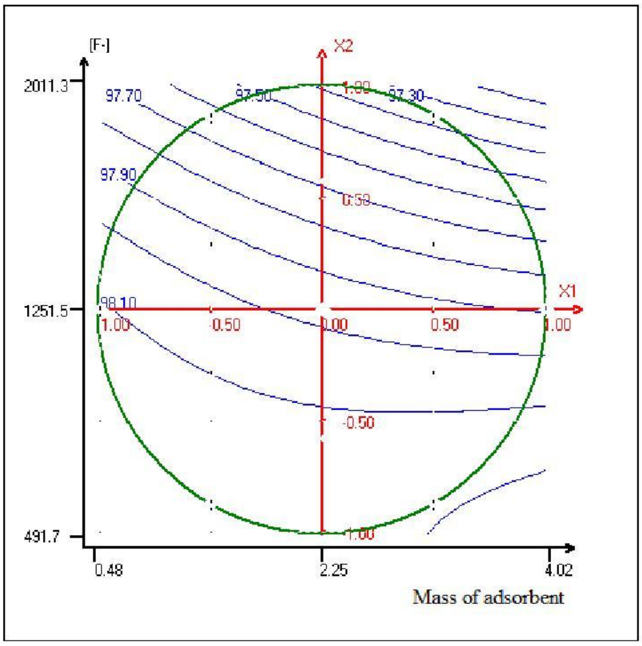

FIG. 3 : DIAGRAM OF ISORESPONSE CURVES OF THE VARIATION OF THE ABATEMENT RATES FLUORINE IN THE PLAN (DOSE ADSORBENT [F^-], FIXED FACTOR : PH = 6.5).

Thus, the optimum conditions adopted are:
adsorbent dose : 3.13 g ;

fluoride ion concentration : 600.7 mg/;
pH = 6.5 ;

AFMW volume : 1 L ;
contact time : 1h 30 min.

Under these conditions, an industrial liquid waste sample was treated and the results obtained are summarized in Table 10.

TABLE 10
COMPOSITION OF THE AFMW AFTER TREATMENT

pH	Conductivity	SO_4^{2-} (mg/L)	SiO_2 (mg/L)	F- (mg/L)	PO_4^{3-} (mg/L)	Ca^{2+} (°F)	Mg^{2+} (°F)
8.90	9.38	12.00	0.23	11.91	3.50	0.00	3.35

Treating an industrial liquid discharge sample according to optimal conditions obtained using the approach of Doehlert shows that the contents of SiO_2, PO_4^{3-} and SO_4^{2-} are increased. The conductivity of the solution decreased as a result of the removal of fluoride ions.

The fluoride ion content decreased dramatically, leading to a reduction rate of 98.05 %. Generally, the adsorption capacity of the adsorbent increases by increasing the initial concentration of the adsorbatemolecules. As the adsorbate concentration increases, the number of collisions between the adsorbatemolecules and the adsorbent functional groups also increases leading to an increase in the adsorption capacity [20, 21].

The influence of adsorbent dose on fluoride adsorption capacity has been demonstrated in a number of studies. Maiti et al. (2011) [22] in a fluoride removal study observed that at fixed pH and initial fluoride concentration the adsorption capacity of chemically.

The decreased adsorption capacity with increasing adsorbent dose was attributed to the non-availability of fluoride ion. Similar results have been reported by Kamble et al. (2009) [23] with chemically modified bentonite for which they have cited two reasons: (i) better utilization of the available active sites at low adsorbent dose in comparison to high adsorbent dose where too many sites are available for limited quantity of adsorbate, (ii) reduced driving force for adsorption as high adsorbent dose causes lower equilibrium fluoride concentration.

So by lowering the pH optimum conditions of full factorial design (set at pH 6.5), an increased reduction rate of fluorine with a final pH of 8.9 could be obtained. The adsorption capacity of a clay mineral is influenced not only by its textural properties (e.g. specific surface area, pore size and pore size distribution) but also by the very chemical nature of adsorbent surface. The surface chemical characteristics of the adsorbents can be significantly altered by the pH of an adsorption system [22, 23].

IV. CONCLUSION

The removal of fluoride ions from an industrial effluent through treatment by adsorption on natural clay using the methodology of experiment design. The graphical analysis of the effects of various factors as well as the study of surface patterns - response curves and isoresponse allowed obtaining the following optimal conditions:

adsorbent dose: 3.13 g ;

fluoride ion concentration : 600.7 mg/L;
pH = 6.5 ;

AFMW volume : 1 L ;
contact time : 1h 30 min.

We have shown that the treatment of strongly acidic and fluoride-rich industrial waste (26,000 mg/L) resulted in good yields of removing fluoride ions, even exceeding 98% of fluorine reduction rate. The removal of fluoride ions by adsorption on clay was shown to be very fast and very effective.

Use of natural clay has often been better or comparable with the existing commercial filter materials, adsorbents, and conventional methods for fluoride removal. Among various process parameters, pH of water is found to be one of the critical factors affecting the sorption process [24].

The amount of clay used has a significant influence on the kinetics and performance of the treatment process.

REFERENCES

[1] A.H. Bannoud et Y. Darwich, Désalination, 2007, 206, 449 - 456.
[2] Méthodes d'analyse, Centre d'expertise en analyse environnementale du Québec, 12 Décembre 2014.
[3] J. Goupy et L. Creighton, Introduction aux plans d'expériences, 3ème Ed., Dunod, Paris, 2006.
[4] J. Cantet, Le cahier des chroniques scientifiques, n° 10, Effluents industriels, Mai 2007.
[5] L.R. Puka, Fluoride Adsorption, MSc dissertation, Faculty of Science, Rand Afrikaans University, 2004.
[6] A. Ezzeddine, A. Bedoui, A. Hannachi, N. Ben salah, Desalination and water treatment, 2015, Vol. 54, Issue 8, 2280-2292.
[7] P.K. Sanjay, D. Priyadarshini, S.R. Sadhana et K.N. Labhsetwar, Desalination, 249, 687 - 693, 2009.
[8] V.K. Meenakshi et al., Journal of Hazardous Materials, 2004, B106, 85 - 97.
[9] V.K. Meenakshi et R.C. Maheshwari, Journal of Hazardous Materials, 2006, B137, 456 - 463.
[10] J.L. Shupe, A.E. Oslon, H.B. JAVMA, 1984, n° 185, 1295 - 1300.
[11] R.K. Hoop, E.C. Böttger et G.E. Pfyffer, Journal of Clinical Microbiology, 1996, 34, 991 - 992.
[12] G.A. Lewis, D. Mathieu et R. Phan Tan Luu, Pharmaceutical Experimental Design, Marcel Dekker, New York, 1998.
[13] Sado, Les plans d'expériences : De l'expérimentation à l'assurance qualité, Afnor Technique, 1991.
[14] D. Mathieu, R. Phan Tan Luu, Approche méthodologique des surfaces réponses, pp. 211 - 278, dans les plans d'expériences, Application à l'entreprise et J.J. Droesbeke, J. Fine et G. Saporta, Ed. Technip, Paris, 1997.
[15] M. Dachraoui, Introduction à la norme ISO/CEI 17025 et guide de validation des méthodes d'analyse, Centre de publication Universitaire, Tunis, Tunisie, 2012.
[16] F. Hellal, M. Benna et M.S. Medimagh, Intern. J. Environment Studies, 1998, 55, 53.
[17] M. Dachraoui, Introduction à la norme ISO/CEI 17025 et guide de validation des méthodes d'analyse, Centre de publication Universitaire, Tunis, Tunisie, 2012.
[18] W.L. Lindsay, Chemical equilibria in soils, John Weley and Sons, New Yord, 1979.
[19] B. Bar-Yosef, I. Afik et R. Rosenberg, Soil Sci., 1988, 145, 194-200.
[20] Q. Guo, E.J. Reardon, Appl. Clay Sci., 2012, 56, 7 - 15.
[21] S. Mandal, S. Mayadevi, J. Hazard. Mater, 2009, 167, 873 - 878.
[22] A. Maiti, J.K. Basu, S. De, Desalination, 2011, 265, 28 - 36.
[23] S.P. Kamble, P. Dixit, S.S. Rayalu, and N.K. Labhsetwar, Desalination, 2009, 249, 687 - 693.
[24] A. Vinati, B. Mahanty and S.K. Behera, Applied Clay Science, 2015, 114, 340 - 348.