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Extraction of sulfite for wastewater treatment and for analytical determination

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ABSTRACT

Due to the international demand for fresh agricultural products, especially fruits, which result in long travel times from the production centers to the final markets, the preservation of these products becomes very important. Within the most common conservation methods, sulfite stands out. However, to preserve the ecosystem and the environment, it is the great interest to remove this substance from residual waters of preservation treatments and to prevent the contamination of layers of water and soils. Due to the great importance of the fruit industry in our country is necessary to develop techniques that allow treating this kind of wastewater to avoid affecting environmental and human conditions. For that reason, in this work we describe a system specially designed to carry out tests of absorption of sulfite by membranes, using a Celgard Liquicel® module, which puts in contact indirect two solutions, a feeding solution with the sulfite to extract and a solution NaOH receptor. The sulfite transferred from the feeding solution to the NaOH solution in the form of sulfur dioxide reacts with NaOH. Later, sulfite can be sensed via electrochemistry using modified reticular carbon electrodes. The best extraction results were obtained for a sodium hydroxide of 0.2 mol/dm^3 and a concentration of 1,500 mg/dm^3 sodium sulfite for the feeding, obtaining about 78% extraction, at a constant flow rate of 0.0083 dm^3/s. By varying the flow rates keeping both concentrations constant, in the levels earlier mentioned, an increase in the extraction was observed from the flow of 0.0042 dm^3/s to 0.0083 dm^3/s, but no appreciable difference between the maximum of 0.0083 dm^3/s and 0.0125 dm^3/s was achieved. In addition, these results can lead to a marketable prototype that includes the separation and removal of sulfite from wastewater from the fruit and agricultural industry quickly and effectively.

Keywords: Analytical determination of sulfite; Membrane contactor system; Sulfite removal; Wastewater treatment

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1. Introduccion

A large part of the food and drink industry uses sulfite as an antiseptic that eliminates wastewater with high sulfite content. In general, wastewaters are complex matrices and consequently, treating the sulfite by oxidation does not allow a full removal of sulfite because the energy applied is used in oxidizing many organic compounds that are also discarded in these wastewaters. Although, it is possible to determine sulfite in those matrices through colorimetric or electrochemical methods, these methodologies are intrincate since most of the wastewater proceed from the drink, wine, and food industries and so contains dyes or easily oxidizable species that mask or block the sulfite measurement.

It is difficult to exactly define a membrane, but a general definition may be: a selective barrier between two phases, being the term "selective" inherent to a membrane or a membrane process. It is worth mentioning that this is a macroscopic definition, while the separation must be considered at a microscopic level. The definition does not discuss the membrane structure or its function. Each membrane separation process is characterized by using a different membrane in particular. The membrane has the ability of transporting a component more easily than to another because of differences in the physical and/or chemical properties between the membrane and the permeable components [1]. A membrane contactor is a devise that achieves gas-liquid or liquid-liquid mass transfer without dispersion of a phase within the other. This is attained by passing the fluids on opposing sides of a microporous membrane. Through a careful control of the pressure difference between the fluids, one of the fluids is immobilized on the membrane pores so that the fluid-fluid interface is localized on the mouth of each pore. Such approach offers a series of important advantages over conventional dispersed phase contactors, including the absence of emulsions, the flooding at high flow speeds, the discharge at low flows, the density difference between the required fluids, and the surprisingly wide interface area. In fact, membrane contactors typically offer 30 times the area that can be reached on gas absorbers and 500 times the area that can be obtained on liquid-liquid extraction columns. On these applications, the process selectivity is primarily given by thermodynamic aspects between the different phases in contact [2]. On the other hand, this study carried out by Park et al., [3] in 2008, the absorption of sulfite, SO_2, was tested from acid gases from the fossil fuel production industry, showing that the HFMC (hollow fiber membrane contactor) system generated efficiencies of around 85% for different SO_2 flows using different inorganic salts as absorbent or receiver solutions by a gas-liquid contactor system. A year later, Morales [4] developed the study to implement a system of membrane absorption for the colorimetric analysis of sulfites in red wine, to develop a technique for sulfite quantification, obtaining extraction results up to 97%. In a simulation study of a sulfite extraction system from wine developed by Silva [5–6], the modelling and simulation of experimental extraction data by SO_2 membranes was carried out. In the work developed by Hasanoğlu et al., [7] it was demonstrated that, for the cases of SO_2 absorption with reaction in the sodium hydroxide receiver solution, the reaction can be considered instantaneous and irreversible, moving the reaction area to the gas-liquid interface of the corresponding receiver solution, a fact that was also demonstrated before by Schultes [8–9] by the SO_2 absorption in a packed bed column using a NaOH counterflow solution.

The method proposed and studied in this work allows the treatment of wastewater for sulfite removal and also its detection by the Ripper Method [10] even if the sample is highly dyed, a fact that is an advantage in comparison with other methods. Also, it is important that the sulfite control and detection is needed due to the negative effects on asthmatic/allergic people [11,12] and on the soil if the industrial waste is not treated.

2. Experimental setup

2.1. Sulfite extraction

The experimental absorption system consists on a hydrophobic hollow fiber membrane that separates two aqueous solutions which circulate counterflowly; sulfite water (wastewater, beverages, or food-water) or, in this case, a model solution that circulates on the case and a solution of NaOH extraction that circulates on the module fibers. Each flask is connected to generate the recirculation of each flow to have extraction in counterflow and continuously, as can be seen in Fig. 1.

Once both solutions are prepared, they are connected to the system and pumped at counterflow within the equipment to set the system. This process is carried out for 1,200 s. Then, the system is stopped (both pumps) and the feeder solution is acidified to pH < 1 with concentrated H_2SO_4. In these conditions, the sulfite becomes sulfur dioxide that goes through the membrane barrier and enters the receiver solution that contains NaOH, where it becomes sulfite anion again. Once the feeder solution is acidified, the flask that contains it must be capped immediately and connected again to the system (both pumps), marking the beginning of the operation time as time zero.

The samples in which the sulfite content is analyzed are obtained from the receiver solution from the receiver flask, extracting a 0.01 dm^3 aliquot by a syringe at previously determined times. Those times were determined as shown in Table 1.

In this way, each experimental determination takes 1,200 s in which 10 samples are extracted. Once the times have passed and the samples have been taken, the pump flows are stopped, and the system is shut down. Then, the samples are analyzed by the Ripper titration colorimetric method.

The system operation conditions are shown in Table 2.

The flows were previously calculated by calibration curves and their determination is shown in Figs. 2 and 3.

3. Results and discussion

3.1. Performance assessment of the absorption by membranes process

3.1.1. Extraction

The results obtained from the concentrations measured at each time, are used to obtain mass data and, therefore, to obtain the extraction percentage, as shown in the following equation:

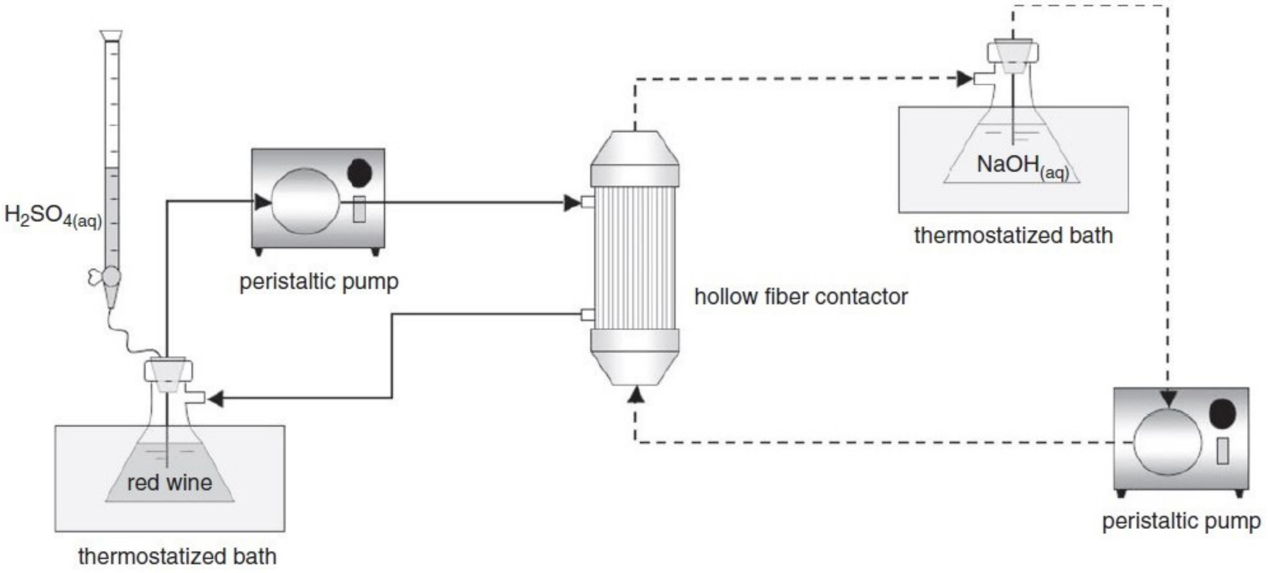

Fig. 1. Sulfite extraction system though hollow fiber membrane contactor [6].

Table 1
Extraction times (in s) during the process of separation by membranes

No. of sample		Time between each extraction (s)	
1st – 2nd		30	
3rd		30	
4th		60	
5th		60	
6th		60	
7th		60	
8th		300	
9th		300	
10th		300	
Sample total	10	Total time (s)	1,200

Table 2
Operation conditions of the procedure

Temperature, *K*	300.15
Total time, s	1,200
Case flow, dm^3/s	$8.33 \cdot 10^{-03}$
Fiber flow, dm^3/s	$8.33 \cdot 10^{-03}$

$$\text{Extraction } \% = \left(\frac{C^{\text{recep}}_{\text{Na}_2\text{SO}_3,t=i} \cdot V^{\text{recep}}_{t=i}}{C^{\text{feeder}}_{\text{Na}_2\text{SO}_3,t=0} \cdot V^{\text{feeder}}_{t=0}} \right) \cdot 100 \tag{1}$$

$C^{\text{recep}}_{\text{Na}_2\text{SO}_3,t=i}$, concentration obtained in the receiver solution at a time "*i*" (mg/dm^3); $C^{\text{feeder}}_{\text{Na}_2\text{SO}_3,t=0}$, initial sulfite concentration in the feeder (mg/dm^3); $V^{\text{recep}}_{t=i}$, receiver solution volume in the flask at a time "*i*" (dm^3); $V^{\text{feeeder}}_{t=0}$, initial solution volume in the feeder (dm^3).

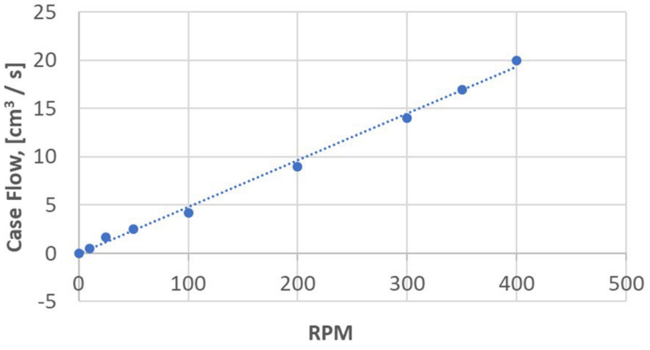

Fig. 2. Calibration curve for sodium sulfite solution pump.

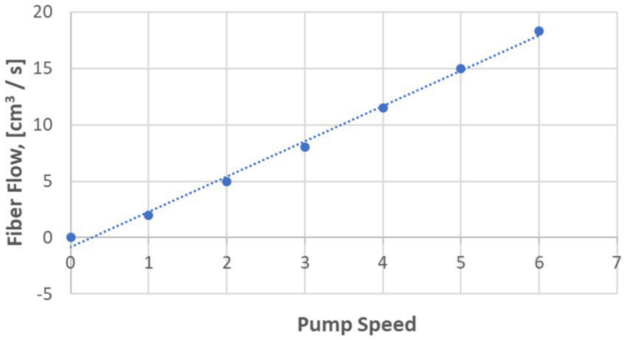

Fig. 3. Calibration curve for sodium hydroxide solution pump.

3.1.2. Mass transference rate

The mass transference rate was calculated by means of the molar flow density that goes through the membrane, based on the Na_2SO_3 concentrations obtained at the time in the NaOH receiver solution. This was carried out by Eq. (2):

$$J = \frac{1}{A} \cdot \frac{d\left(C^{\text{recep}} \cdot V^{\text{recep}}\right)}{dt} \tag{2}$$

where J is the molar flow density (mol/[m^2·s]), A is the transfer area (m^2) and s is the time (s).

As the volume of the receiver solution changes through the process because of the extraction of the corresponding samples, the equation is corrected and Eq. (3) is obtained:

$$J=\frac{1}{A}\cdot\frac{\left[\left(C^{\text{recep}}_{t=t+1}-C^{\text{recep}}_{t=t}\right)\cdot V^{\text{recep}}_{t=t+1}+\left(V^{\text{recep}}_{t=t+1}-V^{\text{recep}}_{t=t}\right)\cdot C^{\text{recep}}_{t=t+1}\right]}{\Delta t} \qquad (3)$$

where $C^{\text{recep}}_{t=t+1}$, sodium sulfite molar concentration in receiver solution at time $t + 1$ (mol/m^3); $C^{\text{recep}}_{t=t}$, sodium sulfite molar concentration in receiver solution at time t (mol/m^3); $V^{\text{recep}}_{t=t+1}$, Receiver solution liquid volume at time $t+1$ (m^3); $V^{\text{recep}}_{t=t}$, Receiver solution liquid volume at time t (m^3).

Since the volume of the receiver solution changes due to the sample taking, an average of the results obtained was calculated in order to obtain an average of the mass transfer velocity.

On the other hand, the optimal concentration of sodium hydroxide must be determined for different sulfite concentrations on the feeder solution to maximize the extraction percentage. For this reason, experiments were developed varying the model Na_2SO_3 solution concentrations that were 500, 1,000, 1,500, and 2,000 mg/dm^3, and were measured with an increasing concentration NaOH receiver solutions, that were 0.02, 0.05, 0.1, and 0.2 mol/dm^3. In each case, the four different sulfite concentration solutions were measured against the same NaOH solution. This was performed to each NaOH solution to determine the optimal sulfite concentration/NaOH concentration relation.

3.2. Assessment of the effect on the solution concentrations at extraction

3.2.1. Na_2SO_3 extraction results

The results of extraction percentages obtained for each combination of concentrations of sodium sulfite feeder model solutions and sodium hydroxide receiver are shown in Table 3.

The first item that calls the attention in Table 3 is the mistake associated to the Ripper method [10], since the sample, at basic pH 12.3 just prepared and measured by the Ripper method, determines a number clearly smaller than the expected according to the preparation. This error varies from 18% to 26.5% for more diluted samples (500 mg/dm^3) and diminishes for the 2,000 mg/dm^3, independently of the NaOH concentration. As in all the cases the solution pH is constant, loss by acidification is not expected, so this variation accounts for the mistake associated to the Ripper method on “clean” samples (without interfering), indicating that even if it is an official measurement method, it produces an important mistake for relatively diluted samples, such as the 500 mg/dm^3 ones. However, considering that the Ripper method is the official method in Chile for sulfite determination, the values measured by this method will be used as “real sample” values. The results here shown refer to that concentration, the one obtained by the Ripper method, considered as the real sample concentration. Secondly, the fourth column, which shows the mass measured from the solution after acidification, is much smaller (practically half) than the one given by the Ripper method, accounting for the loss produced by the SO_2 generation escaping the solution. This loss is real since the difference between the sample measured by the Ripper method

Table 3
Results of assessment of concentration effects on extraction at constant flow

NaOH (mol/dm^3)	Na_2SO_3, (mg/dm^3) prepared solution	Na_2SO_3 feeder, (mg/dm^3) measured solution	Difference between prepared solution and measured by Ripper method (%)	Na_2SO_3 feeder initial mass, after acidification (mg)	Na_2SO_3 extracted mass on receiver (mg)	Extraction percentage (%)
0.02	500	409.50	18.1	204.75	37.21	18.17
	1,000	940.80	6	470.40	199.33	42.38
	1,500[a]	1335.60	11	667.80	369.43	55.32
	2,000[a]	1801.80	9.9	900.90	683.55	75.87
0.05	500	390.60	22	195.30	50.57	25.89
	1,000	924.70	7.5	462.35	313.56	67.82
	1,500	1302.00	13.2	651.00	468.01	71.89
	2,000	1822.80	8.9	911.40	658.43	72.24
0.1	500	367.50	26.5	183.75	69.47	37.81
	1,000	914.90	8.5	457.45	289.43	63.27
	1,500	1348.20	10.1	674.10	487.79	72.36
	2,000	1932.00	3.4	966.00	708.33	73.33
0.2	500	407.40	18.5	203.70	95.59	46.93
	1,000	921.90	7.8	460.95	257.69	55.90
	1,500	1419.60	5.4	709.80	557.76	78.58
	2,000	1869.00	6.6	934.50	708.67	75.83

[a] Sodium hydroxide limiting the reaction.

before and after acidification shows a loss near to 50% in all concentrations. In the fifth column, what is obtained from the extraction flask after 1,200 s of the process is detailed, as explained in Table 2. Finally, in the sixth column the extraction percentage is determined calculated according to Eq. (1).

It is important to point out that after the 1,200 s in all the measurements performed, independently of the sulfite concentration, when the NaOH was in excess, the sulfite remaining in the feeder solution was zero. Namely, all the sulfite is transferred from the feeder flask to the receiver solution, even if in the process there is an associated loss by volatilization of SO_2.

From the results in Table 3, it can be seen that for the same concentration of the NaOH receiver solution, a higher extraction percentage is obtained as the sulfite concentration in the feeder solution increases, which can be due to the generation of gradients of higher SO_2 concentration between both interfaces within the membrane pore, that facilitates the transfer process. On the other hand, it is interesting to note that as the NaOH concentration in the receiver solution increases, the recovery percentage does not vary significantly and did not surpass the 80% of the sodium sulfite mass extraction (according to Eq. (1)), indicating that the increase in the NaOH concentration (over the equimolar concentration needed for the neutralization) is not significant enough to increase the sulfite extraction. Because the reaction represented in Eq. (3) occurs in the gas-liquid interface of the receiver solution in an instant and irreversible manner [5–6], a chemical equilibrium between reactants and product that stops the reaction before a 100% extraction is not generated. However, when a sulfite concentration analysis at time zero and at 1,200 s, in the end of the extraction process, is made to determine the remaining sulfite quantity in the feeder solution, it is worth mentioning that the experiments carried out show in all cases that after the extraction time in the feeder solution sulfite is not detected, concluding that the system achieves a 100% of extraction, even if its recovery in the NaOH solution is less.

According to the simulation of this process made by Silva [5] for the sulfite extraction in wine, it was obtained that for 0.0085 dm^3/s flows using the same solution types used in this research and at a constant temperature of 300.15 K, it is possible to expect an extraction level around 70% until 300 s approximately, so it can be said that similar results were achieved under similar working conditions. It is interesting to note that the reaction is instantaneous. The instantaneousness of the reaction is described in the work by Schultes on SO_2 absorption with sodium hydroxide solution in a packed column, in which the results obtained by comparison of the Hatta number and the E maximum improvement factor demonstrated that the reaction is generated spontaneously and irreversibly in a magnitude such that it can be assumed that the reaction is displaced to the reception gas-liquid interface [8]. The instantaneousness was also demonstrated in the work of Hasanoğlu et al. [7] at concentration much closer to those used in the procedures of this work.

On the other hand, according to the chemical reactions shown as follows and the data obtained by the HSC Chemistry 7 software (Table 4), it is possible to say that the reaction of sodium sulfite formation occurs much faster than the one of sulfurous acid formation, indicating that these are reactions in a series and not reactions that can occur in parallel.

Table 4
Equilibrium constants for SO_2 reactions with receiver solution at 298.15K

K_{eq} formation of Na_2SO_3	K_{eq} formation of H_2SO_3
$3.03 \cdot 10^{19}$	1.06

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O \quad \text{(First reaction)}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad \text{(Second reaction, in absence of NaOH)}$$

The formation of sulfurous acid was verified by measuring the pH of the receiver solution once the process was over. Sulfurous acid was found in the combination of NaOH 0.02 mol/dm^3 concentrations against 1,500 and 2,000 of sodium sulfite, because they show a pH value around 6 for both instances. It is concluded that sulfurous acid is formed because the receiver solution pH presented a value around 6 in both cases, instead of 12 which the common value is obtained. It is worth mentioning that in both processes, using 0.02 of NaOH and in both sodium sulfite concentrations, the component in excess was the sodium sulfite, therefore the explanation for this will be that the transferred sulfite reacts with all NaOH in the receiver solution and begins to react with water to produce the sulfurous acid mentioned.

This result is interesting because with a simple final pH measurement for the receiver solution it can be estimated whether the NaOH concentration used or not suitable, a fact that is highly interesting for unknown samples. Consequently, always it must be provided that this solution has a pH around 12 to secure a complete sulfite extraction from wastewaters.

On the other hand, the times required for a complete sulfite extraction were estimated, obtaining the results that are shown in Figs. 4–7 by using Eq. (1).

In Figs. 4–7 the resulting behaviors of the sulfite extraction through time and particularly for each concentration of each of the solutions can be observed. In most of the cases, it can be seen that after 600 s of extraction, it starts to stop and advance more slowly, mainly because of the diminishing of the mass transfer potential after that period of time. Also, it can be observed that as the NaOH concentration increases, the difference between the extraction percentages obtained for the different sulfite concentrations is less noticeable, as all reach similar percentage over 70%. The reason for this is that the more sodium hydroxide is in the receiver solution, the contact between the NaOH molecules and the SO_2 in the gas-liquid interface of the receiver solution is easier, generating that the transfer potential between the interfaces within the pore is maintained at a higher level than in smaller concentrations of NaOH. This indicates a mass transfer velocity higher when the NaOH concentrations increases, because, as can be seen in Fig. 4, the extractions for sodium sulfite concentrations of 500, 1,000,and 1,500 mg/dm^3 are low, but it is expected that with more working time they reach the maximum of extraction for this system. On the contrary, it can be seen in Figs. 5, 6, and 7 that the increase in the NaOH concentration favored the transfer velocity reaching almost at all sulfite concentrations, a percentage near to the maximum possible.

It is worth to mention that the standard deviation of the process is ±2,78%, which is obtained by the repetition of one of the experimental series, randomly chosen, to obtain a general value for the process carried out.

To conclude, a statistical analysis was developed that demonstrated with a 99% of accuracy that the most significant variable for the concentration combination is the sodium sulfite concentration in the feeder. In the graph of normal probability (Fig. 8) it can be seen how the sulfite concentration is the most significant variable on the extraction results, while in a much minor degree, the hydroxide concentration will affect the extraction in relation to the quantities used in the experimental design of this work.

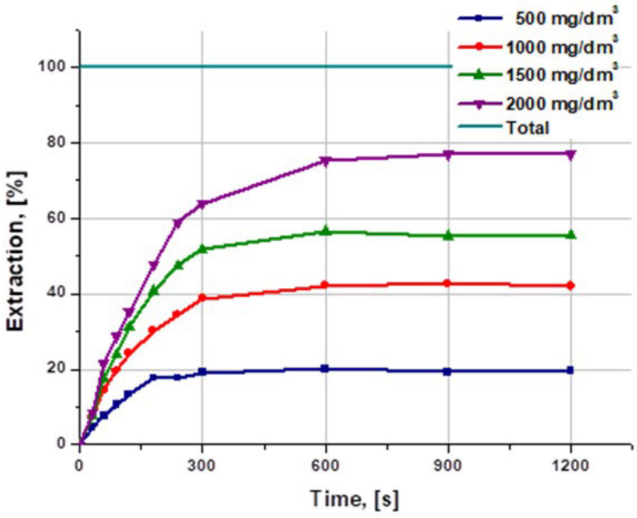

Fig. 4. Extraction percentages obtained at different sulfite solution concentrations and 0.02 mol/dm³ NaOH solution vs. time. Hydroxide concentration 0.02 mol/dm³.

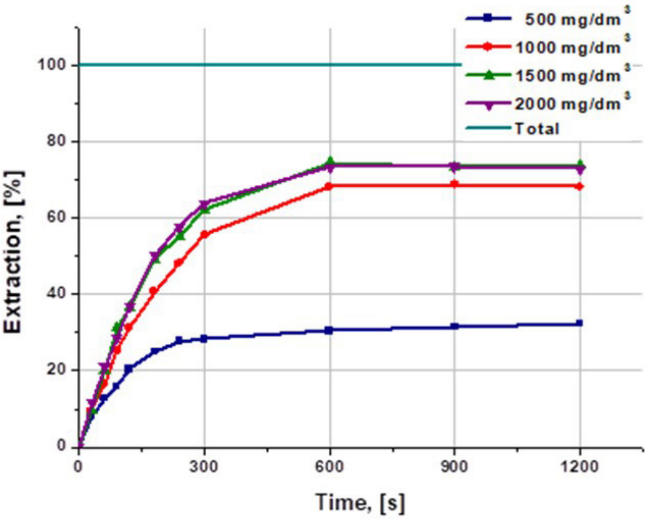

Fig. 5. Percentages of extraction obtained at different sulfited solution concentrations and NaOH 0.05 mol/dm³ solutions vs. time. Hydroxide concentration 0.05 mol/dm³.

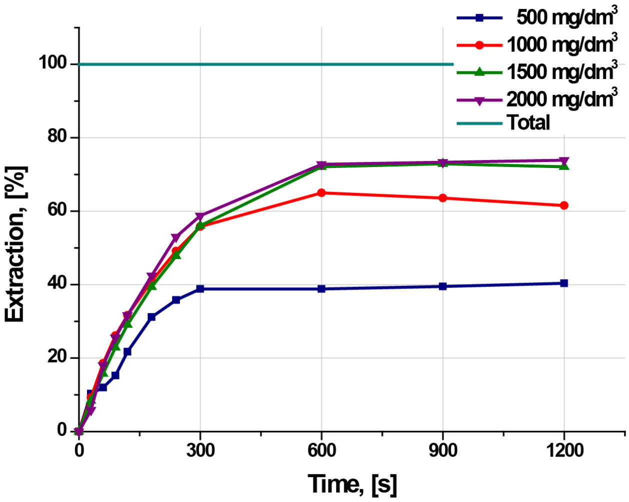

Fig. 6. Percentages of extraction obtained at different sulfited solution concentrations and NaOH 0.1 mol/dm³ solution vs. time. Hydroxide concentration 0.1 mol/dm³.

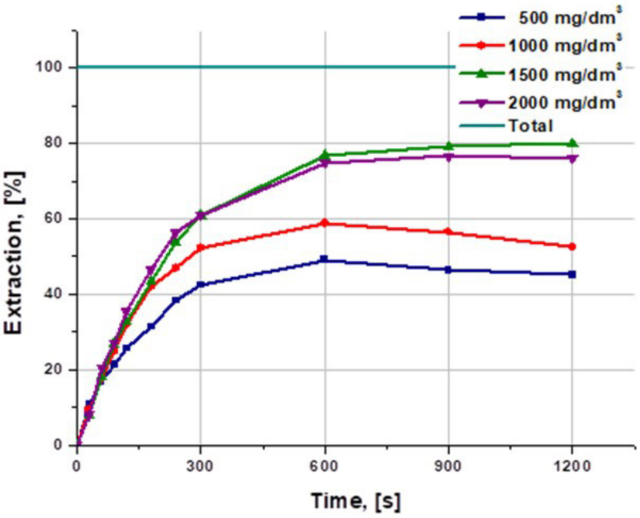

Fig. 7. Percentages of extraction obtained at different sulfited solution concentrations and NaOH 0.2 mol/dm³ solution vs. time. Hydroxide concentration 0.2 mol/dm³.

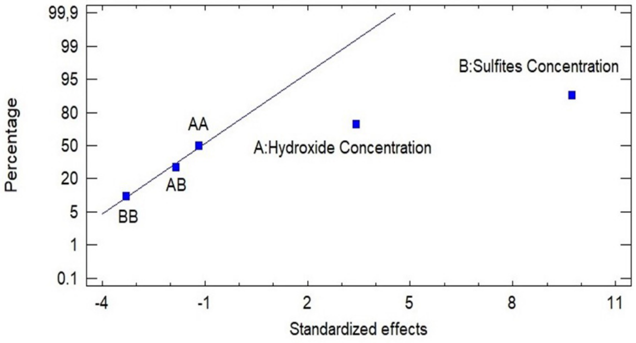

Fig. 8. Graph of normal probability to evaluate the effect of concentrations on extraction.

3.3. Na_2SO_3 transfer rate results

For the measurement and comparison of mass transfer rates in the system, the average flow densities for each experimental series developed were calculated, results that can be observed in Table 5.

According to the results on Table 5, it can be observed that the mass transfer process is governed by the feeder phase resistance and the change in its concentration which generates an increase in the transfer potential. On the contrary, for the same sodium sulfite concentration, the NaOH concentration is not influential for the molar flow density, being an insignificant variable for mass transfer.

On the other hand, the fact that the detachment of the gaseous SO_2 obeys to the Henry law [1], generates a very favorable factor for the system and for the passing of SO_2 to the gas phase within the pore, due to the fact that SO_2 presents a high pressure (78.899 [Pa m^3/mol]) at the working temperature. Given the easiness in the transfer of SO_2 from the solution to the pore, high partial pressure gradients are generated each time in the pore, according to the increase on sulfite concentration on the feeder, so the transfer stage from the pore is probably the one that less contributes in terms of resistance to the SO_2 passing. In this manner, the first stage of the system of the feeder boundary layer, is the one that more influence the process, given that the values that are obtained for the mass transfer coefficient for the feeder boundary layer are 10,000 times smaller than the ones obtained for the mass transfer coefficient in this system membrane, as simulated in the work reported by Silva [5], representing similar flows to those used, practically the 1% of the total system resistance, possible being that percentage smaller given that the flows used in this process are smaller than the ones used in the simulation performed [5–6]. Afterwards, in the gas-liquid interface of the receiver solution, the instant and irreversible reaction described for the previous results is generated, easing even more the extractive process because its immediateness makes the partial pressure in such interface to stay constant in a null or zero value, generating a practically free passing of SO_2 through the membrane given that it maintains the transfer potential at its maximum.

The normal probability graph analysis in Fig. 9 for molar flow densities shows that, for a high mass transfer to happen, the most important variable, keeping the flow of both solutions constant, is the sodium sulfite concentration differences generated by the concentration on the feeder. Namely, with 99% accuracy, the most significant variable is sodium sulfite concentration, verifying that the sodium hydroxide concentration does not have a high relevance when there is an excess of it, corroborating what was mentioned in Schultes, Hasanoğlu, and Flagiello et al., [7–9]. works about the immediateness of the reaction in the receiver solution interface

Once the best combination to maximize the absorption sulfite process is achieved, the next step was to vary the flows of the feeder and receiver solutions so to obtain the best extraction result regarding a high, medium, and low flow. For this, the flows listed in Table 6 were tested.

It is worth to mention that the result for the medium flow corresponds to the one obtained in the previously mentioned experiments.

3.4. Assessment of the optimal flow for solutions

3.4.1. Results of extraction by varying the levels of flows

Since the biggest extraction percentage was obtained at 0.2 mol/dm^3 sodium hydroxide and 1,500 mg/dm^3 sodium sulfite, this was the concentration combination used for the extraction analysis in terms of the flow of both currents. The results obtained are listed in Tables 7 and 8.

The results in the extraction percentages for the flow variation shown in Table 8, for the concentrations of 1,500 mg/dm^3 sodium sulfite model solution and 0.2 mol/dm^3 sodium

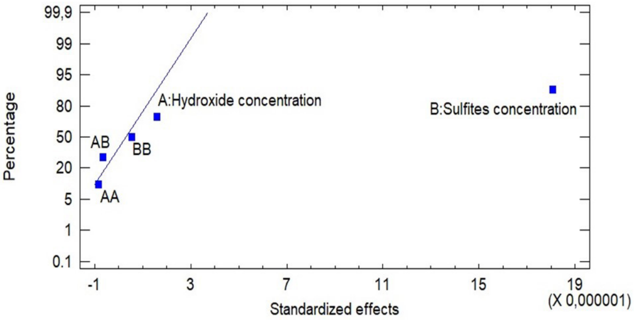

Fig. 9. Normal probability graph for the concentration effects on average molar flow density.

Table 6
Flow levels and their corresponding flow

Flow levels	Flow (dm^3/s)
High	0.0125
Medium	0.0083
Low	0.0042

Table 5
Average molar flow densities at different concentration combinations

Na_2SO_3 (mg/dm^3)	Average molar flow density (mol/[m^2·s])			
	0.02 mol/dm^3 NaOH	0.05 mol/dm^3 NaOH	0.1 mol/dm^3 NaOH	0.2 mol/dm^3 NaOH
500	$1.314\cdot10^{-06}$	$1.755\cdot10^{-06}$	$2.333\cdot10^{-06}$	$3.093\cdot10^{-06}$
1,000	$6.350\cdot10^{-06}$	$9.151\cdot10^{-06}$	$8.941\cdot10^{-06}$	$8.592\cdot10^{-06}$
1,500	$1.205\cdot10^{-05}$	$1.443\cdot10^{-05}$	$1.322.10^{-05}$	$1.534\cdot10^{-05}$
2,000	$2.025\cdot10^{-05}$	$2.065\cdot10^{-05}$	$2.001\cdot10^{-05}$	$2.057\cdot10^{-05}$

hydroxide receiver, indicate that at the same 1,200 s of working time, an increase between the flow of 0.0042 dm^3/s and 0.0125 dm^3/s was obtained, as it was theoretically expected. However, the sodium sulfite quantity obtained for the 0.0042 dm^3/s and 0.0125 dm^3/s flows is similar, corroborating that for the extractive or absorption process of the sulfur dioxide produced by sodium sulfite, a maximum extraction percentage of 78% is achieved, which is not very far from what Silva simulated. This can be seen also in Fig. 10 in which for both flows mentioned the same maximum is reached, nevertheless, in the same figure, it can be seen that the effect of the increase in the flow principally consists in an increase in the mass transfer velocity, since that even if in both cases the extraction maximum is the same, the one that corresponds to 0.0125 dm^3/s is obtained 300 s before than the one obtained at the medium flow. For this, it is necessary to observe Fig. 11 that shows the difference among the molar flow density averages that explains that at 0.0125 dm^3/s the maximum of extracted mass is obtained before, given that the mass flow density is favored, in this case, by the increase in the solution flows. This is explained because, as the process is governed by the resistance to mass transfer from the feeder solution, the increase in the flow of such solution improves the mass transfer, because generates a reduction in the feeder limit layer, facilitating the SO_2 transfer through it.

By the Sherwood calculation (Sh) it is possible to verify that the chosen configuration is the correct one in regard to the chosen areas for the passing of the solutions, besides confirming an increase in the mass transfer coefficient as the flows increase. This can be observed in Table 9, in which it is corroborated that the Sh at the 3 flow levels studied are higher in the cases that the sulfite solution circulates on the casing, compared with hypothetical cases in which it circulates through the fibers, in addition to increase according to the feeder flow increasing.

In addition, on Silva's simulation work [5] was theoretically verified that the flow variation of the receiver NaOH solution does not generate a noticeable increase on the SO_2 extraction transferred by membrane. The reason for this is that the mass transfer in the receiver gas-liquid boundary layer is principally conditioned by the instant reaction between sulfur dioxide and sodium hydroxide, moving the reaction plane towards the gas-liquid interface. The contribution of the receiver solution to the mass transfer is highly independent of its flow, because for this 0.2 mol/dm^3 case the sodium hydroxide is found in excess, being this maximum for all time and space.

Thus, the increase in the Reynolds number and consequently Sherwood's, are the main factor that explains the

Table 7
Concentrations used for the assessment of the flow effect on extraction

NaOH (mol/dm^3)	Na_2SO_3 (mg/dm^3)
0.2	1,500

Table 8
Extraction percentages results for flow variations at constant concentrations

Flow (dm^3/s)	Na_2SO_3 feeder (mg/dm^3)	Initial mass Na_2SO_3 (mg)	Extracted mass Na_2SO_3 (mg)	Extraction percentage (%)
0.0042	1302.00	651.00	347.45	53.37
0.0083	1419.60	709.80	557.76	78.58
0.0125	1365.00	682.50	530.15	77.68

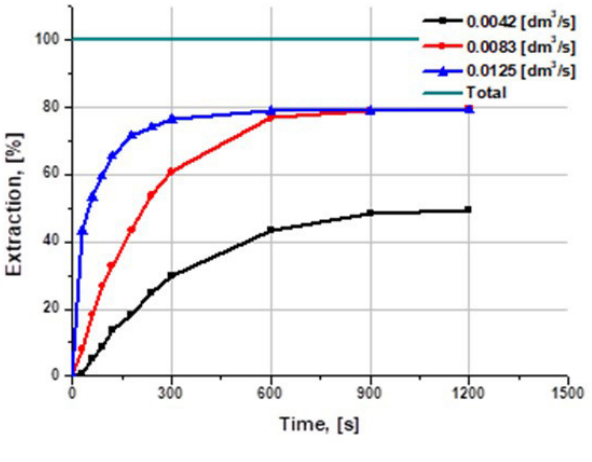

Fig. 10. Result of punctual extraction percentages for flow variations at constant concentrations.

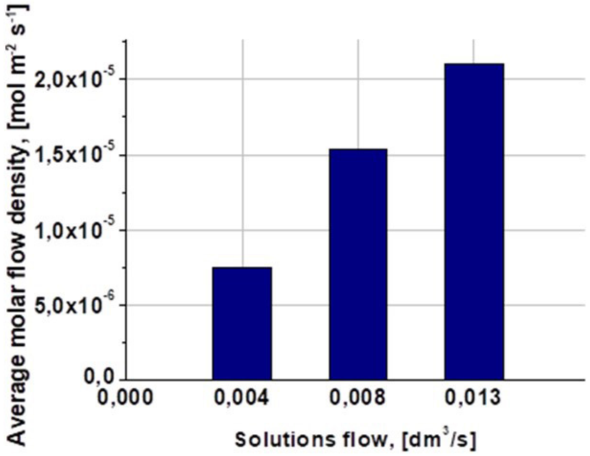

Fig. 11. Average molar flow densities at different flows and constant concentrations.

Table 9
Comparison of dimensionless parameters as the feeder solution goes through the case or the fibers.

Flow (dm^3/s)	Re		Sc		Sh	
	Case	Fibers	Case	Fibers	Case	Fibers
0.0042	2.54	3.53	543.31	543.31	5.11	5.02
0.0083	5.08	7.06	543.31	543.31	5.31	5.16
0.0125	7.62	10.58	543.31	543.31	5.47	5.28

Re, Reynolds calculation; Sc, Schmidt calculation; and Sh, Sherwood calculation.

increase in the mass flow density in function to the increase of the solutions flow, as shown in Fig. 11, translating this into a faster extraction that can be seen in Fig. 11, given its effect on the convective coefficient of mass transfer.

It is important to note that, in parallel, a chemical reaction of oxidation in heterogeneous phase was carried out. For this, different catalyzers to diminish the reaction activation energy that occurs in the electrode-solution phase can be used. The catalyzers can be adsorbed on the electrode or be in the solution [13–14]. In this research, modified electrodes were used because their use requires a smaller potential to oxidize the sulfite. A controlled potential electrolysis at 0.73 V vs. Ag/AgCl was carried out, obtaining, in this case, a sodium sulfate solution that enables the sulfite disposal from the waste water system. Before performing the controlled potential electrolysis, the system was studied by cyclic voltammetry. The electrode used was a reticulated vitreous carbon one and on that electrode nickel tetrasulfonated phthalocyanine (II) (polyNiTSPc) was electropolymerized.

In Fig. 12 the current increase (red line) and the 0.02V potential displacement towards less positive potentials of the oxidation wave (positive sweep, from –1.0 to 1.0 V vs Ag/AgCl) at 0.73 V is shown, indicating electrocatalysis towards sulfite oxidation reaction at pH 12 by the modified electrode.

In this way, an electrochemical system that can be coupled to the separation by membrane system is obtained, and therefore, the two technologies can be connected for the making of a mayor scale product, taking into consideration that in this work electrooxidation of sodium sulfite solutions under 500 mg/dm^3 was achieved.

In comparison with the preconcentration and analysis method [15] proposed by Wu et al., the advantageous the developed system is that the membrane separation system is eventually coupled to an electrochemical system is convenient operation, good reusability, and cost efficient. This makes a good alternative because pre-concentration is not used, extraction is used in optimal working conditions and it is easy to use. In addition, sulfite analysis is performed with electrochemical techniques from which much information can be obtained, not only the quantification but also the sulfite removal from the wastewater.

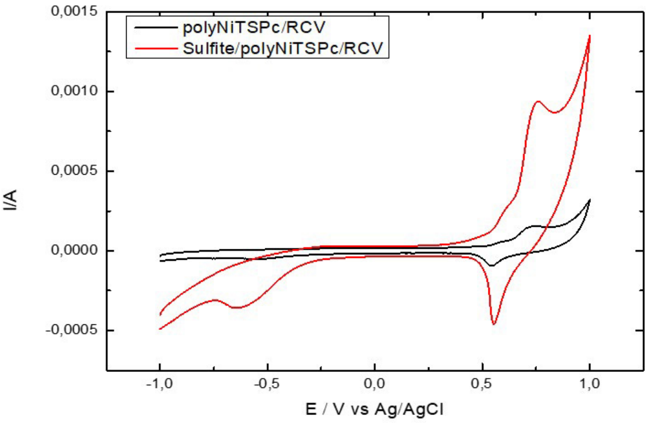

Fig. 12. Voltammetric response for the NiTSPc/RCV reticular carbon modified electrode in absence (black line) and presence (redline) of sulfite at 500 mg/dm^3 at 0.1 V s^{-1}. Cicle 1.

4. Conclusions

Sulfite is an important chemical that is widely used in the processing and conservation of foods of vegetable and animal origin. It is also known as a disinfectant or antiseptic agent. It gained popularity as a preservative due to its apparent lack of toxicity in mammals [16]. However, the sulfites are attributed various adverse effects in humans, such as headache, breathing difficulties, diarrhea, allergic reactions, fatigue, irritation, and swelling of the face, lip or throat; In recent years there has been an increase in intolerance or high sensitivity to SO_2, related to its ingestion, particularly in sensitive or vulnerable persons such as asthmatics and children [17,18].

In the present study it was possible to stablish a membrane extraction or adsorption system for sulfite from aqueous solutions, at laboratory level, that allows its subsequent removal through its oxidation to sulfate once it pass to the receiver NaOH solution.

The major transference rate or molar flux density is obtained at major concentrations of the Na_2SO_3 model solution independent of the concentration of sodium hydroxide used, demonstrating that the existence of an immediate and instantaneous reaction in the gas-liquid interface of reception generates that the extraction results becomes independent respect to the NaOH concentrations when is in excess.

According to the variation of flows at a constant NaOH concentration of 0.2 mol/dm^3 and constant Na_2SO_3 concentration of 1,500 mg/dm^3, it is possible to increase the extraction from 0.0042 dm^3/s of flow to 0.0083 dm^3/s (from 53% to 78%). While from 0.0083 to 0.0125 dm^3/s there was not an appreciable difference in the maximum level of extraction, but an increase was observed in the velocity at which this peak is reach. This proves that the rise in the flow reduces the time needed to obtain the maximum extraction.

The concentration on the feeder solution is what influences the mass transfer process. Moreover, Eq. (1) does not account for the 100% of extraction that is achieved with the system.

The best extraction results are obtained when high amounts of sodium sulfite are treated, keeping the concentration of sodium hydroxide always in excess.

Therefore, the system can extract and remove sulfite from waste waters and measure the concentration in water from food or wines. Finally, these results can lead to a marketable prototype that includes the separation and removal of sulfite from wastewater quickly and effectively.

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