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The regeneration of the pre used ashes in the elimination fluorides ions from the underground waters

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Abstract
After studying the mechanisms and optimization of the conditions of adsorption of soluble fluoride in groundwater (Youssoufia-Morocco) on fly ash [1], interest has been focused on the regeneration performance of these pre-used ashes to estimate their lifetime. The results showed, firstly, that the desorption is possible and effective step proceeds using a basic solution of ammonia and lime. The optimum desorption conditions are a breakthrough time of at least 30 minutes and a concentration around 1M for lime and 4M for ammonia, with a desorption percentage of 92% .In the second time we have shown that the number of successive adsorption cycles tolerated by the ash is at least 10 cycles. Finally, some parameters influencing the desorption such as the concentration of lime, volume to implement, the desorption kinetics were optimized.

Keywords: Fly ash, Fluoride, kinetics of desorption, Ground water

1. Introduction
The deposit of black phosphate in Youssoufia (Morocco) is characterized by the presence of underground water in yards. This water, known as mine water is pumped to the outside of the mine to allow the exploitation of these deposits [1, 2]. The observation in recent years the relationship tonnage / debit dewatering foreshadowed a rate of more than 35 000 m^3/day from the 2000 [2]. This mine water of Youssoufia is characterized by a chemical composition more or less variable and is particularly loaded by fluorides ($[F^-]>>2$ mg/l). We note that the fluoride concentration is exceeding the levels recommended by the Moroccan National Office of Drinking Water [3] and the World Health Organization (WHO) [4]. The maximum concentration of fluoride ions must be less than 1.5mg/l, which represents an ongoing risk to the rural population using only groundwater (wells) for daily consumption [5-6].
After studying the sorption mechanisms under static conditions, including allowing optimizing the operating conditions for fluoride sorption from the mine water (groundwater) black phosphate of the city of Youssoufia - Morocco on fly ash, interest has focused on the regeneration performance of such pre-ash used to estimate the lifetime. The fly ash used is the main by-product of solid waste from thermal power Lafar Jorf in El Jadida (Morocco) [7].

2. Materials and methods
2.1 *Characterization of mine water of Youssoufia*
All water samples are stored at 4°C in plastic vials and analyzed in the laboratory within 24 hours according to the French standard methods (The French Association for Standardization) [8] and Rodier J [9].

For dosing fluorides, several methods can be used including titrimetry, spectrometry and fluorine activation analysis. In this study, the fluoride ions were measured by potentiometric method using an solution of Titre Ionic Strenght Adujsting Buffer (TISAB), a specific electrode and a reference electrode (Ag/AgCl), according to The French Association for Standardization [8] (T_{90-004}). It has the advantage of being simple, rapid response and lends them to serial testing. The apparatus used was an Orion pH model SA 520 with specific electrode fluoride ions. The assay solutions were prepared in plastic beakers in accordance with the following volumes: 10 ml of the sample+10 ml of TISAB solution. After magnetic stirring for 3 minutes, the readings are taken and values are brought to the calibration curve to determine the concentrations of ions F^- in mg/l [8].

2.2 *Chemical analysis of fly ash*

In the city of El Jadida (Morocco), located 115 km from the city Youssoufia (Morocco), we have large quantities of fly ash from the power plant at Jorf Lasfar [7]. The Chemical analysis (major components) of fly ash was performed using a fluorescence spectrometer brand X Rays Siemens Type SRX 3000, equipped with a tube with Rhodium anode.

2.3 *Study of the sorption-adsorption*

2.3.1 *Choice of the concentration of the eluent*

A preliminary test in the selection of an eluent was made by the following steps: saturated ash is mixed with 100 ml of the eluent solution (NH_4OH and lime). The mixture is stirred for one hour at 300r/min. Finally, the resulting solutions, after filtration, were analyzed according to the previously described method [10].

2.3.2 *Kinetics of desorption*

A mass of saturated ash (10g) is put in contact with 1liter of lime solution (0.25M, 0. 5 M and 1M). The whole is subjected to mechanical agitation with Jart-test at a speed of 300 rpm at room temperature. At a defined time, there a sub-sample is used to determine the residual concentration of fluorides.

2.3.3 *Cycles of the adsorption-desorption of fluoride*

10 g of ashes were placed in a beaker containing 1liter of fluoride riche water. The stirring speed was 300r/min. the tests were carried at room temperature. This quantity of ash successively undergoes several sorption and desorption cycles. The objective of the test is to provide a large number of sorption-desorption cycles. To achieve the sorption phase, a water containing 3.50 mg/l of fluoride was used. The amount of fluoride retained by ash is given by the difference between the initial and final concentration of the treated water.

The desorption phase is as follows: 10 g of fluorides saturated ash are placed in 1liter of eluent solution of lime. After stirring for 30 min at 300r/min, the fly ash is removed and rinsed with water and reused again.

3. Results and discussion

3.1. *Characterization of fly ash*

The chemical composition of fly ash from the power plant at Jorf Lasfar, in El Jadida is listed in Table 1. We note that the silica SiO_2 and Al_2O_3 alumina is present in very large quantities [7]. This type of ash rich in silica and alumina is called Silico-Aluminous ash, and it belongs to the class F according to the files American Standard Methods (ASTM) [11,12]. The complete characterization namely; SEM, IR, RX at different temperatures, the analysis of heavy metals and metallic elements of the fly ash was carried out in the following study [7]. We can also be added that the Leaching of fluorides from fly ash has been studied at different conditions (ash/water distilled ratios, variable temperature and for one interval of the very precise pH). The contents of the trace elements in the washed waters have also been evaluated [13].

Table 1: Chemical composition of fly ash from the thermal power station of JORF-LASFAR-Morocco [7, 13]

Oxide	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	Na_2O	K_2O	MgO	SO_3
Mass%	50	25	1,5	6	6	0,34	1,5	1	1,5

3.2. *Characterization of the studied water (mine water)*

Table 2 shows the average physicochemical analysis of certain parameters. Indeed, these waters have highly concentrated levels of fluorides from the standards [14,15]. It is noted that these waters have a concentration of fluoride that exceed the standards of the World Health Organization (WHO) and those the National Office of Drinking Water in Morocco (NODWM) [3,4]. The maximum concentration of fluoride ions must be less than 1.5mg/l.

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Table 2: Physico-chemical composition of groundwater from Phosphate region.

Parameters	pH	EC* ms/cm	F^- mg/l	Cl^- mg/l	SO_4^{2-} mg/l	NO_3^- mg/l	HCO_3^- mg/l	Na^+ mg/l	K^+ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l
Average values	7,67-8.10	1,21-1.34	2,4-4.4	173-197	140-179	9-32	281-305	58-87	3-12	60-100	55-88

EC*: Electrical Conductivity

3.3. *Study of desorption*

The results obtained according to the eluent solution, their concentration are reported in Table 3. The efficiency of desorption is the percent fluoride desorbed with respect to the quantity contained in the 10g of fly ash.

Table 3: Efficacy of the desorption as a function of the eluting agent

Eluent Agent	NH_4OH						Lime			
Concentration	12 M	8 M	4 M	2M	1M	0,5M	10 M	5 M	2 M	1 M
Efficiency (%)	82	80	76	72	70	62	94	91	93	90

We see that the basic environments are very favorable for the desorption of fluoride ions with fairly important efficiencies for Ammonia (NH_4OH) and Lime ($CaCO_3$) for the different concentrations used. These initial results pushed us very far, to optimize their use as agent eluent.

3.4. *Desorption in lime*

Efficiency values (Table 4) indicating that the volume of lime does not alter the desorption efficiency. It is the maximum when the volume of implement is maximum and the lime concentration is 0.5M. For the rest of the work, we take lime (0.5M) as eluting agent.

Table 4: Efficacy of desorption of fluoride with lime according to the volume used in 1M and 0.5M.

Volume (ml)	20	30	50	60	80	120
Lime 1M	85	90	92	91	90	90
Lime 0.5 M	82	93	91	90	90	90

3.5. *Kinetic desorption*

A first series has been traced by varying the concentration of the lime. 10 grams of saturated ashes are put with 1liter of lime (0.5 M; 0.25M and 1 M) under stirring of 300 rpm. Samples are withdrawn made regularly. The solutions are analyzed. The curves obtained are shown in Fig. 1.

These graphs provide interesting information on the kinetics of desorption. Firstly, the maximum efficiency is reached very rapidly since at after of 30 minutes, concentrations practically not change more in the solution for the two concentrations of lime used (0,5 and 1 M), it is with 92% of fluorides have been sorbed. Finally, increasing the concentration of the lime of 0.25M to 1 M also has an effect on the kinetics of desorption.

3.6. *The effect of dose of fly ash*

It is noted in Figure 2 that the quantity of ash for the same volume of the lime has an effect on the kinetics of desorption. The quantity of fluoride to be desorbed is important when the mass of the ash increases. The effect on the desorption kinetics corresponds to an increase of the time required to achieve equilibrium. We will therefore use lime as eluting agent, a very fast and very efficient desorption even at low concentrations.

3.7. *Adsorption and desorption cycles*

The results of Figure 3 show that the sorbed and desorbed quantity of fluoride is t the same for 10 cycles. Sometimes the desorbed quantity is greater than the fixed amount. This can be explained by the imprecise of the measurements, it is estimated at 3% (Fig. 3).

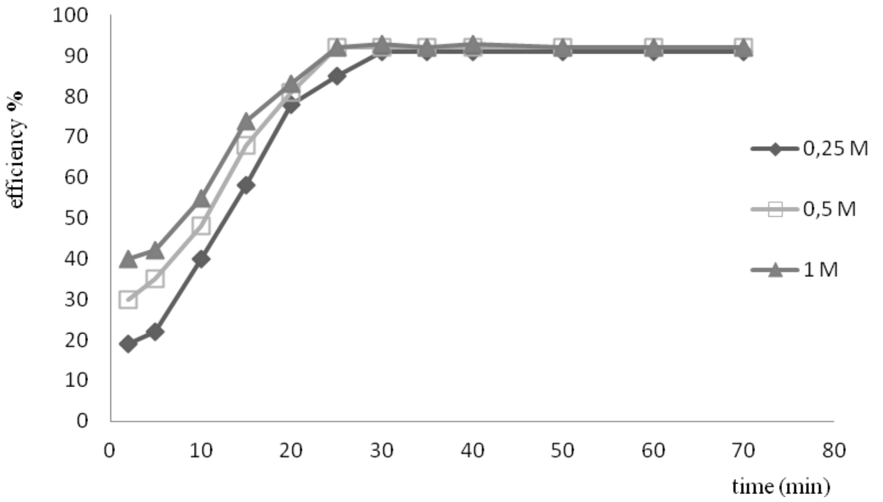

Figure 1: Kinetics of the desorption of the fluoride by lime

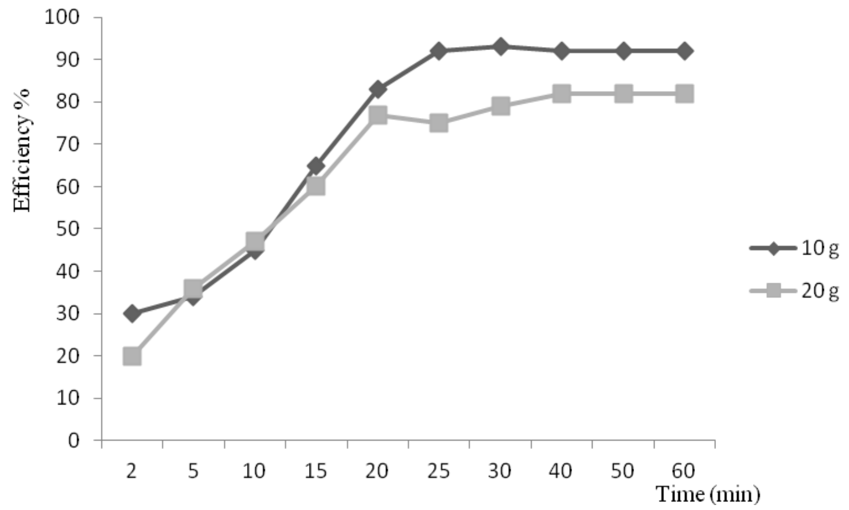

Figure 2: Effect of the quantity of ash on the desorption lime (0.5M)

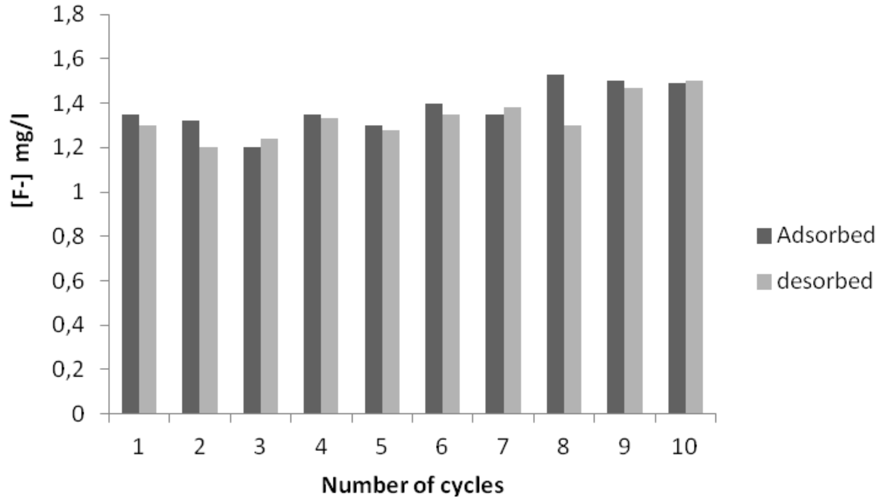

Figure 3: Sorbed and desorbed quantity of fluoride in the 10 cycles sorption-desorption

Conclusion

The results obtained in this work show:

First time, desorption is a possible and effective method step. This can be done using basic solution of ammonia and lime. Optimal desorption conditions are a contact time of at least 30 minutes and a concentration at about 0,5M to lime and 4M for ammonia.

Second time we have shown that the number of successive cycles of adsorption tolerated by the ashes is at least 10 cycles.

Finally, we optimized some parameters influencing this desorption (concentration of lime, volume to implement, the desorption kinetics). All these findings are interesting in view of the use of fly ash stored for defluoridation existing groundwater in large whose amount (without any previous treatment) for agriculture since it is possible to work with these ashes several times in the adsorption-desorption cycle.

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