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Cr(III) REMOVAL FROM AQUEOUS SYSTEMS BY FLOTATION WITH ATYPICAL COLLECTOR

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Lucrarea prezintă rezultatele obținute prin aplicarea flotației ca metodă de separare a Cr(III) din sisteme apoase folosind acid cafeic (CA) ca reactiv colector. Proprietățile tensioactive ale CA s-au investigat din izotermele de tensiune superficială, ale căror aluri descendente indică proprietăți tensioactive. Funcția de complexare s-a studiat în raport cu ionii Cr(III) cu care au format specii insolubile, care au fost separate prin flotație şi precipitare. S-a realizat studiul factorilor de influență: pH, raport molar [AC]:[Cr(III)], volum de aer, folosind soluții sintetice. Rezultatele obținute (eficienta de separare, R > 95%), confirmă capacitățile CA de complexare şi posibilitatea utilizarii drept colector în flotație.

The paper presents the results obtained by flotation applying as Cr(III) separation method from aqueous systems using caffeic acid (CA) as collector reagent. Surface properties of CA were investigated from surface tension isotherms, whose downward shapes indicates surface properties. Complexing function was studied in relation with Cr(III) ions with that was formed insoluble species, which were separated by flotation and precipitation. Was performed the study of influence factors: pH, molar ratio [CA]:[Cr(III)], air volume, using synthetic solutions. The results obtained (separation efficiency, R > 95%), confirming complexing capacities of CA and the possibility of using it as collector in flotation.

Keywords: flotation, caffeic acid, Cr(III)

1. Introduction

The possibility of applying flotation in order to recovering clean up of the diluted aqueous systems (10^{-6}-10^{-2} M), but poor quality from the point of view of the environmental protection is one of the characteristics of this method which, join simplicity, rapidity, efficiency, sustain its applicability [1,2].

At the same time, dilute aqueous systems, through the wide range of contamination agents, soluble or insoluble, with iono-molecular or colloids size

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can often be a real source of useful substances. In the case of aqueous systems impurified with metallic ion, the diversification of technologies that generate pollutants requires the study of collector reagents with high quality in comparison with the new collectors [1].

In flotation, collector reagents, by their heteropolar structure, with long hydrocarbonate chain, function as superficial active agents, and by polar group/groups behave as ligand for metallic ions that represent separation object [1,2].

In recent years, regarding the study of new classes of collector reagents, the literature mentions the specialists to study the concerns of some **atypical collectors**, reactives with more polar complexing (chelating) groups, which can facilitate the separation process by flotation, in general, reagents with different structure from the typical collectors [1,2].

Atypical collectors are collectors which deviating from the characteristics of classic collectors, in that: apolar group is nonlinear (or may be absent), molecular weight less than 200 u.m.a., polar group is polyvalent [1].

In order to introduce the flotation practice of such atypical collectors, in this paper was studied the acid 3-(3, 4-dihydroxyfenil) propenoic, $C_9H_8O_4$ (CA), as potential atypical collector for flotation separation of Cr(III) from aqueous solutions.

CA selection in this study took into consideration that it is found in nature in medicinal plants (root Spinarum Carissa L. (wild plum) [3], Ixora Javanica flowers (flower Bunge Soka) [4], Centaurium Umbellatum Gil (Tintaura) [5], fruits, vegetables and spices. CA could be extract from vegetable scraps [6].

The CA structure contains a benzene ring that is grafted two hydroxyl groups in vicinal positions (3, 4), so it is a good complexing agent of metal ions, the behaviour is different depending on the nature of the metal [7].

These considerations support the study opportunity on the possibility of metal ions complexation from aqueous systems followed by separation by flotation of the complexes formed.

Regarding interaction with metal ions from the system, are important CA species in solution at different pH [8-10].

In the literature there are data [9, 21] that refer to the CA ionization steps, acidity constants and speciation at different pH values.

$$H_3CAF \overset{pH=4,5}{\underset{-H^+}{\leftrightarrow}} \underset{ka_1}{H_2CAF^-} \overset{pH=8,4}{\underset{-H^+}{\leftrightarrow}} \underset{ka_2}{HCAF^{2-}} \overset{pH=12,4}{\underset{-H^+}{\leftrightarrow}} \underset{ka_3}{CAF^{3-}} \qquad (1)$$

Considering this informations have studied the complexation of Cr(III) with CA, followed by complex isolation from the system by flotation, aspect none mentioned in the studied literature.

Literature information [7,8,10-16] indicates the formation of CA complexes with di- [7,12-14] and trivalent metal ions [8,10,14,16]. About complexation of Cr(III) with CA there are few informations and its refer to the reaction mechanism [11,16].

Although in small amounts, Cr(III) is essential for the body: Cr(III) enhances insulin action, so having the metabolism of carbohydrates, proteins and lipids (daily requirement of Cr: 50-200 μg). In large amounts, Cr(III) is toxic: biodisponibility and metal toxicity is not represented by their total concentration, but depend on the chemical forms under which they are present; thus, Cr(VI) is more toxic than Cr(III). Long exposure by inhalation of chromium compounds leads to the appearance of skin ulcers, dermatitis, perforation of nasal septum and hypersensitivity respiratory manifestations [16,18,19].

Cr(III) presence, concentration and environmental forms depend on various physical and chemical processes such as hydrolysis, complexation, redox reactions and adsorption [20].

According to Romanian law NTPA 001/2005, for industrial and urban waters that are discharged into natural receivers, Cr(III) concentration should not exceed 0.9 $mg\cdot dm^{-3}$, and according to NTPA 002/2005, in waste water which is discharged sewerage networks of settlements, Cr(III) concentration should not exceed 1.3 $mg\cdot dm^{-3}$.

The paper studies the Cr(III) separation from model aqueous solutions by flotation, using the CA as atypical collector. The study will continue with the interaction of Cr(III) with CA on the formation of insoluble species separated by flotation. The order of reagents addition was: the sample (solution $Cr_2(SO_4)_3$) + (NaOH + CA) + pH regulator (NaOH) ± flocculant, and the main factors influencing the flotation separation process with maximum efficiency in order to establish the optimum parameters.

2. Experimental procedure

Reagents

- $Cr_2(SO_4)_3$ p.a.; were prepared stock solution (5000 $mg\cdot dm^{-3}$) and work solution (10 – 500 $mg\cdot dm^{-3}$);
- NaOH p.a; were prepared 0.1 M and 2M solutions;
- Praestol 610 BC, weak cation flocculant, was prepared 0.02% solution;
- C_2H_5OH p.a.;
- CA p.a.;
- (CA + NaOH) alcoholic solution (water: ethanol = 70:30% vol), $1.25\cdot 10^{-2}$ M.

Equipments

- Kruss K11 tensiometer for surface tension determination;
- Heidolph Vibramax 100 stirrer, with variable speed;
- 290A ORION pH-meter;
- Laboratory installation for flotation experiments [1];
-UNICAM PAY SP9 atomic absorption spectrophotometer for Cr(III) determination.

Collector selection

Surface tension of solution, σ, was determined in relation to the surface tension of the solvent (water), at 20°C, $\sigma_o = 73$ dyn·cm^{-1}, determined through the ring method using Kruss K11 tensiometer. With the obtained values, the curve $\sigma = f(c)_T$ was plotted.

Flotation

A volume of Cr(III) aqueous solution (0.1/0.15/0.2 dm^3) was contact with CA and NaOH solution while stirring, to obtain insoluble specie (sublate). pH was corrected (with NaOH) while stirring (10 min), the sample was diluted with in advance pressurized water, and then was separation by flotation occurs. The effluent was sampled for Cr(III) analytical control of separation and was calculated separation efficiency using the formula (2):

$$R = (1 - \frac{C_t}{C_0})100 \qquad (2)$$

where: C_0 - Cr(III) initial concentration in solution;
C_t - Cr(III) concentration in solution after flotation, at *t* time.

The experimental data processing was done by Excel program, and the Student method for statistical processing was applied.

3. Results and discussions

Collector selection

For CA surface properties testing, surface tension of solutions with different CA concentrations was studied, CA being unstudied as collector reagent.

Collector function of a substance is ensured by its surface properties; therefore, in the study of a new class of collector reagents the surfactant substance qualities are primarily determined by interpreting of surface tension isotherms. The CA surface tension isotherm, is shown in Fig.1.

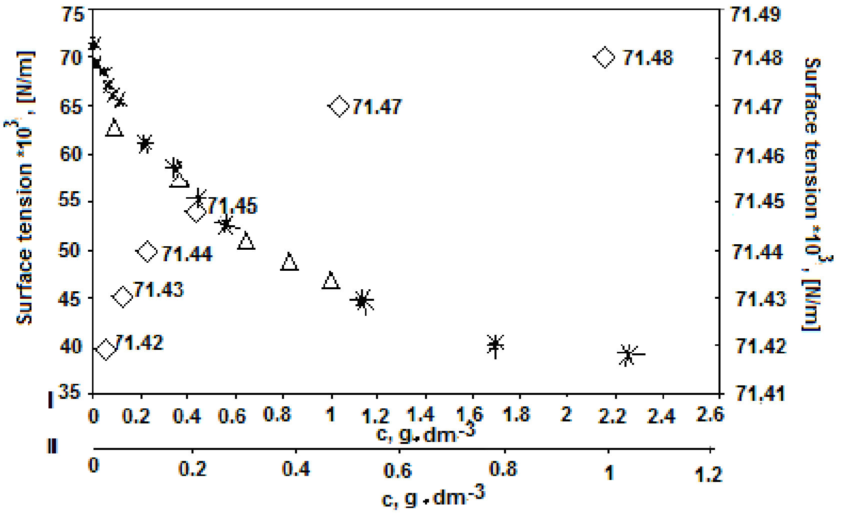

Fig. 1 - Surface tension isotherms, $\sigma = f(c)_t$ (t = 20°C):
(*) CA-water aqueous solutions, (◊) aqueous solutions $Cr_2(SO_4)_3$, (△) CA- $Cr_2(SO_4)_3$ system;
I. CA-water aqueous solutions ; CA- $Cr_2(SO_4)_3$ system ;
II. $Cr_2(SO_4)_3$ solutions

In the case of CA-water system (Fig. 1, ◊), surface tension isotherm has a downward shape at low concentrations of aqueous solutions, that suggesting surface-active properties of CA and the opportunity to be tested as a collector reagent in the flotation. $\sigma=f(c)_T$ isotherms of inorganic salts solutions have upward shape, which was verified in the case of $Cr_2(SO_4)_{3aq}$ (Fig. 1, ◊). For the Cr(III)-CA system with Cr(III) constant concentration (250 $mg{\cdot}dm^{-3}$) and variable CA concentration at different molar ratios [CA]:[Cr(III)] = 2:1, 1,5:1, 1.25:1, 1:1, $5{\cdot}10^{-1}$:1 surface tension isotherm is downward shape (Fig. 1, △), which confirms the CA surfactant qualities.

Influence factors

Flotation pH. Literature [1] mentions that optimum flotation pH is placed in the precipitation pH range of species that are formed in collector - metal ion interaction. In the case of Cr(III)-CA interaction there is not information about the precipitation pH.

Optimum pH value, that for which its obtain maximum separation efficiency in flotation, is typical for each collector-coligand system and depends on the nature of existing species in the system, on the mutual interaction and precipitate stability.

Experiments were performed with the Cr(III) solution of 250 mg·dm^3 (taken sample volume has been between 0.1-0.2 dm^3, depending on the molar ratio) at different pH values in the pH range from 5.0 to 9.0, and different molar ratios [CA] : [Cr(III)] = 2:1; 1.5:1; 1.25:1; 1.1:1; 1:1; 5·10^{-1}:1; 10^{-1}:1; 5·10^{-2}:1; 10^{-2}:1. For each pH value and molar ratio was studied R(%) = f(pH) dependence.

Each system was studied in two versions: with and without flocculant, that was introduced into the system to mass ratio pollutant: flocculant = 100:1. In the case of excess and stoichiometric molar ratios, maximum separation efficiency is obtained in the pH range from 5.8 to 6.5, and for understoichiometric molar ratios from 6.5 to 7.5 (Fig. 2-5). Both areas are valid for the systems with flocculant used, because experimental data are homogeneous. Insoluble sublate with surface-active properties, green-veined colour and strong hydrophobia, is fast concentrated on foam.

At the stoichiometric and excess molar ratio, maximum separation efficiency is in the range 98.25% - 98.98% for cases with flocculant. These molar ratios are likely to develop flotation after an ion flotation mechanism. The Cr(III) concentration in solution after flotation (C_t=2.55 mg·dm^{-3}) is over the limit allowed by the law in force (C_t = 0.9 mg·dm^{-3}, according NTPA 001/2005, C_t = 1.3 mg·dm^{-3}, according NTPA 002/2005).

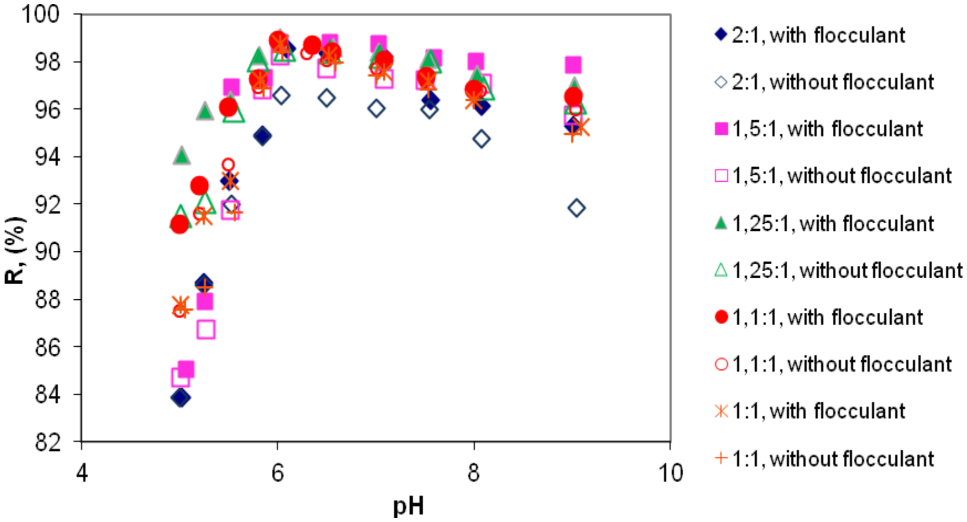

Fig. 2 – R(%)*vs* pH for CA- Cr(III) system at different stoichiometric molar ratios (with and without flocculant)

Higher separation efficiency (R(%) = 98.63- 99.93) are obtained at understoichiometric molar ratios, when the flotation process follows a precipitate flotation mechanism, the concentration in the effluent after flotation fulfilling requirements of legislation in force (C_t=0.18 mg·dm^{-3}).

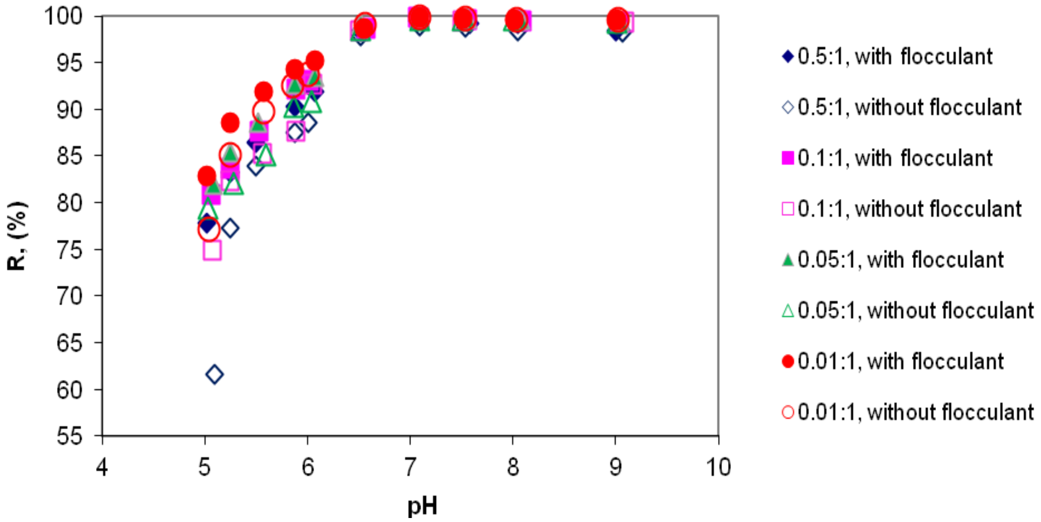

Fig. 3 –R(%) *vs* pH for CA- Cr(III) system at different understoichiometric molar ratios (with and without flocculant)

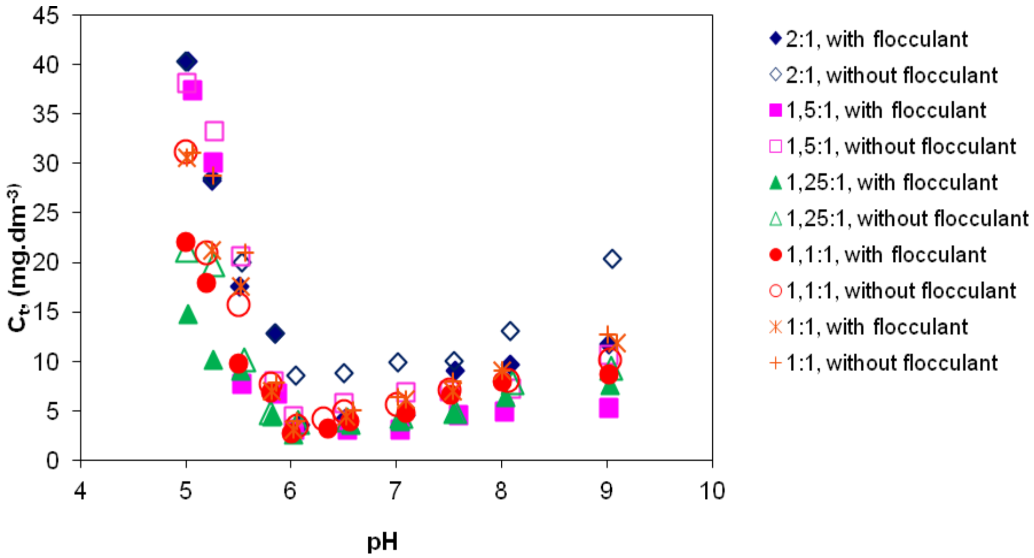

Fig. 4 - C_t *vs* pH for CA- Cr(III) system at different stoichiometric and excess molar ratios (with and without flocculant), C_0=250 mg·dm^{-3}

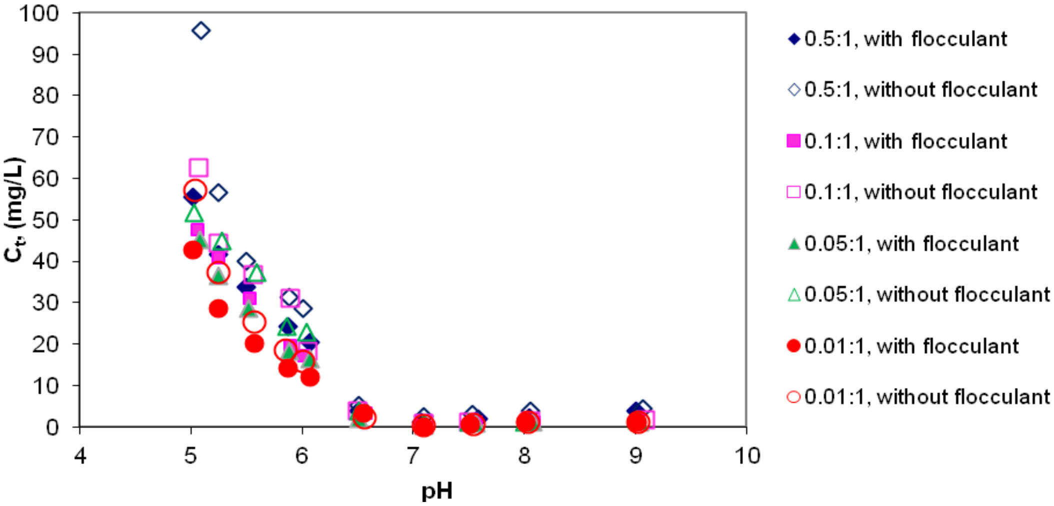

Fig. 5 - C_t *vs* pH for CA- Cr(III) system at understoichiometric molar ratios (with and without flocculant) C_0=250 mg·dm^{-3}

Flocculant Presence. After the experimental data processing was observed that in “with flocculant” version higher efficiency were obtained in comparison to the “without flocculant” version for both cases: stoichiometric and excess molar ratios and understoichiometric molar ratios (Fig. 2-5). Therefore, further study of influence factors were performed in the version with flocculant to the optimal parameters set.

The obtained results maintain the flocculant action of particle agglomeration and increase the separation efficiency. The flocculants, like adjuvants in precipitation-flotation process, have the role to accelerate the particles aggregation, favouring the increase of hydrophobic species [22].

Molar ratio [CA]:[Cr(III)]. In ion flotation (I.F.) the collector consumption is stoichiometric also requiring an excess as in the precipitation reactions. A well consumption can be predicted on the range of pH value in that the Cr(III) is found as aquacomplexes. By pH increasing aquacomplexes structure changes due to the oxolation and olation equilibrium are involved, when forming polymer species that require a stoichiometric collector consumption. Therefore, a study of ion flotation collector consumption is justified.

In the precipitate flotation (P.F.) collector consumption is understoichiometric and insoluble species that are separated by flotation have a hydrophobia resulted from the precipitation reaction, which allows their concentration in the foam. Collector introduced in the system acts on the surface properties on the one hand, but on the other hand can substitute ligands from hydroxospecies, leading to a sublate that is fast concentrated in the foam (with minimum redispersion tendency) as collar form to the liquid surface.

The influence of concentration collector study on separation efficiency was performed according to the pH flotation and anticipated mechanism. For ion flotation $C_o = 250\ mg \cdot dm^{-3}$, optimum flotation pH was 6.0 at different molar ratios [CA]:[Cr(III)] = 2:1; 1.5:1; 1.25: 1; 1.1:1; 1:1. For precipitate flotation, optimum flotation pH was 7.0 at different molar ratios [CA]:[Cr(III)] = $5 \cdot 10^{-1}$:1; 10^{-1}:1; $5 \cdot 10^{-2}$:1; 10^{-2}:1.

The experimental results when maintaining constant stirring and flotation times are shown in Table 1.

Table 1

Molar ratio for I.F. and P.F. in CA- Cr(III) system

Separation method	Flotation conditions	Molar ratio [CA]:[Cr(III)]	R_{max} (%)
I.F.	pH=6,0 Stirring time= 6 min. Flotation time= 13 min. $V_{sample}:V_{water} = 3:1$ $p = 4 \cdot 10^5\ N \cdot m^{-2}$ $C_0 = 250\ mg \cdot dm^{-3}$	2:1	98.56
		1.5:1	98.78
		1.25:1	98.98
		1.1:1	98.91
		1:1	98.76
P.F.	pH = 7,0 Stirring time= 6 min. Flotation time= 13 min. $V_{sample}:V_{water} = 3:1$ $p = 4 \cdot 10^5\ N \cdot m^{-2}$ $C_0 = 250\ mg \cdot dm^{-3}$	$5 \cdot 10^{-1}$:1	99.52
		10^{-1}:1	99.82
		$5 \cdot 10^{-2}$:1	99.82
		10^{-2}:1	99.92

Collector consumption should be closely correlated with Cr(III) ions concentration, because collector excess may be a new pollutant. Thus, to avoid collector excess, research is performed at minimum optimum molar ratios. In this case, the optimum molar ratio, [CA]:[Cr(III)], for precipitate flotation is 10^{-2}:1.

Separation reproducibility

Separation optimal parameters for the CA- Cr (III) system in ion and precipitate flotation versions were examined on 10 identical samples for solutions ($C_0 = 250\ mg \cdot dm^{-3}$) for calculating the separation reproducibility by Student method (Tables 2 and 3).

Table 2

Reproducibility of Cr(III) separation with CA by I.F.

No.	Flotated sample characteristics	C_t, [mg·dm^{-3}]		Statistical probability	
		with flocculant	without flocculant	with flocculant	without flocculant
1	C_o=250 mg·dm^{-3} V_{sample} = 0.2 dm^3 pH ≅ 6,0 [CA]:[Cr(III)]= 1.25:1 V_{sample}:V_{water} = 3:1 p= 4·10^5 N·m^{-2}	2.55	3.74	$\overline{X}$ =2.54 S=0.0171 $S_{\overline{X}}$ =0.0054 **P=95%** t·$S_{\overline{X}}$ =0.0172 **C_t=2.54 ± 0.0172** **P=99%** t·$S_{\overline{X}}$ =0.0121 **C_t=2.54 ± 0.0121**	$\overline{X}$ =3.75 S=0.0193 $S_{\overline{X}}$ =0.0061 **P=95%** t·$S_{\overline{X}}$ =0.0194 **C_t=3.75 ± 0.0194** **P=99%** t·$S_{\overline{X}}$ =0.0136 **C_t=3.75 ± 0.0136**
2		2.56	3.76		
3		2.52	3.75		
4		2.56	3.71		
5		2.56	3.74		
6		2.53	3.76		
7		2.53	3.78		
8		2.52	3.77		
9		2.56	3.76		
10		2.55	3.75		
11	C_o=250 mg·dm^{-3} V_{sample} = 0.2 dm^3 pH ≅ 6,0 [CA]:[Cr(III)] = 1.1:1 V_{sample}:V_{water} = 3:1 p= 4·10^5 N·m^{-2}	2.73	3.44	$\overline{X}$ =2.72 S=0.0103 $S_{\overline{X}}$ =0.0033 **P=95%** t·$S_{\overline{X}}$ =0.0104 **C_t=2.72 ± 0.0104** **P=99%** t·$S_{\overline{X}}$ =0.0073 **C_t=2.72 ± 0.0073**	$\overline{X}$ =3.42 S=0.0808 $S_{\overline{X}}$ =0.0256 **P=95%** t·$S_{\overline{X}}$ =0.0810 **C_t=3.42 ± 0.0810** **P=99%** t·$S_{\overline{X}}$ =0.0570 **C_t=3.42 ± 0.0570**
12		2.72	3.41		
13		2.71	3.45		
14		2.70	3.45		
15		2.71	3.47		
16		2.72	3.48		
17		2.73	3.43		
18		2.73	3.44		
19		2.72	3.46		
20		2.71	3.20		

$\overline{X}$ - mean selection

S - standard deviation of one measurement

$S_{\overline{X}}$ - standard deviation of the mean selection

C_t - Cr(III) concentration in solution after flotation

P - probability that C_t be within a range of values

t – *t* (Student) variable

Table 3

Reproducibility of Cr(III) separation with CA by P.F.

No.	Flotated sample characteristics	C_t, [mg·dm^{-3}]		Statistical probability	
		with flocculant	without flocculant	with flocculant	without flocculant
1	C_o=250 mg·dm^{-3} V_{sample} = 0.2 dm^3 pH ≅ 7.0 [CA]:[Cr(III)] = 10^{-2}:1 V_{sample}:V_{watert} = 3:1 p= 4·10^5 N·m^{-2}	0.18	0.20	$\overline{X}$=0.17 S=0.0135 $S_{\overline{X}}$=0.0043 **P=95%** t·$S_{\overline{X}}$=0.0135 **C_t=0.17 ± 0.0135** **P=99%** t·$S_{\overline{X}}$=0.0095 **C_t=0.17 ± 0.0095**	$\overline{X}$=0.21 S=0.0127 $S_{\overline{X}}$=0.0040 **P=95%** t·$S_{\overline{X}}$=0.0127 **C_t=0.21 ± 0.0127** **P=99%** t·$S_{\overline{X}}$=0.0090 **C_t=0.21 ± 0.0090**
2		0.15	0.21		
3		0.18	0.19		
4		0.16	0.21		
5		0.19	0.20		
6		0.17	0.21		
7		0.18	0.18		
8		0.16	0.21		
9		0.19	0.22		
10		0.18	0.22		
11	C_o=250 mg·dm^{-3} V_{sample} = 0.2 dm^3 pH ≅ 7.0 [CA]:[Cr(III)] = 5·10^{-2}:1 V_{sample}:V_{water} = 3:1 p= 4·10^5 N·m^{-2}	0.44	0.99	$\overline{X}$=0.43 S=0.0201 $S_{\overline{X}}$=0.0064 **P=95%** t·$S_{\overline{X}}$=0.0202 **C_t=0.43 ± 0.0587** **P=99%** t·$S_{\overline{X}}$=0.0142 **$C_{tCr(III)}$=0.43 ± 0.0142**	$\overline{X}$=1.00 S=0.0833 $S_{\overline{X}}$=0.0263 **P=95%** t·$S_{\overline{X}}$=0.0835 **C_t=1.00 ± 0.0835** **P=99%** t·$S_{\overline{X}}$=0.0587 **C_t=1.00 ± 0.0587**
12		0.40	1.10		
13		0.45	0.80		
14		0.44	1.08		
15		0.46	0.99		
16		0.44	1.06		
17		0.45	1.01		
18		0.43	0.98		
19		0.40	0.96		
20		0.43	0.98		

In ion flotation, the best reproducibility value, calculated on the experimental results, was obtained for 1.25:1 ratio, in version with flocculant for P =95% and P=99%.

In precipitate flotation, the best reproducibility value, calculated on the experimental results, was obtained for 10^{-2}:1 ratio, in version with flocculant for P =95% and P=99%.

Interpreting the results of statistical processing it observed that the presence of flocculant influences both separation efficiency and reproducibility of separation.

7. Conclusions

The results obtained in the research performed sustain the possibility of CA using as atypical collector in flotation.

High separation efficiency obtained for precipitate flotation (R(%)=98.63-99.93, C_t=0.18 mg·dm^{-3}) sustain the possibility of this reagent using in the recuperative separation of Cr(III) by flotation. The use of a stoichiometric molar ratio is justified only to study the separation mechanism, this option being uneconomical for pilot scale or industrial application. The option for precipitate flotation was for economic reasons (understoichiometrical reagents consumption and smaller flotation times), in the event of industrial-scale application. The present of flocculant is not a disadvantage because it is used in the case of typical collector.

Further, will perform theoretical and experimental studies obout systems containing metal ion in the presence of other ions, dynamic aspects of the process, the Cr(III)-CA interaction mechanism at two pH flotation values, and will check the optimal conditions established for synthetic solutions on real samples.

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