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REMOVAL OF TARTRAZINE (E102) FROM AQUEOUS SOLUTIONS BY SORPTION-FLOTATION

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This paper presents the possibility to remove orange yellow azo dye (tartrazine E102), from aqueous solution by using Fe(II)aq ions to form an „in situ” adsorbent support. In order to establish the optimum experimental conditions for sorption process, the influence of pH, amount of adsorbent, contact time, initial concentration and stirring rate was examined. The dye loaded adsorbent was separated from the liquid phase by flotation. To this end, the following parameters were studied: amount of collector, initial dye concentration, pressure in the pressurized recipient, dilution ratio V_{sample}:V_{water} and flotation time. The obtained data, suggests that tartrazine (E102) can be succesfully removed from synthetic aqueous solutions by sorption-flotation (> 99.00%).

Keywords: tartrazine removal, sorption-flotation, Fe(II)aq, aqueous solution

1. Introduction

The removal of organic dyes (usually containing azo and aromatic groups) from aquatic systems is a very important issue in terms of environmental protection, because most of this type of dyes are toxic and have mutagenic, teratogenic and carcinogenic effects on living organisms from the aquatic environment [1].

The main problem in treating wastewaters containing azo-dyes is related to the high stability of these species, since they are resistant to moderate oxidizing agents and light, and cannot be removed completely by conventional methods of anaerobic degradation. The procedures most commonly used for the treatment of wastewaters containing azo-dyes are: coagulation-flocculation, ozonization, membrane separation and adsorption [2, 3]. Considering the disadvantages of the conventional treatment methods (i.e. incomplete removal, high operating costs,

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high reagent and/or energy requirements, generation of toxic sludge etc.), as well as the hazardous effects of these dyes, new competitive, effective separation methods should be studied.

The present paper is an attempt to remove a hazardous dye from aqueous systems. Because of its composition, E102 has a number of adverse effects, most occurring to asthmatic people or allergic to aspirin. There are a number of countries that do not allow the use tartrazine (E102) in food industry, due to the harmful efects on human health [4, 5].

In this study, we investigated the removal of orange yellow azo dye (tartrazine - E102) a coloring agent commonly used in food industry, from synthetic aqueous solutions by sorption-flotation and the overall objective was to establish the optimum experimental conditions.

2. Experimental

2.1. Reagents

Trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonato phenylazo)-*H*-pyrazole-3-carboxylate(tartrazine), an azo dye (CI Number = 19140, EEC Number = E-102) with molecular formula $C_{16}H_9N_4Na_3O_9S_2$ and molecular weight 534.4 was obtained from STERA CHEMICALS Bucharest.

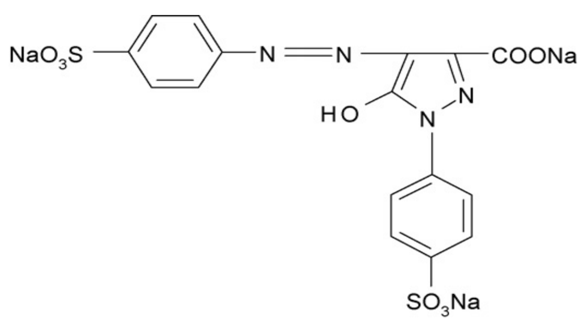

Fig.1. Chemical structure of tartrazine, [1]

- Fe(II)aq solution, 0.2 M was used to form an ,,in situ" adsorbent support and was prepared by dissolving $FeSO_4 \cdot 7H_2O$ into distilled water.
- Sodium oleate ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COONa$), of 0.0125 M was used as collector agent.
- The pH of the solutions was adjusted by addition of H_2SO_4 0.1 M or NaOH 0.2M solutions. All reagents were of analytical reagent grade.

2.2. Equipments

The sorption-flotation experiments were carried out by using a:

- HEILDORPH VIBRAMAX 100 shaker;
-ORION 290 a pH-meter ;
-UV-VIS spectophotometer (UNICAM UV2-100)
-Dissolved air flotation (DAF) unit, composed of a flotation cell fitted with glass column and a pressure source [6].

2.3. Methods

Different experiments were carried out in batches, under various conditions of pH, molar ratio [dye]:[Fe(II)], adsorption time, initial dye concentration, stirring rate for adsorption and respectively, amount of collector, pressure, dilution ratio and flotation time.

Experiments to investigate the influence of pH on tartrazine removal efficiency were carried out in the pH range 7-9, for samples of 100 mg/L initial concentration. This pH range was selected because at pH 7, Fe(II) start to precipitate. To investigate the influence of initial concentration (5-500 mg/L) samples of 200 mL were used. In order to identify the optimum stirring rate, batch sorption experiments were performed by varying the stirring rate from 100 to 300 rpm. The dye loaded adsorbent was separated from the liquid phase by dissolved air flotation (DAF). The removal efficiency of the sorption-flotation process was calculated according to the following equation:

$$Y = \frac{C_f - C_i}{C_f} \times 100,\% \quad (1)$$

where Y – removal efficiency (%);
Ci – tartrazine initial concentration (mg/L);
Ct – tartrazine time t concentration (mg/L).

3. Results and discussion

The objective of the combined sorption-flotation process was to study the influence of the main factors that influences each method, adsorption, respectively, flotation. Since the flotation process was applied subsequently after adsorption, the only factors that were studied for this process were those that ensure the concentration of the dye loaded adsorbent in the foam.

The flotation experiments were carried out at the optimum parameters established for the adsorption process.

3.1. Adsorption

3.1.1. pH

The pH for the solution is very important factor in the adsorption process because it contributes to modification of the adsorption capacity of adsorbent support.

The influence of pH on tartrazine removal efficiency using ions Fe(II)aq to form an ,,in situ" adsorbent support at the different molar ratios [dye]:[Fe(II)], adsorption time 5 minutes , initial tartrazine concentration: 100mg/L, sample volume:200 ml, stirring rate 200 rpm, temperature (20ºC), was studied in the pH range 7-9 and is represented in Fig. 2.

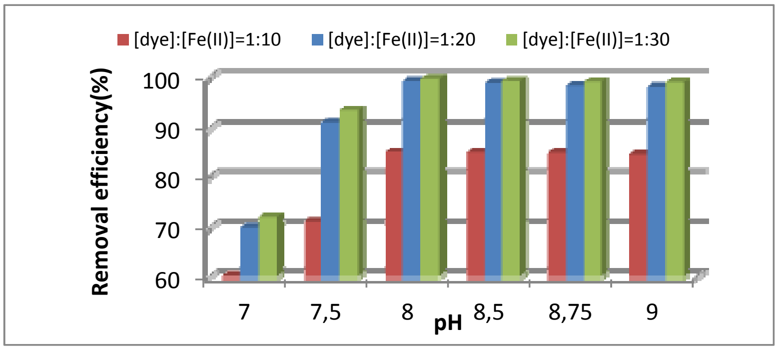

Fig. 2. Influence of pH on tartrazine removal efficiency by sorption

From Fig. 2. it can be seen that maximum removal efficiencies of tartrazine 85.02%, 99.29% and 99.75% were obtained at pH 8. The pH 8 was selected as optimum for tartrazine removal by sorption using ions Fe(II)aq to form an ,,in situ" adsorbent support due to the fact there were not observed significant increases of the removal efficiency at higher pH values.

3.1.2. Adsorbent dose

The adsorbent dose is another factor that significantly influences the adsorption process (Fig. 2).

The obtained results show that the removal efficiency of the sorption process presents high percentages (> 90%) in all the three cases, reaching maximum at the molar ratio [dye]:[Fe(II)] =1:30, (99,03%). It can also be noticed that the removal efficiency slightly increased with the increase of the molar ratio [dye]:[Fe(II)]. Due to the fact that obtained values were very close, the molar ratio [dye]:[Fe(II)] =1:20 (99,29%) was selected for further experiments.

3.1.3. Adsorption time

The influence of contact time on tartrazine removal efficiency was investigated in the range of 1–20 minutes, in the following experimental conditions: pH=8, molar ratio [dye]:[Fe] =1:20, initial tartrazine concentration :100 mg/L, sample volume: 200 ml, stirring rate 200 rpm, temperature (20ºC).

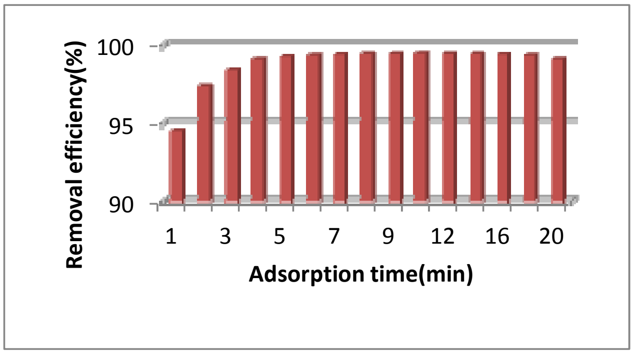

Fig. 3. Influence of adsorption time on tartrazine removal efficiency by sorption

From Fig.3. it can be observed that tartarzine removal from aqueous solution using ions Fe(II)aq to form an „in situ” adsorbent support, increased with increasing contact time, reaching after 5 minutes. It can be noticed that tartrazine adsorption is a rapid process since the maximum is reached after the first minutes and after this time interval the removal efficiency remains almost constant **.**

3.1.4. Initial tartrazine concentration

Experiments to evaluate the influence of initial concentration were carried out in the concentration range of 5-500 mg/L (Fig. 4.). The tests were conducted for samples of 200 mL, under batch conditions at pH=8, molar ratio [dye]:[Fe(II)]=1:20, adsorption time 5 minutes, with continuous stirring at 200 rpm and room temperature (20ºC).

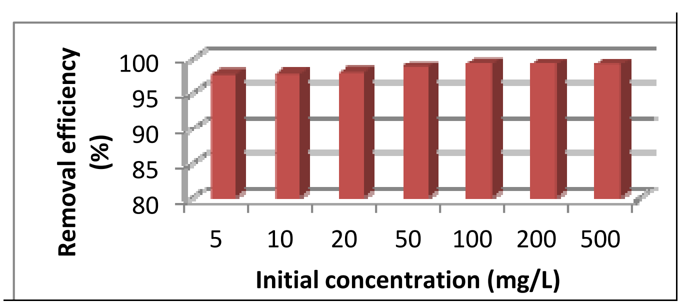

Fig. 4. Influence of initial dye concentration on tartrazine removal efficiency by sorption

From Fig.4. it can be observed that the removal efficiency increases with increasing in initial dye concentration.The concentration was varied in the range 5-500 mg/L. The maximum removal efficiency values varied between 97.6% and 99,16% , which shows that tartrazine sorption from aqueous solution using ions Fe(II) aq to form an ,,in situ" adsorbent support is effective for the whole range of concentration .

3.1.5. Stirring rate

In order to identify the optimum stirring rate, batch sorption experiments were conducted by varying the stirring rate from 100 to 300 rpm, at pH=8, molar ratio [dye]:[Fe(II)]=1:20, adsorption time 5 minutes, initial tartrazine concentration :100 mg/L, temperature 20ºC. The influence of stirring rate on the tartrazine removal efficiency is illustrated in Fig.5.

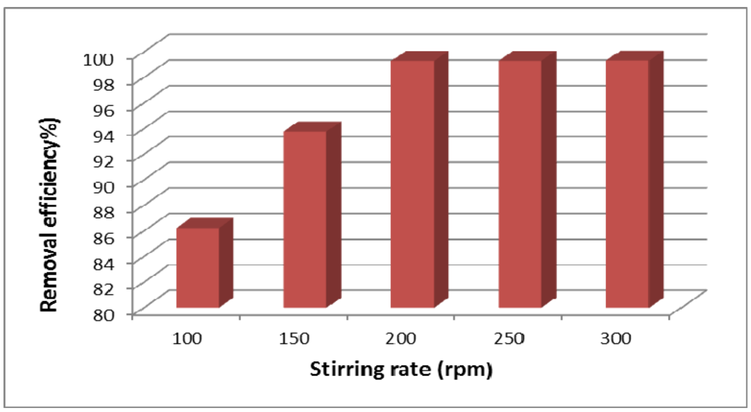

Fig. 5. Influence of stirring rate on tartrazine removal efficiency by sorption using

From Fig.5, it can be seen that the increase of the agitation rate leads to a slight increase of the removal efficiency of adsorption, reaching maximum at 300 rpm (99.32%). Further increase of the stirring rate over 200 rpm (99.29%) did not produced significant changes of the removal efficiency, therefore 200 rpm was selected as optimum stirring rate.

3.2. Flotation

In order to separate the dye loaded adsorbent from the liquid phase and to observe if there are any improvements of the removal efficiency the suspension resulted after adsorption was subjected to a floatation .To establish the optimum parameters of separation process by flotation the following factors were investigated: collector amount, initial dye concentration, pressure, dilution ratio and flotation time.

3.2.1. Collector amount

In order to evaluate the influence of the collector amount on the tartrazine separation from aqueous solutions by sorption-flotation, different molar ratios [colector]:[dye] were studied in the following conditions: initial tartrazine concentration: 100 mg/L, sample volume: 200 mL, pH 8, molar ratio [dye]:[Fe(II)],=1:20, adsorption time 5 minutes, stirring rate 200rpm, pressure p=4 $\times 10^5$ N/m^2, Vsample:Vwater =3:1, flotation time 5 minutes temperature 20ºC).The obtained results are illustrated in Fig. 6.

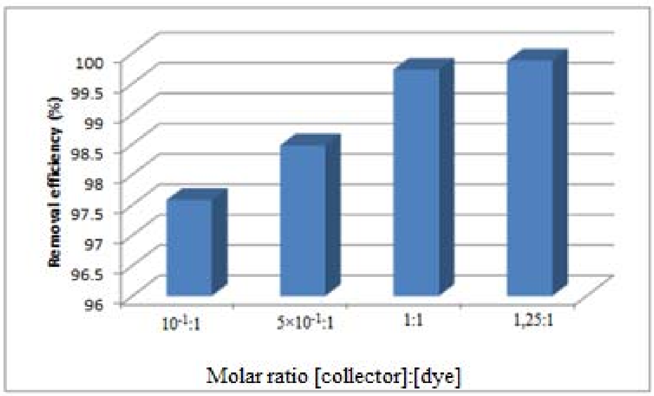

Fig. 6. Influence of initial collector amount on tartrazine separation by sorption-flotation

From Fig.6. it can be seen that the maximum removal efficiencies of tartrazine by sorption-flotation were obtained for the molar ratios [collector]:[dye] of 1:1 and 1.25:1 (99.73% and respectively, 99.88%). Since, the difference in terms of removal efficiency between the two molar ratios was insignificant, the molar ratio [collector]:[dye] of 1:1 was selected as optimum.

3.2.2. Initial dye concentration

Fig.7. shows the influence of initial dye concentration on tartrazine removal efficiency by sorption-flotation using 0.025M sodium oleate as collector agent. The experimental conditions were: sample volume: 200 mL, pH 8, molar ratio [dye]:[Fe(II)],=1:20, adsorption time 5 minutes, stirring rate 200rpm, molar ratio [collector]:[dye],=1:1, pressure p=4 $\times 10^5$ N/m^2, V_{sample}:V_{water}=3:1, flotation time 5 minutes, temperature (20ºC).

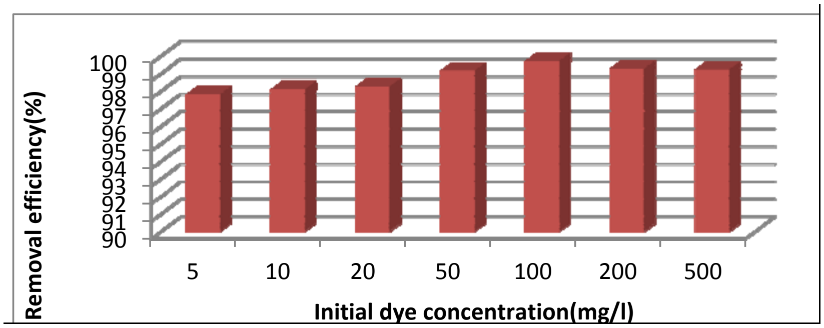

Fig. 7. Influence of initial dye concentration on tartrazine removal efficiency by sorption-flotation

From Fig.7. it can be observed that the maximum removal efficiency of tartrazine by sorption-flotation, 99.73% was obtained for an initial concentration of 100 mg/L. It can also be noticed that the flotation stage applied to the considered system tartrazine-Fe(II), after adsorption leads to a minor improvement of the separation efficiency.

3.2.3. Pressure

The influence of pressure on the tartrazine separation from aqueous solutions, was studied in the range of 2-4.5×10^5 N/m^2 (Fig.8). Experimental conditions: initial tartrazine concentration: 100 mg/L, sample volume: 200 mL, pH 8, molar ratio [dye]: [Fe(II)]=1:20, adsorption time 5 minutes , stirring rate 200 rpm, molar ratio[collector]:[dye],=1:1, V_{sample}:V_{water} 3:1, flotation time 5 minutes, temperature (20ºC).

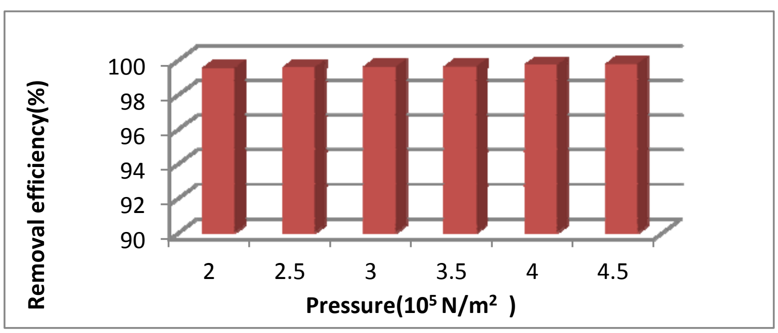

Fig. 8. Influence of pressure on tartrazine removal efficiency by sorption-flotation

Fig.8 shows that the increase of the pressure in the range of 2-4.5 ×10^5 N/m^2 does not seem to significantly affect tartrazine separation by sorption flotation. However, it was observed that the best yields were obtained at pressure values of 4-4,5×10^5 N/m^2 .

3.2.4 Dilution ratio

In order to evaluate the influence of dilution ratio (V_{sample} :V_{water}) on tartrazine removal efficiency, in the following experimental conditions: initial tartrazine concentration: 100 mg/L, sample volume: 200 mL, pH 8, molar ratio [dye]:[Fe(II)]=1:20,adsorption time 5min, stirring rate 200 rpm, molar ratio[collector]:[dye]=1:1, p=4 $\times 10^5$ N/m^2, flotation time 5 minutes. The influence of dilution ratio on tartrazine removal efficiency is presented in Fig. 9.

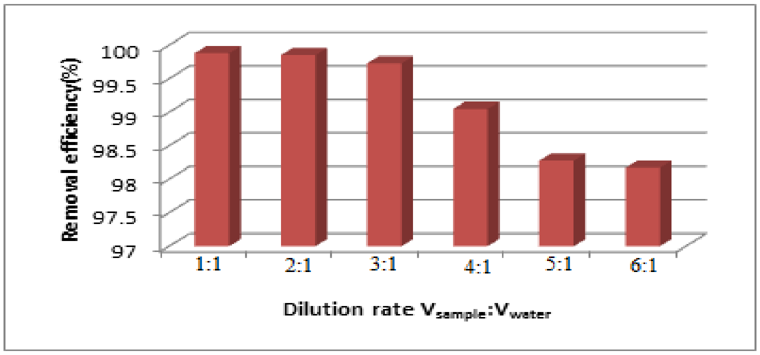

Fig. 9. Influence of dilution rate on tartrazine removal efficiency by sorption-flotation

Fig.9. shows that the highest removal efficiencies were obtained for the following dilution ratios: 1:1, 2:1, 3:1 (99.88%, 99.85%, 99.73%). From **Fig.9**. it can also be observed that the removal efficiency slightly decreases for the dilution ratios: 4:1, 5:1 and 6:1. Considering that there were not recorded significant changes of the removal efficiencies and also from economical reasons, the dilution ratio 3:1 was selected as optimum and was used for further experiments.

3.2.5. Flotation time

Another important factor that influences the separation process is the flotation time. The influence of flotation time on tartrazine removal efficiency by sorption-flotation is presented in Fig.10. Experimental conditions was: initial tartrazine concentration: 100 mg/L, sample volume: 200 mL, pH 8, molar ratio [dye]:[Fe(II)]=1:20, adsorption time 5 minutes, stirring rate 200 rpm, molar ratio [collector]:[dye],=1:1, pressure p=4×10^5 N/m^2, V_{sample}:V_{water}=3:1, temperature (20ºC).

From Fig.10. it can be seen that the separation process is rapid, reaching in only 5 minutes a removal efficiency of 99.73%.

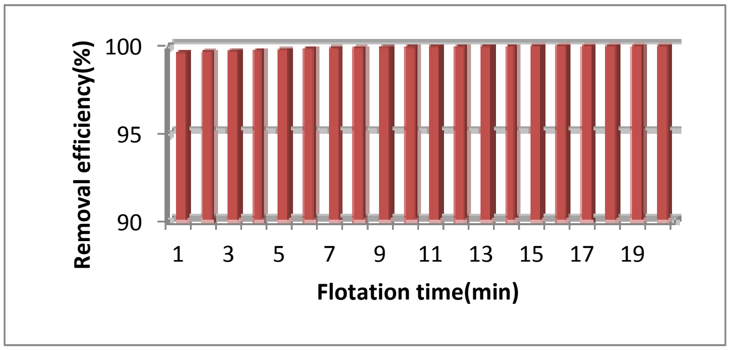

Fig. 10. Influence of flotation time on tartrazine removal efficiency by sorption-flotation

It was observed that after this time interval the agglomerates that contains adsorbent loaded with tartrazine has tendency to fall down. Therefore, 5 minutes was selected as optimum flotation time necessary for the separation of the dye loaded adsorbent.

4. Comparison with others decontamination techniques

A **c**omparison between the removal efficiency of tartrazine by some previously investigated decontamination techniques and the results obtained in this study is given in Table 1.

Table 1

Comparison between the removal efficiency of tartrazine by some previously investigated decontamination techniques

Technique	Adsorbent	Removal efficiency, %	References
Adsorption	Hen feathers	100	[7]
	Bottom Ash	77.30	[8]
	De-Oiled Soya	85.31	[8]
	Saw dust	97	[9]
	Soil	9	[10]
	Colloidal silica	10	[11]
	Magnetic molecularly imprinted polymer	95	[12]
Ion exchange	Amberlite IRA-900[1]	49.88[3]	[13]
	Amberlite IRA-910[2]	49.96[4]	[13]
Photodegradation	-	93.57	[14]
Catalytic decolorization	-	97.5	[15]
Electrocoagulation	-	100	[16]
Electrochemical degradation	-	95.1	[17]
Coupled electrocoagulation and ZnO photocatalyst methods	-	99.70	[18]
Sorption-flotation	Fe(II)	99,73	This study

[1, 2] Ion exchange resins, [3,4] Sorption capacity, mg/g

By comparing the results obtained in this study with those reported in the literature (Table 1) in terms of removal efficiency, we estimate that tartrazine removal by sorption-flotation is an effective process that can be successfully used as decontamination technique for aqueous systems.

5. Conclusions

This study was focused on tartrazine (E102), a toxic azo-dye removal from aqueous solution by sorption-flotation using ions Fe(II)aq to form an ,,in situ" adsorbent support.

In order to establish the optimum operating parameters, the influence of pH, sorbent dosage,adsorbtion time, initial dye concentration, strring rate on the sorption process was investigated. The maximum removal efficiency of tartrazine by sorption-flotation was 99.73% and was obtained in the following conditions: at pH = 8, molar ratio [collector]:[dye]=1:1, Ci = 100mg/L, $p=4\times10^5$ N/m^2, dilution ratio:3:1, flotation time=5 minutes. It can also be observed that the flotation stage applied to the considered system (tartrazine-Fe(II)) after adsorption leads to an improvement of the removal efficiency (> 99%).

The obtained results indicate that Fe(II)can be successfully used to form an ,,in situ'' adsorbent support for tartrazine removal.

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