Levigates ions separation by sorbtion-flotation

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INTRODUCTION

- **Levigates represent liquid media with complex composition and can contain pollutants concentrations more than legal limits. Levigates from agricultural area have large quantity of** $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and $P\text{-}PO_4^{-3}$.

- **Selection of levigate treatment technology had in view both composition of speciations and costs in case of application in industrial scale. The technologies who are mention in literature are diverse with selective efficiency.**

- The presence of contaminated agents in levigates in less concentrations (10^{-2}-10^{-6} M), but inadequate regarding water quallity regarding environment protection, imposed the study of separation methods which assured *cleaning* and *useful compounds recovering*, when it is the case.

- In this context the group of separation methods by adsorptive bubbles generally and ion flotation with its variants (precipitate flotation, colloidal adsorption flotation etc) specially, represent an alternative because of some characteristics which confer priority up another methods.

CHARACTERISTICS OF FLOTATION

- **Diversity of species**-as nature and structure- susceptible to be separated by these methods;
- **High separation efficiency**;
- **Low consumption of reactive agents** for the formation of insoluble high hydrophobic and low specific weight;
- **Simplicity, rapidity and economicity**;
- **Equipments flexibility and fiability**;
- **Recovery of useful compounds** by processing the resulted foam.

OBJECTIVES

- **The present paper reports a systematic study based on adsorption and flotation characteristics.**

- **For adsorption process study were introduced the solid support with both adsorptive and ion exchange capability.**

- **For flotation process was selected dissolved air flotation technique (DAF). The influencing factors like: optimum pH, optimum molar ratio, ions concentration, necessary air have been studied, regarding establish the optimum parameters, in synthetic solutions.**

OBJECTIVES

- **The option for combinated technology adsorption-decantation-flotation (ADF) was justified by:**

- **- reused of adsorptive support after desorption of pollutants and Na$^+$ activation;**

- **- used of Romanian natural rock like as adsorptive support.**

METHODS AND REACTANTS

A. Methods for pollutants removal

Adsorption-Decantation-Flotation (ADF) on **Romanian volcanic material** and synthetic solutions **NH_4NO_3** ($C_{i\ NO3}^-$=77.5 mg·L^{-1}, $C_{i\ NH4}^+$=22.5 mg·L^{-1}) and **$Na_3PO_4\cdot12H_2O$** (C_{iP}=41.4 mg·L^{-1})

B. Methods for determination of pollutants concentrations

• Spectrophotometric methods.

STUDIED FACTORS

STIRRING RATE

The model samples were prepared with different stirring rates (200 ; 300 ; 400 and 600 turation/min.) for 10 min. Immediatly were decanted and resulted effluents were flotated resulting the second effluent. Both effluents were analised and experimental date were showed in fig 1.

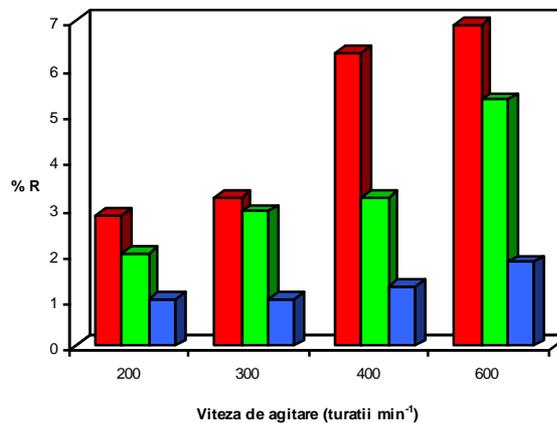**Stirring rate not influence very much separation efficiency and finaly it was choose slowly stirring 200 tur/min.**

Fig 1. %R=f(stirring rate) to $C_{i\ NO3^-}$=77,5 mg·L^{-1} (a) ; $C_{i\ NH4^+}$=22,5 mg·L^{-1} (b) ; $C_{i\ P\ total}$=41,4 mg·L^{-1} (c)
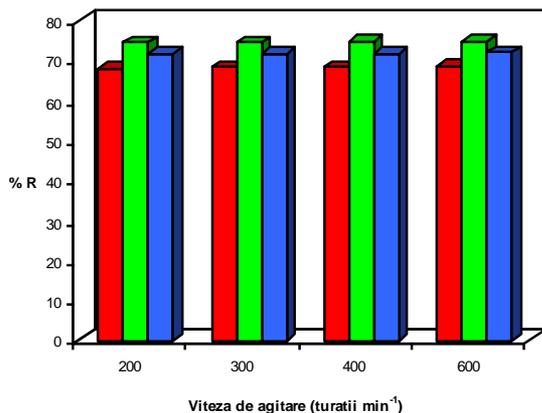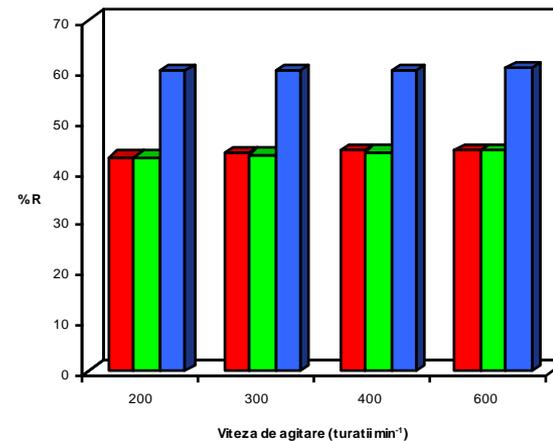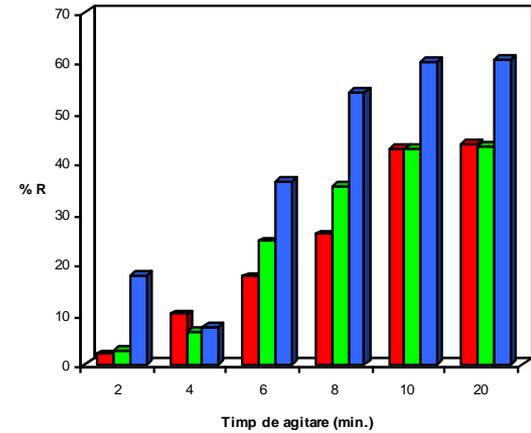
STIRRING TIME

The model samples were prepared to the same stirring rate 200 tur/min., with different stirring times (2 ; 4 ; 6 ; 8 ; 10 ; 20 min.). The samples after contact to these stirring times were decanted and flotated. The experimental data were presented in fig. 2.

The separation efficiency increase with stirring time until 10 min. After this minor time increase of separation efficiency was not justify.
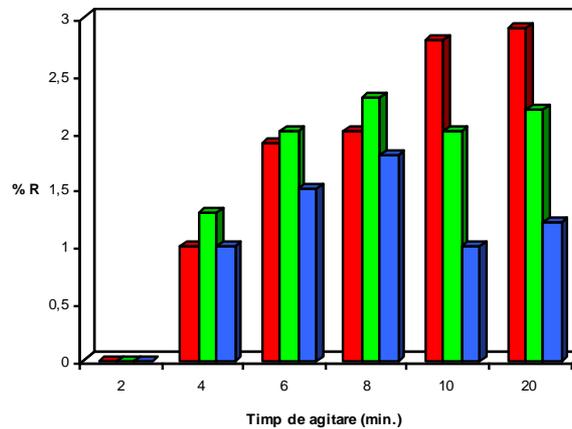
Fig 2. %R=f(stirring time) to $C_{i\ NO3}^{-}$=77,5 mg·L^{-1} (a) ; $C_{i\ NH4}^{+}$=22,5 mg·L^{-1} (b) ; $C_{i\ P\ total}$=41,4 mg·L^{-1} (c)
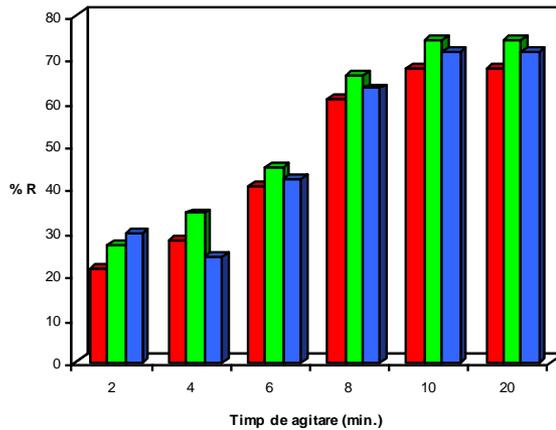
STATIONARY TIME FOR DECANTATION

Stationary time for decantation were determined for model samples with stirring rate 200 tur/min., stirring time 10 min. and diff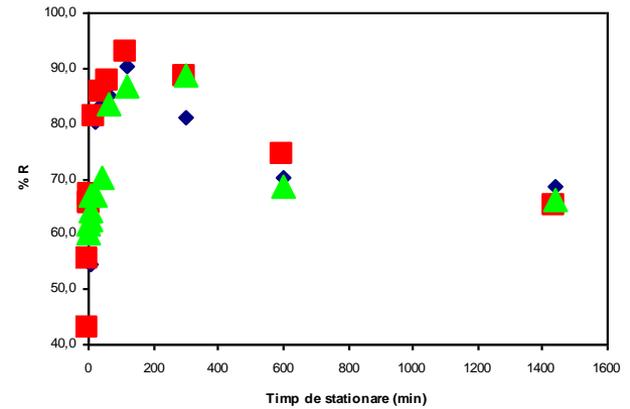erent stationary times for decantation (0 ; 2 ; 4; 6 ; 8 ; 10 ; 20 ; 40 ; 60 ; 120 ; 300 ; 600 ; 1440 min.). Each sample was decantated and flotated. Experimental data are showed in fig 3.

Fig.3 %R = $f(t_s)$ to $C_{i\ NO3^-}$=77,5 mg·L^{-1} (a) ; $C_{i\ NH4^+}$=22,5 mg·L^{-1} (b) ; $C_{i\ P\ total}$=41,4 mg·L^{-1} (c)
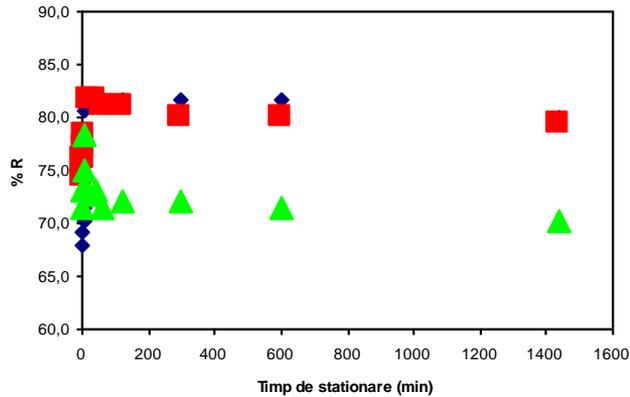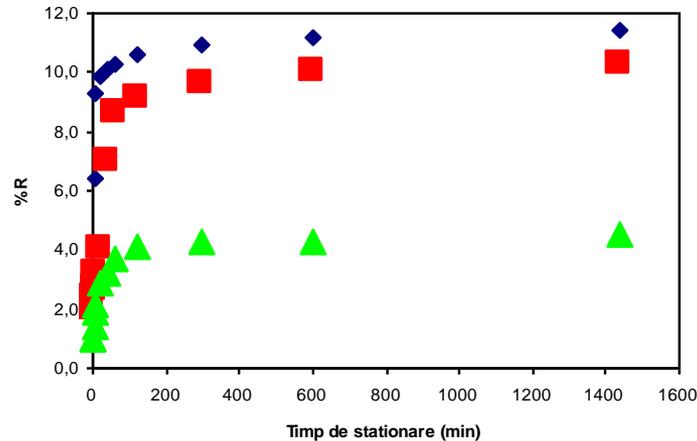
• After $t_d > 60$ min the separation efficiencies were similary in all experiments on adsoptive support;

• The final time for AD separation is 70 min;

pH FLOTATION

Optimum pH for obtained maximum separation efficiencies is characteristic for each collector-colligend system and depend species nature from system, reciprocally interaction and sublate stability.

In case of studied aqueous systems **pH $\cong$ 7,0** because this value resulted from the first contact AD with NaOL (anionic collector) to molar ratio $C_c : C_{ion} = 10^{-3}$, accepted value for this quality indicator to effluent evacuation in natural receptors. Also majority of supports were stable to this pH value.

MOLAR RATIO $C_C : C_{ion}$

In this paper the **molar ratio $C_C : C_{ion}$ was understoechiometrical** because was introduced in system for its tensio-active role. Collector consumption were correlated with ion concentration because an excess of collector could constituted a new pollutant. For collector excess avoided minimum molar ratio worked.

- **EQUILIBRIUM PRESSURE AND DILUTION RATIO $V_{SAMPLE}:V_{WATER}$**

After pH established sample was introduced in flotation cell and bublles gase were generated by pressurised water destintion. For this reason was necessary the study of pressure on separation efficiency (%R). Its were done flotation experiments to different pressures p (4,5 10^5; 4,0 10^5; 3,5 10^5; 3,0 10^5 N m^{-2}) and constant dilution ratio (**$V_{sample}:V_{water} = 1 : 3$**) from theoretical and another experimental data. These experimental data were presented in fig.4.

Fig 4. %R=f(p) to $C_{i\ NO3^-}$=77,5 mg·L⁻¹ (a) ; $C_{i\ NH4^+}$=22,5 mg·L⁻¹ (b) ; $C_{i\ P\ total}$=41,4 mg·L⁻¹ (c)
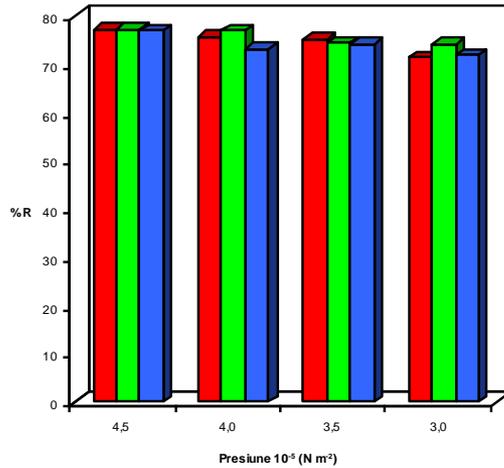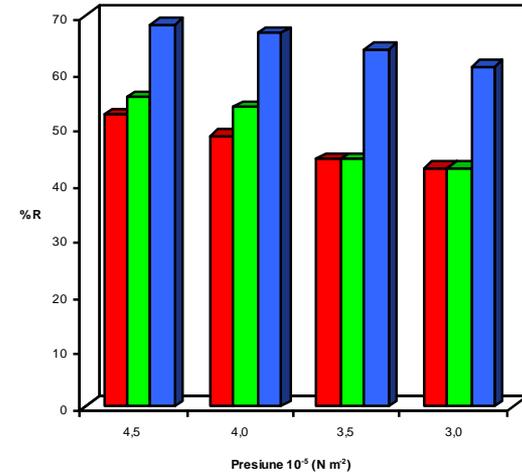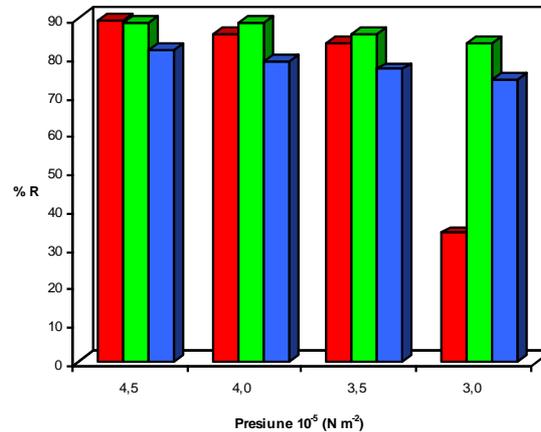
The increase of pressure required constructive precaution for pressure recipient. For this reason in all flotation experiments were established a suprapressure given the minimum atmospherical pressure which ensure maximum efficiency. In another way a suprapressure, $p > 4 \cdot 10^5$ N m^{-2} could provoc a turbulence with negative effects on studied ion separation. From experimental data its observed more than $4 \cdot 10^5$ N m^{-2} was not justify.

SEPARATION PARAMETERS

Separation parameters	Adsorbtion-Decantation on adsorbent support	Flotation
Granulometric fraction (mm)	0,2	-
Molar ratio $C_{Fe}^{3+}:C_{NO3}^{-}$; $C_{Fe}^{3+}:C_{NH4}^{+}$	5	-
Stirring rate (tur/min)	200	-
Stirring time (min.)	10	-
Decantation time (min.)	60	-
Total contact time (min.)	70	-
pH	5,5	7,0
Molar ratio $C_C : C_{NO3}^{-}$, $C_C : C_{NH4}^{+}$	-	$10^{-3}:1$
Ion concentration $N-NO_3^{-}$, $N-NH_4^{+}$, $P-PO_4^{-3}$	$C_{i\,NO3}^{-}=77,5$ mg/L ; $C_{i\,NH4}^{+}=22,5$ mg/L ; $C_{i\,P}=41,4$ mg/L	$C_{f\,ion}$ from AD :• $C_{fAD/NO3}^{-}=14,17$ mg/L; $C_{fAD/NH4}^{+}=3,34$ mg/L$C_{fAD/P}=37,14$ mg/L • $C_{f\,ion}$ from F: • $C_{fNO3}^{-}=8,65$ mg/L; $C_{fNH4}^{+}=1,60$ mg/L$C_{fP}=1,98$ mg/L
Stirring time (min.)	-	3
Dilution ratio $V_{sample}:V_{water}$	-	3 :1
Equilibrium pressure (N/m^2)	-	$4,0\ 10^5$
Flotation time (min.)	-	10

Fig. 5. ADF process block on Romanian volcanic material

Influent   ($C_{tPO_4^{3-}}$=77,5 mg/L ; $C_{tNH_4^+}$=22,5 mg/L)

Influent-adsorbent contact

Rapid decantation — Solid

pH control   Effluent 1   Desorbtion — Solution   loaded
pH ≅ 5-6   (muddy solution)   with pollutants

Washing

Colector NaOL   TAS contact   Support activation   Recirculation

Pressurised water   FLOTATION   Foam
4 atm, dil. ratio 3:1

Effluent 2

$C_{tPO_4^{3-}}$=8,65 mg/L < 25,00 mg/L NTPA 001

$C_{tNH_4^+}$=1,60 mg/L < 2,00 mg/L NTPA 001
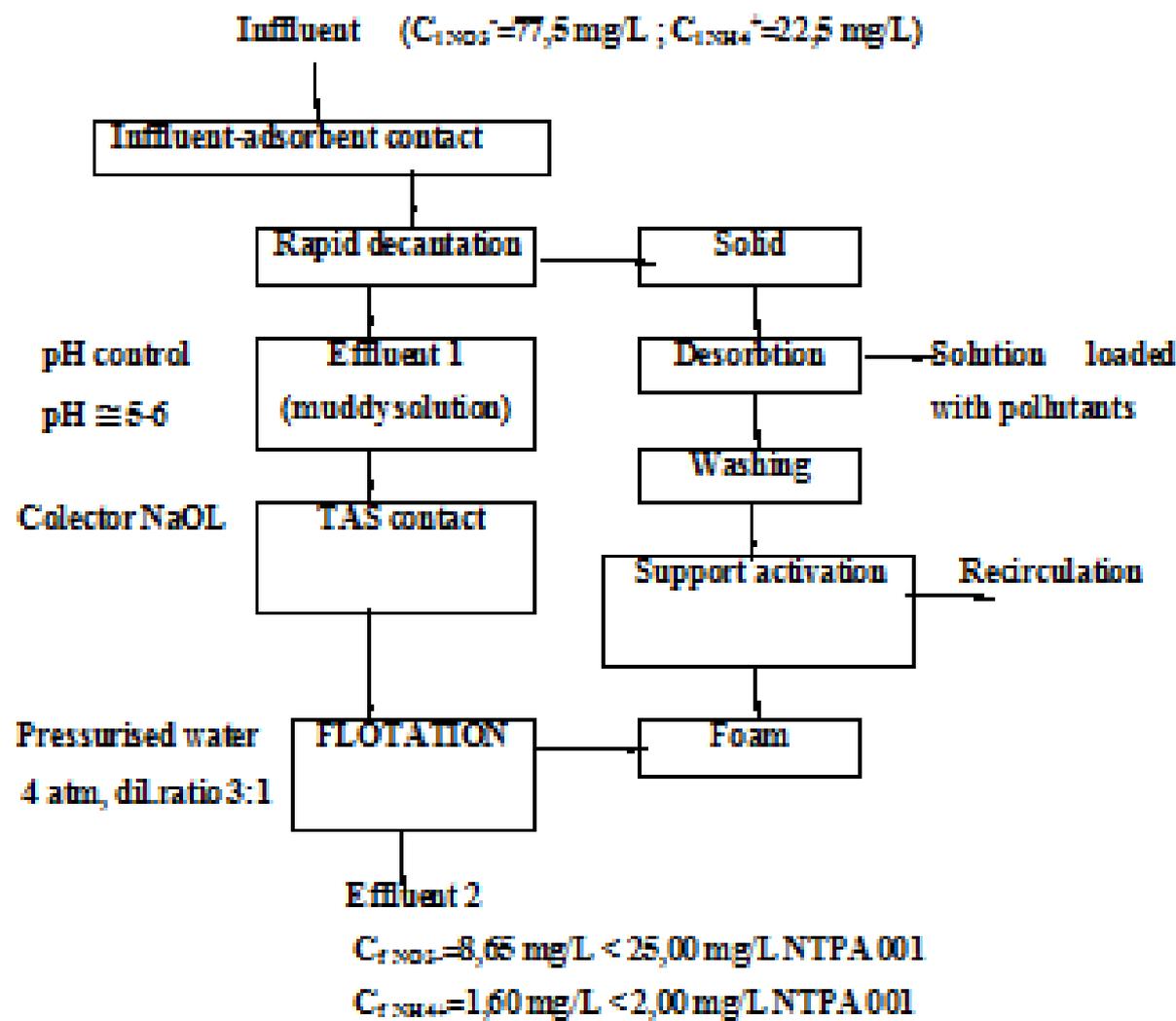
CONCLUSIONS

1. In this paper was studied separation of $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and $P\text{-}PO_4^{-3}$ from mono and multicompounds model aqueous systems by adsorbtion-decantation-flotation (ADF)-DAF technique- in order to apply the proposal technology on real systems;

2. The posibility of adsorbent support recirculation sustain the efficiency of proposal technology because of good separation efficiencies by decrease of pollutant initial concentrations;

3. The possibility of adsorbent support recirculation done reduced costs for generally treatment process.