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FLUORIDE REMOVAL FROM AQUEOUS SOLUTIONS BY SORBTION-FLOTATION

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S-a studiat îndepărtarea ionului fluorură din sisteme apoase prin sorbție pe oxohidroxid de fier urmată de flotație. Pentru procesul de sorbție s-au studiat echilibrul de separare şi factorii de influență (pH-ul, viteza de agitare, cantitatea de adsorbant, timpul de contact şi concentrația inițială de ioni fluorură) în vederea stabilirii parametrilor optimi. Ecuațiile izotermelor Langmuir şi Freundlich fitează datele experimentale obținute pe tot domeniul de concentrații studiate. Efluenții rezultați după adsorbție s-au flotat în scopul creşterii eficienței procesului. În acest scop s-au studiat: presiunea în vasul de presurizare, raportul de diluție V_{proba}:V_{apa}, *timpul de flotație, şi s-au stabilit parametrii de separare. După aplicarea tehnicii de sorbție-flotație eficiența de îndepărtare maximă obținută a fost de 92%.*

The removal of fluoride ion from aqueous system by sorption on ferric oxyhydroxide and flotation was studied. In order to establish the optimum process parameters for sorption process the separation equilibrium and the influence of the factors: pH, stirring rate, amount of the adsorbent, contact time and initial concentration of the fluoride ions were examined. Langmuir and Freundlich isotherm equations fit the experimental data on the whole range of studied concentrations. In order to increase the removal efficiency effluents resulted from adsorption were floated. For this reason, pressure in the pressurized recipient, dilution ratio V_{sample}:V_{water}, *flotation time were varied, and the separation parameters were established. After applying the sorption-flotation technique, the maximum removal efficiency obtained was 92%.*

Keywords: sorption-flotation, ferric oxyhydroxide; fluoride ion, wastewaters treatment

1. Introduction

High fluoride levels in drinking water has become a critical health hazard of this century as it induces intense impact on human health including skeletal and dental fluorosis [1].

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Of all elements, fluorine is the most electronegative and most reactive. Because of its high reactivity, fluorine is not found in Nature in its elemental state and exists as fluorides [2] and is harmful to human health. Besides natural sources fluorides may also be derived from mining or industrial activity in some areas.

According to the World Health Organization (WHO) guidelines, the upper limit of fluoride concentration in drinking water is 1.5 mg/L [3]. The most commonly used methods for the defluorination of water are precipitation, adsorption, ion-exchange, nano-filtration and electrodialysis [4-12]

Precipitation of fluoride with calcium and aluminum salts [13, 14] has been intensively used to remove fluoride from industrial wastewaters. Typically, lime is used as a calcium source, and firstly reduces the fluoride concentration down to 10–20 mg/l. The Ca^{2+} ions released from calcium salts interact with fluoride and form CaF_2 precipitate. The final concentration of fluoride in the water treated using this method greatly depends on the solubility of precipitated fluoride. The solubility constant of CaF_2 is theoretically $K_{sp\ CaF2} = 3.45 \cdot 10^{-11}$ (at 25°C), therefore, even when a large dosage of calcium is used, the concentration of fluoride in water is still greater than 5mg/l (F^- limit from NTPA 002), and the pH of treated water is at a relatively high value, resulting in a supplementary difficulty of eliminating excess chemicals [15].

Adsorption is considered one of the most efficient technologies for fluoride removal in drinking water when compared to other technologies for fluoride removal based on initial cost, flexibility and simplicity of design, and ease of operation and maintenance [16]. The efficiency of this technique mainly depends on adsorbents.

Recent attention of scientists has been devoted to the study of low cost, but friendly reagents, from this reason, in the past years, considerable attention has been focused on the study of fluoride removal using natural, synthetic, and biomass materials such as activated alumina [17], fly ash [18], alum sludge [19], chitosan beads [20,21], red mud [22], zeolite [23], calcite [24], hydrated cement [25], and layered double hydroxides[26].

In this paper, FeO(OH) was used as sorbent material to remove fluoride from aqueous solutions in order to obtain a cost efficient water treatment and to reduce the concentration of F^- in water according to environmental legislation. Studies were carried out in synthetic fluoride solutions with the objective of establishing optimum parameters for adsorption-flotation.

2. Experimental

2.1. Reagents

- NaF Carlo ERBA (Italy) p.a., $10.53 \cdot 10^{-3}$M stock solution of fluoride (1000mg/l). Standard solutions with varying NaF (from 0 to 200mgF^-/l) concentration were prepared by appropriate dilution of the stock solution. Distillated water was used for preparing the solutions.

- FeO(OH) WISUTEC (Germany) with 0.2mm particle size;
- H_2SO_4 (1.5M) for pH adjustment;
- FR2510 (Henkel) anionic flocculent polyacrylamide type, aqueous solution 0.2% concentration;
- NaOL Fluka (Hungary) p.a., $2.5 \cdot 10^{-2}$ M solution, as collector agent.

2.2. Equipments

-UV-VIS spectrophotometer SPECORD 205 for determine the concentration of fluoride;

-pH-meter type Orion 420A+ for pH determinations;

- A dissolved air flotation unit (DAF) with the cell dimensions: $h = 30$ cm, $\Phi = 4.5$ cm was used for flotation [27];
- Kruss K11 tensiometer for surface tension determinations.

2.3. Methodology

The batch adsorption-flotation study was conducted for the optimization of various experimental conditions like pH, stirring rate, contact time, initial fluoride concentration, adsorbent dose for adsorption and dilution ratio $V_{sample}:V_{water}$; equilibrium pressure in pressure recipient and time for flotation.

Measured volumes (100 ml) of test samples were mixed with different quantities of FeO(OH) using a shaker. After the addition of adsorbent, the content was mixed at different speeds for various periods of time. At the end of the stirring period, the samples were removed from the shaker and the contents were allowed to settle for 60-480 min. After settlement of adsorbent, the supernatants were carefully decanted and analyzed for residual fluoride by spectrophotometric method [28]. Adsorption effluents were then floated varying the pressure, flotation time and dilution ratio.

3. Results and discussion

3.1. Adsorbent selection

For adsorption studies FeO(OH) with fraction size of $\square \leq 0.2$ mm was selected, because the adsorption capacity of different adsorbent materials from iron oxides category have shown good separation yields for fluoride removal.

For this synthesis absorbent was performed an X-ray diffractogram analysis that has shown a solid amorphous and homogeneous material. X-ray diffractogram of the ferric oxyhydroxide is presented in Fig. 1.

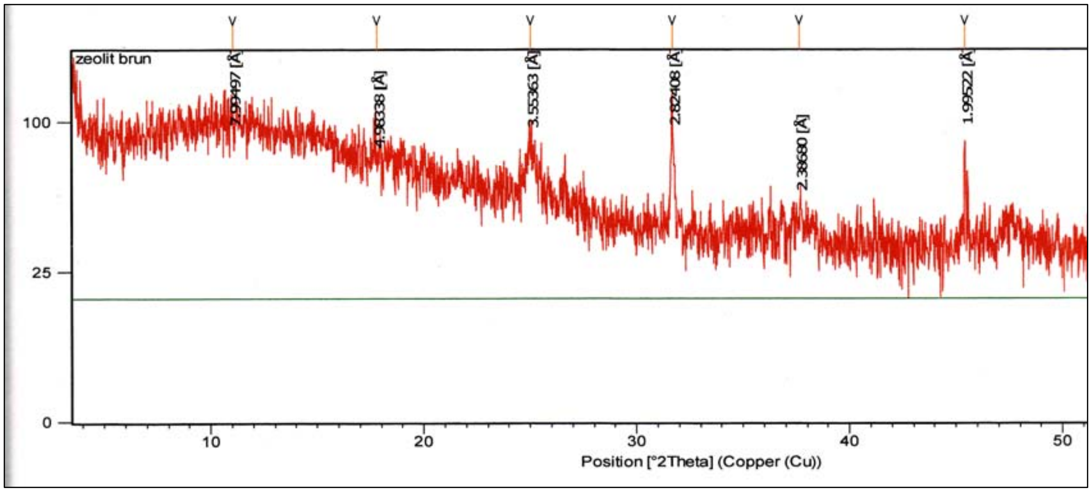

Fig. 1. X-ray diffractogram of the ferric oxyhydroxide [28]

Surface charge of iron hydroxide indicates a pH modification between 6.4 and 7.4.

Ferric oxyhydroxide chemical composition expressed in % weight was: Na_2O 13.64%; Al_2O_3 1.585%; SiO_2 1.033%; SO_3 1.755%; Cl 4.23%; CaO 0.183%; TiO_2 36.35%; Fe_2O_3 37.38% [28].

Adsorption equilibrium isotherms for F^- on ferric oxyhydroxide

Adsorption process can be described by various models. Empirical models provide descriptions of adsorption data. An adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption process reaches an equilibrium state in batch investigations.

Maximum adsorption capacity is an important parameter to characterize the performance of an adsorbent. Adsorption capacity is based on mass balance in the system adsorbent - adsorbate, considering that the adsorbate which is not found in the solution is retained by the adsorbent and is calculated with equation (1) [29]:

$$q_e = \frac{V \cdot (C_i - C_e)}{m} \qquad (1)$$

Were: q_e – equilibrium adsorption capacity;
C_i - initial concentration of adsorbent;
C_e - adsorbent equilibrium concentration;
V - volume of contacting solution;
m -mass of adsorbent.

The analysis of the isotherm data by fitting to different isotherm models such as Langmuir and Freundlich is an important step to find the suitable model that can be used for design purposes. The Langmuir and Freundlich isotherms and their linearized forms are given in Table 1.

Table 1

Isotherms and their linear forms

Isotherm	Form	Linear form	Plot	Ref
Langmuir	$qe = (q_m K_a C_e)/(1+K_a C_e)$	$C_e/q_e = 1/q_m C_e + 1/K_a q_m$	$1/q_e$ vs. $1/C_e$	[30]
Freundlich	$qe = KFCe^{1/nF}$	$\log(q_e) = \log(K_F)+1/n_F \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	[31]

Where: C_e – equilibrium solute concentration, mg/l; q_e – amount of contaminant sorbed at equilibrium mg/g; K_F – Freundlich isotherm constant (mg/g)· (l/g) · 1/n_F; n_F – Freundlich exponent; q_m – maximum sorption capacity, mg/g; K_a – Langmuir constant related to energy of adsorption, l/mg.

Adsorption experiments for process equilibrium study were conducted in discontinuous system, at the following parameters: initial fluoride concentration 50mg/l, adsorbent dose 1g/100 ml, pH 4.5, agitation speed 200 rpm, dynamic contact time 10 min, static contact time 60 min, flotation time 5 min, dilution ratio V_{sample}:V_{water} 3:1 and pressure 4 atm.

To appreciate how well correlates these mathematical model with experimental data obtained, experimental data fitting was performed with Langmuir and Freundlich isotherms equations. The results are presented in Figs. 2, 3 and 4:

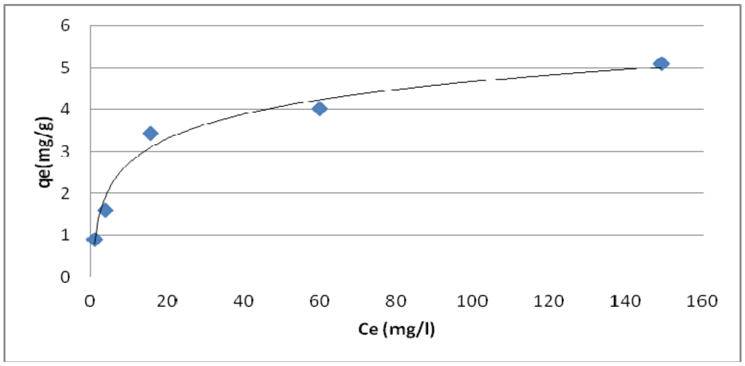

Fig. 2. Adsorption isotherm for fluoride adsorption on FeO(OH) at pH 4.5; mass ratio C_{F}-:C_{ads} 1:20; Ci_{F}- 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure 4atm

From Fig. 2 results that the maximum adsorption capacity for F^- ion is 5mg/g.

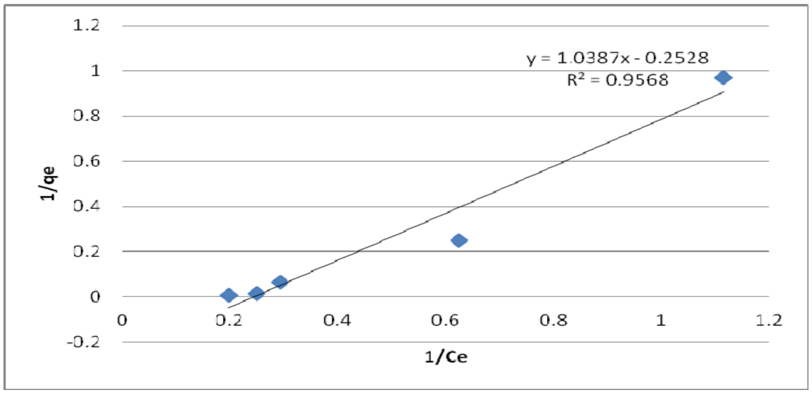

Fig. 3. Langmuir isotherm at pH 4.5; mass ratio C_{F}-:C_{ads} 1:20; Ci_{F}- 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4 \cdot 10^5 N/m^2$

Because coefficient of correlation (R^2) value exceeds 0.950 result that Langmuir equation characterized satisfactory the adsorption process.

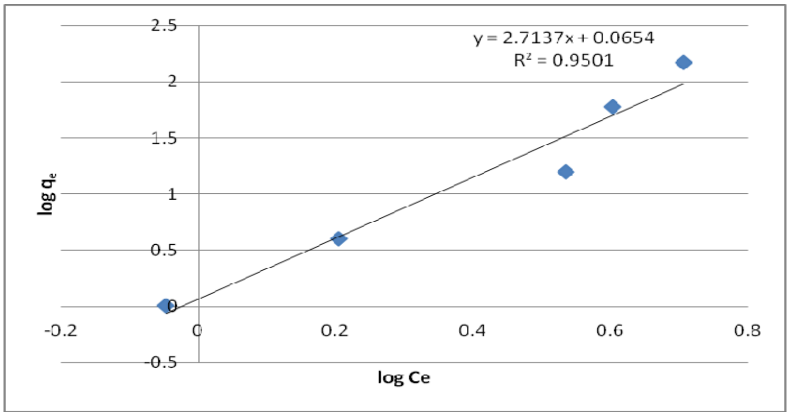

Fig. 4. Freundlich isotherm at pH 4.5; Mass ratio C_{F}-:C_{ads} 1:20; Ci_{F}- 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4 \cdot 10^5 N/m^2$

The regression value (R^2 = 0.950) indicate that the adsorption data for fluoride removal fitted Freundlich isotherm for the concentration studied.

It is evident from a comparison of the values of coefficient of correlation (R^2) that the equilibrium adsorption equations Freundlich and Langmuir satisfactory characterize adsorption process for the whole range of concentrations studied.

F^- removal by sorption-flotation experiments

To establish the optimal parameters for F^- removal by sorption-flotation were studied the adsorption influencing factors under various conditions: stirring rate; mass ratio C_{ion}:C_{ads}; F^- initial concentration; dynamic contact time and static contact time. Then, samples resulted from adsorption were flotated and flotation influencing factors were studied: dilution ratio V_{sample}:V_{water}; equilibrium pressure in pressurized recipient; flotation time. The experiments were done on synthetic solutions of NaF.

3.1. Adsorption

pH

The pH of the aqueous solution is a very important factor in the adsorption process because it contributes to modification of the adsorption capacity of adsorbent support. Thus, the role of pH at 4.2, 4.5, 5.0, 6.0 and 7.0 was observed. The pH was maintained at desired value by adding 1.5M H_2SO_4 in 100 ml of prepared solution of 50 mg/l of fluoride solution for contact time of 70 min with a dose of 1g/100 ml of FeO(OH), flotation time 10 min, dilution ratio V_{sample}:V_{water} 3:1 and pressure $4 \cdot 10^5 N/m^2$. The influence of pH on extent of sorption is shown in Fig. 5.

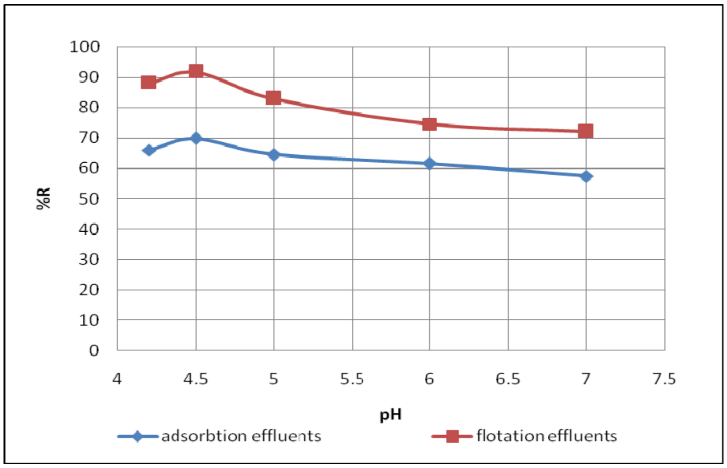

Fig. 5. pH effect on separation yield at mass ratio C_{F^-}:C_{ads} 1:20; Ci_{F^-} 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4 \cdot 10^5 N/m^2$

As described in Fig.5, it was observed that the maximum adsorption $\%R_{ads}$ of 92 % is achieved at pH 4.5. A decrease in the extent of removal of fluoride ions was observed with increase in the pH of the solution. Thus, pH of 4.5, which gave maximum fluoride removal, was taken into consideration for further studies.

Adsorbent dose

Studies on effect of adsorbent doses were conducted by varying adsorbent doses at 0.25; 0.5; 0.75; 1.0; 1.25 and 1.5 g/100 ml. The other parameters were maintained constant. Fig. 6 shows that an increase in the adsorption occurs with the corresponding increase in the amount of adsorbent. The increase in the removal efficiency with simultaneous increase in adsorbent dose is due to the increase in surface area, and hence more active sites were available for the adsorption of fluoride.

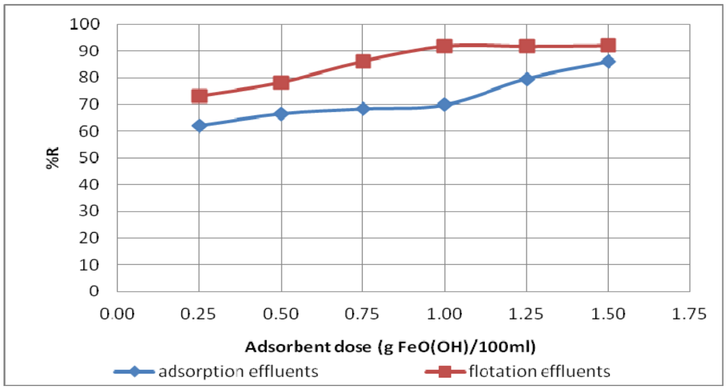

Fig.6. Adsorbent dose effect on separation yield at pH 4.5; Ci_F- 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4\cdot10^5$N/m^2

There was found less significant fluoride ion removal after applying dose of 1.0 g/100 mL (Mass ratio C_{F^-}:$C_{FeO(OH)}$ 1:20) and hence, this dose was selected for further studies.

Initial Fluoride Concentration

Studies on the effect of initial fluoride concentration were conducted at: 10; 20; 50; 100 and 200 mg/l F^- keeping adsorbent dose of 1g/100 ml, pH of 4.5, stirring rate of 200 rpm, contact time of 70 minutes, flotation time 10 min, dilution ratio V_{sample}:V_{water} 3:1 and pressure 4 10^5 N/m^2. The results are showed in Fig.7. The data presented in Fig. 7 indicate that the percentage removal of fluoride ion decreases with increase in initial fluoride ion concentration. This is probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited, thereby adsorbing almost the same amount of fluoride.

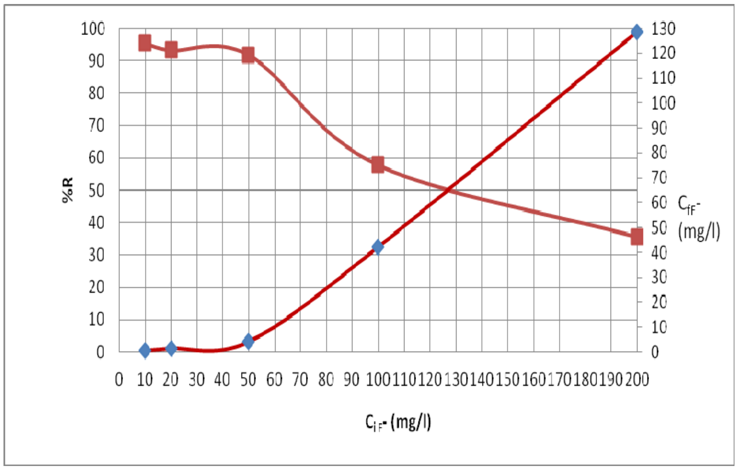

Fig. 7. Fluoride initial concentration effect on separation yield and on final fluoride concentration at pH 4.5; mass ratio C_{F^-}:C_{ads} 1:20; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4{\cdot}10^5$N/m^2

Concentrations below the legal limit of 5mg/l are obtained only in case of using the model fluoride solutions with concentrations of up to 50mg/l, and therefore will continue to work with 50 mg/l initial concentration of F^-.

Stirring rate

Studies on the effect of stirring rate (150; 200; 250; 300; 350; 400 rpm) were conducted maintaining the other adsorption and flotation parameters constant. The influence of stirring rate on the extent of adsorption is shown in Fig. 8.

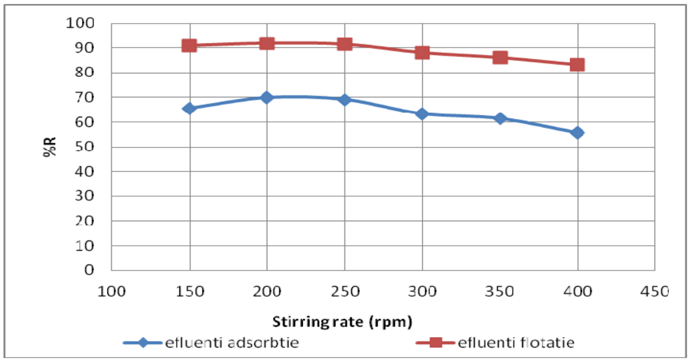

Fig. 8. Stirring rate effect on separation yield at pH 4.5; mass ratio C_{F^-}:C_{ads} 1:20; Ci_{F^-} 50mg/l; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4{\cdot}10^5$N/m^2

Fig. 8 reveals that fluoride removal is a function of stirring rate. The removal (%$R_{ads)}$ is 70% at 200 rpm and decrease at 56% at 400 rpm. The adsorption extent for stirring rate of 200 rpm show a significant decrease and hence stirring rate of 200 rpm was considered for further study.

Dynamic contact time

Dynamic contact time is one of the effective factors in batch adsorption process. In this stage, all of the parameters except dynamic contact time, including adsorbent dose (1 g/100 ml), pH (4.5), initial fluoride concentration (50 mg/l), stirring speed (200 rpm), static contact time, flotation time, dilution ratio V_{sample}:V_{water} 3:1 and pressure $4 \cdot 10^5$ N/m^2 were kept constant. The effect of different dynamic contact times (10; 20; 30; 45; 60 min) on fluoride adsorption efficiency is showed in Fig. 9.

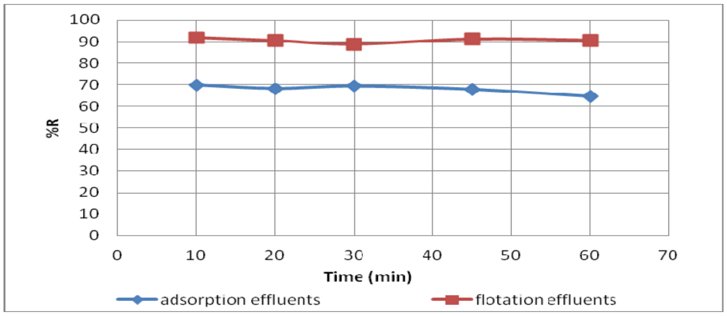

Fig. 9. Dynamic contact time effect on separation yield at pH 4.5; Mass ratio C_{F^-}:C_{ads} 1:20; Ci_{F^-} 50mg/l; stirring rate 200 rpm; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4 \cdot 10^5 N/m^2$

As it is shown in Fig. 9, there was no significant change in adsorption removal efficiency after 10 minutes of stirring.

Static contact time

A plot of percentage adsorption versus static contact time is shown in Fig. 10. Were done experiments at 60, 120, 240; 360 and 480 min and the other parameters were maintained constant.

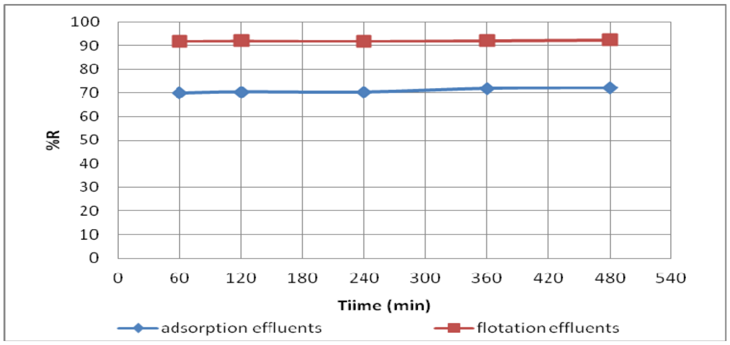

Fig. 10. Static contact time effect on separation yield at pH 4.5; mass ratio C_{F^-}:C_{ads} 1:20; Ci_{F^-} 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; dilution ratio V_{sample}:V_{water} 3:1; flotation time 5 min; pressure $4 \cdot 10^5 N/m^2$

From Fig. 10, the plot reveals that the maximum adsorption (%R_{ads} of 70%) occurred after 1h and there was almost no adsorption beyond this time. This is probably due to a larger surface area available at the beginning of the adsorption of fluoride ions. The fluoride removal efficiency is 92% for flotation effluents.

Adsorption reproductibility

Selected adsorption parameters for F^- separation were verified on 5 identical samples with $C_{i\ F^-}$ = 50 mg/l. For adsorption reproducibility was used Student method (Table 2).

Table 2

Adsorption reproducibility

Sample nr.	**CONDITIONS**	**$C_{f\ F}^-$ (mg/L)**	***ADSORPTION REPRODUCTIBILITY***
1	pH 4.5; Mass ratio C_F-:Cads 1:20; Ci_F-50mg/l; Stirring rate 200 rpm; Dynamic contact time 10 min; Static contact time 60 min	15.25	$\bar{x}$ = 15.11
2		15.04	P = 95%, t = 2.57
3		15.11	Cf_F^- = 15.11 ± 0.10
4		15.02	P = 99%, t = 4.03
5		15.13	Cf_F^- = 15.11 ±0.16

3.2. Flotation

Because fluoride is difficult to be separated from the liquid phase only by adsorption, in order to obtain fluoride values below legal limit of 5mg/l, the separation of residual fluoride by flotation was experimented.

For flotation process was selected **dissolved air flotation** technique. The flotation process was carried out in a dissolved-air-flotation unit [27]. Water saturated with air in the saturator and kept under pressure of $4 \cdot 10^5 N/m^2$ was introduced to the cell base. When releasing water to the atmospheric pressure, fine air bubbles were generated, appropriated for solid/liquid separation.

In this paper we use sodium oleate (NaOL), a common anionic surfactant agent. The importance of oleate solution chemistry in the flotation process results from the fact that the oleic acid in aqueous solution undergoes hydrolysis and forms complex species which exhibit markedly different solubility and surface active characteristics [28].

In batch adsorption experiments was used a constant dose of anionic flocculent (FR 2510).

Pressure in the pressurized recipient

Fig. 11 presents results of experiments conducted on studying effect of pressure on fluoride removal efficiency at 3.0; 3.5; 4.0; 4.5 and 5.0 $\cdot 10^5 N/m^2$.

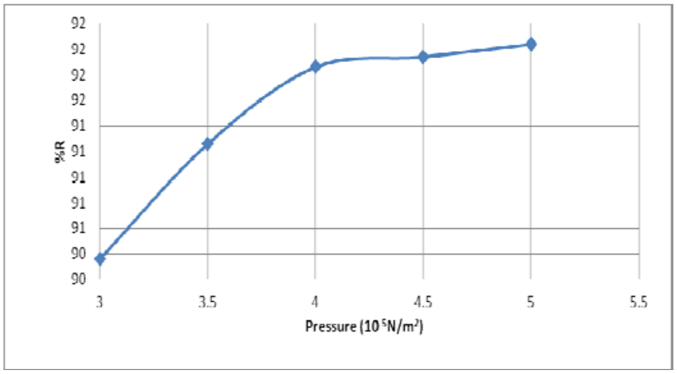

Fig. 11. Pressure effect on separation yield at pH 4.5; mass ratio $C_{F^-}:C_{ads}$ 1:20; Ci_{F^-} 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio $V_{sample}:V_{water}$ 3:1; flotation time 5 min

From the Fig. 11 we observe a maximum efficiency at $4 \cdot 10^5 N/m^2$ pressure after which it decreases, probably due to turbulence caused by pressure higher values.

Dilution ratio (sample volume: water volume)

Dilution ratio $V_{sample}:V_{water}$ was studied by varying it at 1:1; 2:1; 3:1; 4:1; 5:1. Fig. 12 shows the influence of dilution on F^- separation efficiency.

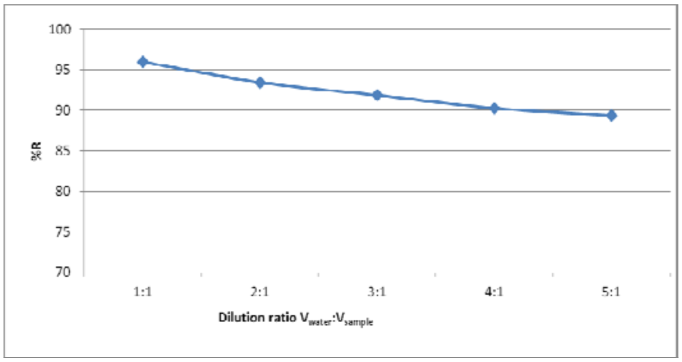

Fig. 12. Dilution ratio $V_{sample}:V_{water}$ effect on separation yield at pH 4.5; mass ratio $C_{F^-}:C_{ads}$ 1:20; Ci_{F^-} 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; flotation time 5 min; pressure $4 \cdot 10^5 N/m^2$

As expected with increasing of the amount of added water the flotation removal efficiency grows to 96% at $V_{water}:V_{sample}$ 1:1 dilution ratio, but for economical reasons we will take into consideration for further studies the dilution ratio $V_{water}:V_{sample}$ 1:3 were flotation separation yield is 92%.

Flotation time

Another factor which influences the flotation process is flotation time. The influence of flotation time (2; 5; 10; 15; 20 min.) on F^- removal efficiency is shown in Fig. 13.

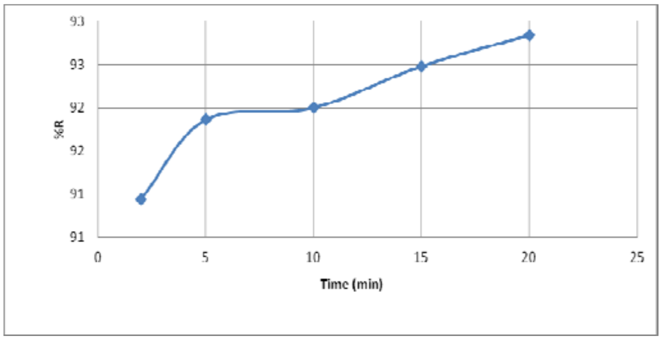

Fig. 13. Flotation time effect on separation yield at pH 4.5; mass ratio C_{F^-}:C_{ads} 1:20; Ci_{F^-} 50mg/l; stirring rate 200 rpm; dynamic contact time 10 min; static contact time 60 min; dilution ratio V_{sample}:V_{water} 3:1; pressure $4 \cdot 10^5 N/m^2$

It can be seen from Fig. 13 that the separation process is very fast, in only 5 minutes is achieved a flotation removal efficiency of 92%.

3.3. Optimum parameters

The optimum parameters affecting the adsorption-flotation of fluoride ions, on FeO(OH) are presented in table 3.

Table 3

Adsorption-flotation optimum parameters

FACTORS	F^- sorption-flotation on FeO(OH)	
	Adsorption	Flotation
pH	4.5	-
Stirring rate (rpm)	200	-
Mass ratio Cion:Cads	1:20	-
F^- initial concentration (mg/L)	50	-
Dynamic contact time (min)	10	-
Static contact time (min)	60	-
Dilution ratio V_{sample}:V_{water}	-	3:1
Equilibrium pressure in pressure recipient (atm)	-	$4 \cdot 10^5 N/m^2$
Flotation time (min)	-	5

3.4. Process Scheme Adsorption-Flotation of F^- on FeO(OH)

Considering the influence of the analyzed parameters in the sorption-flotation technique, it was proposed the followed process scheme.

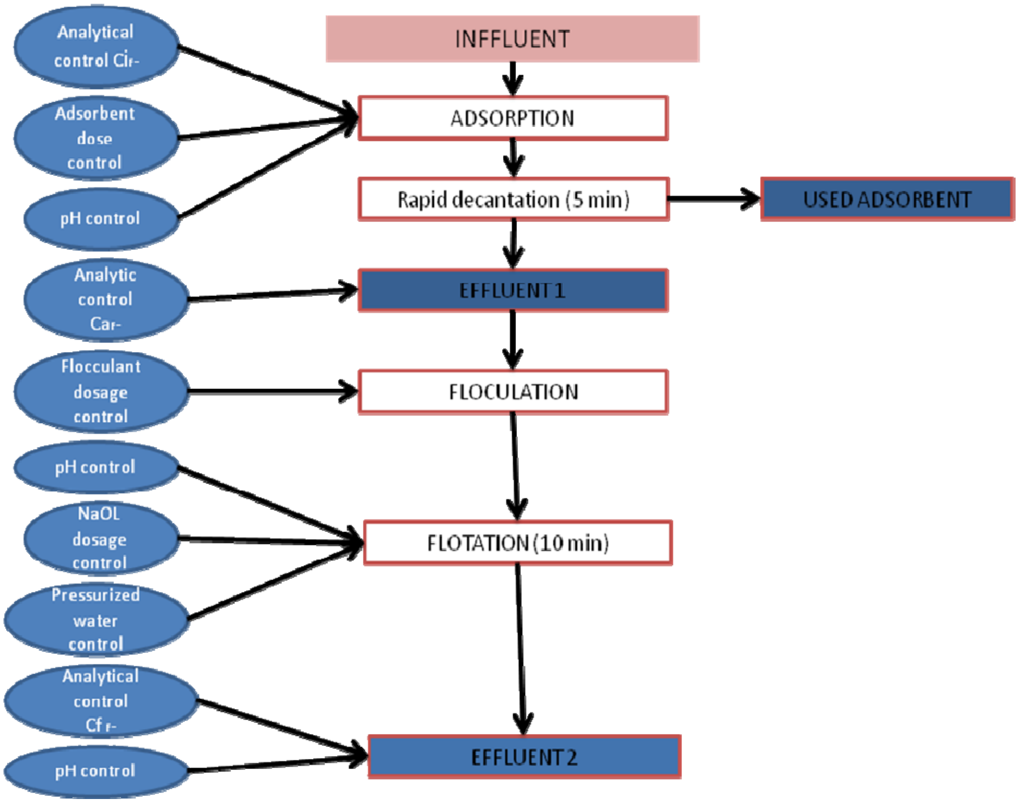

Fig.14. Process scheme adsorption-flotation F^- on FeO(OH) as sorbent

4. Conclusions

FeO(OH) has been examined like sorbent in removing fluoride from aqueous environment. Its granular structure, high surface area and effective capacity of fluoride removal make this adsorbent a highly potential media to be used in removing the fluoride from aqueous systems. The adsorption capacity of FeO(OH) for fluoride was 5mg/g. The sorption process equation was fitted well with both Langmuir and Freundlich isotherm models (the correlation coefficient was slightly higher for Langmuir isotherm than Freundlich isotherm). The optimum fluoride removal was observed at pH 4.5 indicating that FeO(OH) has potential utility in practical application.

70% adsorption separation efficiency was obtained, showing that FeO(OH) is a promising material for fluoride removal from polluted aqueous systems. Therefore, combining adsorption with flotation leads to an increase in flotation removal efficiency up to 92%.

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