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Treatment of dissolved sulfides in water by combined process using ozone and activated carbon

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ABSTRACT

Hydrogen sulfide is a malodorous compound affecting the quality of water and making its treatment necessary. This work aims at developing, at a laboratory scale, a process coupling the powerful oxidizing character of ozone and the activated carbon adsorptive character for dissolved sulfides treatment. Different cases of ozone/activated carbon were studied in this paper. The ozone activated carbon coupling (OZAC) process proved its efficiency in removing dissolved sulfides; in fact, the aqueous solution was ozonated in gas-liquid stirred reactor and pumped in a controlled continuous flow circulation through a fixed bed of granular activated carbon. The outlet of the adsorption column was recycled to the reactor of ozonation continuously. Depletion of sulfides in water was measured over time under different conditions of ozone concentration, recirculation flow and granular bed height. By the studied OZAC, total sulfides conversion was reached for an initial sulfides concentration of 123 mg/l, with 1.19 g of O_3/g of sulfides and 970 g of AC/m^3 of treated water in 16 min under our specified operating conditions. A kinetic model was developed to predict the depletion of sulfides along the adsorption-reaction.

Keywords: Water treatment; Adsorption; Ozone; Sulfides

1. Introduction

Ground water is a natural reservoir for drinking water and irrigation needs worldwide. Even though it is invisible, it is susceptible to some pollutants causing quality deterioration like organic volatile compounds [1] and sulphur compounds such as mercaptans and hydrogen sulfide, coming from bacteria activities or underground hydrocarbon reservoirs. Hydrogen sulfide (H_2S) is a toxic colorless gas with a strong rotten eggs odor [2]. It is present in contaminated water under three forms depending on pH: H_2S, HS^- and S^{2-} [3,4]. Ingestion of sulfides through drinking water can result in stomach discomfort, nausea and vomiting [5]. Corrosion problems are also detected on its presence [6].

To control the sulfides in water, the oxidation process was applied with chlorine dioxide, hydrogen peroxide, oxygen and ozone (O_3) which is one of the strongest available oxidizing agents that has been used

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successfully in the field of water treatment [7–9]. Adsorption by activated carbon (AC) is also widely used for removing contaminants like metals and organic compounds from water [10–13]. Some researchers proved that activated carbon acts as an effective adsorbent for dissolved sulfides from water [14].

To improve the efficiency of the ozonation process, the interest of the scientific community has recently been focused on coupling the oxidant effect of ozone with the adsorptive effect of activated carbon for many applications like the decolourisation of aqueous solution [15–18], the treatment of sulfonated aromatic compounds, and the removal of pesticides from water. However, to our knowledge this treatment for dissolved sulfides has not been cited in previous published works.

The aim of this work was to develop the use of ozone/activated carbon coupling for dissolved sulfides treatment. Different experimental parameters were studied. A kinetic model describing the depletion of dissolved sulfides over time was developed based on experimental data.

2. Experimental

2.1. Methods

Aqueous solution of sulfides prepared by dissolving an amount of sodium sulfide Na_2S in distillated water was used. The dissolved sulfides were analyzed by titration method [19]. In the present work, a commercial activated carbon was used in granulated form; its textural properties were estimated from nitrogen adsorption isotherm at 77 K (Table 1). The produced sulfate ions by ozone-sulfides reaction was measured by the turbidimetric method using barium chloride ($BaCl_2$) [20]. The concentration of ozone in the gas phase was measured by an automatic ozone analyzer based on the characteristic of wave adsorption at 254 nm and calibrated with the iodometric standard method [8].

2.2. The dynamic adsorption test

A batch adsorption test was performed to evaluate the equilibrium time and the adsorption capacity at equilibrium. Then, the dynamic test was carried out to evaluate the activated carbon capacity to adsorb the dissolved sulfides in water: The synthetic solution of sulfides with a concentration equal to 123 mg/l was pumped at a continuous flow rate of 20 ml/min through a glass column 1 cm in diameter containing the granular activated carbon (GAC) with a bed height of 16 cm. The process was stopped when the fixed GAC bed was saturated.

2.3. Ozonation pre-treatment followed by adsorption

Aqueous solution of sulfides with a concentration of 123 mg/l was put in a 2 l stirred reactor (total volume). A continuous flow of oxygen with a fixed inlet concentration of ozone 2.4 mg/Nl of O_2, fed the reactor. The ozone was produced from pure oxygen in a cold plasma generator built in laboratory. The residual ozone concentration was monitored by an automatic analyzer. After 1 h, the ozonation was stopped and the solution was pumped at 20 ml/min to the adsorption GAC bed which is 16 cm high.

2.4. Experimental unit of the OZAC process

The synthetic solution of sulfides was treated by a process designed by OZAC combining ozonation and adsorption. The experimental apparatus used is shown in Fig. 1. The aqueous solution containing 123 mg/l of sulfides was put in the gas-liquid stirred reactor. A continuous flow of oxygen with a fixed inlet ozone concentration was supplied to the reactor. The solution was continuously pumped to the fixed bed column filled by GAC; the treated water leaving the column was recycled to the ozonation reactor continuously.

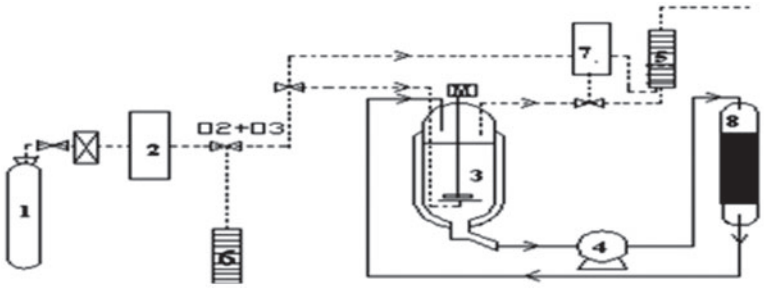
3. Results and discussion

3.1. Batch adsorption

The batch test confirmed the affinity of activated carbon to adsorb dissolved sulfides from water. After 30 min of contact time (Fig. 2), the adsorption process achieved the equilibrium with an adsorption capacity of 15.75 mg/g for the GAC.

Table 1
Textural properties calculated from nitrogen adsorption isotherm at 77 K

S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Micropores volume (cm^3/g)	Apparent density (cm^3/g)
989	0.548	0.479	0.49



1	Oxygen cylinder	5,6	Ozone destructor
2	Cold plasma reactor	7	Ozone analyzer
3	Ozonation reactor	8	Fixed bed of GAC
4	Peristaltic pump		

Fig. 1. Schematic diagram of the experimental apparatus (OZAC process).

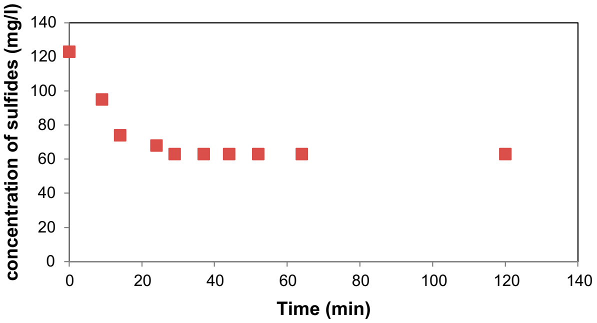


Fig. 2. Batch adsorption test for $C_e = 123$ mg/l, $T = 25$°C, $W_{CA} = 0.5$ g.

Before reaching equilibrium, the adsorption kinetics of the dissolved sulfides follows the first order-kinetics represented by the following equation:

$$\frac{dq}{dt} = K\ (q_e - q_t) \tag{1}$$

The value of the first-order constant of adsorption was estimated by the slope of the plot of ln $(q_e/(q_e - q_t))$ vs. t (Fig. 3). The first-order rate constant (K) for adsorption in our operating conditions is $K = 0.088$ min^{-1} which would be used in the modeling section.

3.2. Dynamic adsorption behavior of dissolved sulfides

The evolution of relative outlet sulfides concentration was presented vs. the treated water volume (Fig. 4). The adsorption capacity (q) of dissolved sulfides was estimated using the concentration of an adsorbat, the flow rate, the breakthrough time, and the mass in the bed. Eq. (2) was used to calculate the adsorption capacity.

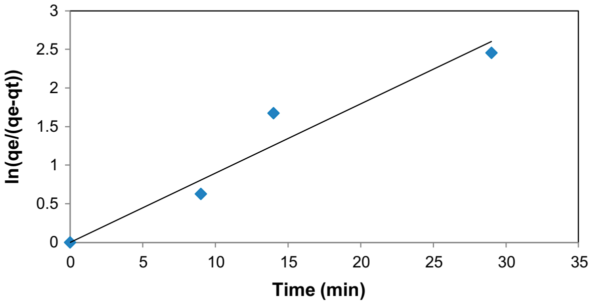


Fig. 3. Adsorption kinetics of the dissolved sulfides for $C_e = 123$ mg/l.

$$q = \frac{L}{W_{CA}} \int_0^t (C_e - C_s(t))dt \tag{2}$$

The activated carbon adsorbed about 16.08 mg of sulfides/g of activated carbon through the dynamic test in the given conditions.

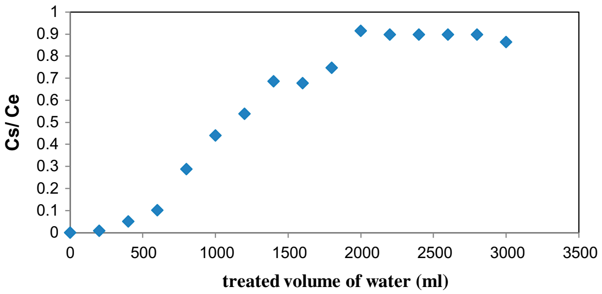


Fig. 4. Example of the breakthrough curve of dissolved sulfide ($L = 20$ ml/min, C_e =123 mg/l, $H_l = 16$ cm).

3.3. The ozonation pre-treatment followed by adsorption

When we supplied a concentration of ozone equal to 2.4 mg of O_3/Nl of O_2 to the reactor containing 123 mg/l of sulfides during 1 h, we found that the residual concentration was 93 mg/l. After ozonation the solution was pumped to the carbon bed for adsorption at 20 ml/min. The results clearly show that the activated carbon was not fully saturated with sulfides as shown in Fig. 5.

When the flow rate of the pre-ozonated solution was varied from 10 ml/min to 30 ml/min, we found that it had no evident effects on the kinetic step emerging in the breakthrough curves. We suggested that the limiting step of the adsorption process was the internal process, and the external mass transfer resistance around particles had a low effect in the operating conditions.

3.4. Continuous process coupling ozonation-adsorption (OZAC process)

The described experimental OZAC apparatus (Fig. 1) was used in three experimental ways: the first was a simple oxidation with ozone; the second consisted in a simple adsorption by GAC, the last was a combined action of ozone and activated carbon. These different processes were tested under the same operating conditions (Table 2). Depletion of sulfides along the reaction-adsorption was measured over time. The results for the three processes are illustrated in Fig. 6.

Comparison of the three treatment ways provided that the use of simple ozonation for the treatment of sulfides has an important effect; about 60% of the initial concentration of sulfides was treated in 16 min. In the second case, the simple adsorption via GAC (without the action of O_3) has a similar effect as the one using only O_3. Coupling the action between AC and ozone, made the depletion of sulfides faster than in the two previous cases, and the removal of dissolved sulfides reached 100% at about 16 min. The OZAC process is efficient for sulfides treatment. The effect of the operating conditions on the process would be studied later.

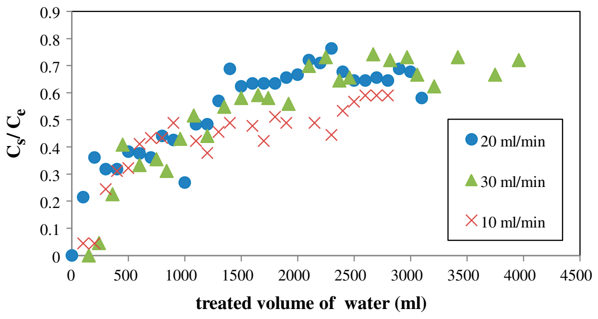


Fig. 5. The effect of pre-ozonation on the fixed bed $C^e_{O_3}$ = 2.3 mg/Nl of O_2, C_e = 93 mg/l.

Table 2
Initial conditions

Oxygen flow	40 Nl/h
Inlet ozone concentration	30 mg/Nl of O_2
Recycling solution flow rate	750 ml/min
Bed height of GAC	16 cm

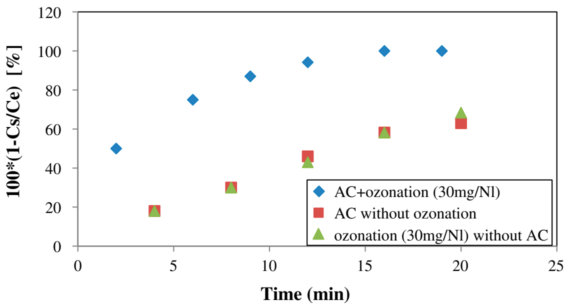


Fig. 6. Conversion rate of sulfides for the three treatment processes C_e = 123 mg/l, L = 750 ml/min, G = 40 Nl/h.

3.4.1. The effect of oxygen on the OZAC process

The experimental apparatus described previously was used without the action of ozone. Only oxygen was introduced into the reactor and different combinations were studied. All the operating conditions are similar to those cited in Table 2 expect the ozone concentration which is equal to zero.

It is noteworthy that the action of oxygen solely, without activated carbon has a very low effect on the removal of dissolved sulfides from water, as

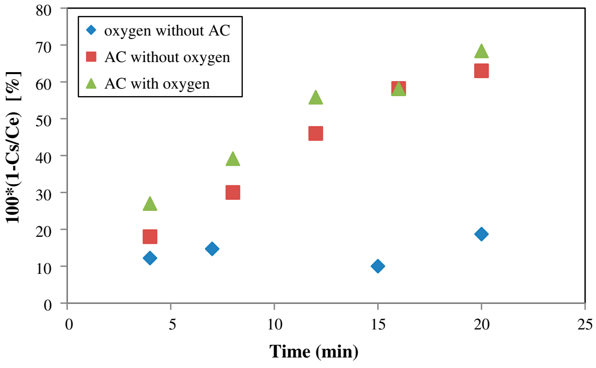


Fig. 7. The effect of oxygen on the removal of sulfides C_e = 123 mg/l, L = 750 ml/min, G = 40 Nl/min.

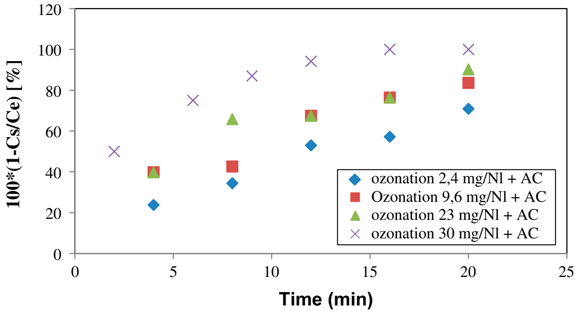


Fig. 8. The effect of the ozone concentration at the inlet gas on the process $C_e = 123$ mg/l, $H_l = 16$ cm, $G = 40$Nl/h and $L = 750$ ml/min.

shown in Fig. 7. Comparison between the action of simple adsorption and combined effect of activated carbon and oxygen showed that the depletion of sulfides improved by 8% only in the presence of activated carbon. It can be deduced that oxygen is not a powerful oxidant for sulfides treatment in the studied process.

3.4.2. The effect of the ozone concentration on the process

Several experiments were conducted to investigate the action of ozone on the removal of dissolved sulfides by the OZAC process. The ozone was supplied continuously to the reactor. The gas flow rate was maintained at 40 Nl/h and the ozone concentration at the inlet ranged from 2.4 to 30 mg/Nl of O_2. The other operating conditions are cited in Table 2.

The results depicted in Fig. 8 clearly show that when the ozone was introduced, the dissolved sulfides reacted rapidly with it. The removal of sulfides rose with the increase of the ozone concentration in the inlet gas. Indeed, the highest concentration of ozone was 30 mg/Nl of O_2 which made the dissolved sulfides reach 0 mg/l in 16 min.

To compare different operating conditions, the consumption of ozone was estimated for all the experiments during 16 min, In fact, the outlet ozone concentration was measured in the outlet gas every 3 min; then, it was calculated by integrating Eq. (3) below.

$$C_{O_3\ \text{consumption}}(t) = C^e_{O_3} \times G \times \int_o^t \left(1 - \frac{C_{O_3}}{C^e_{O_3}}\right) \times \mathrm{d}t/C_e \times V \tag{3}$$

Table 3
The consumption of ozone under the different combinations ozone/AC P_{CA}: (+/−) presence/absence of activated carbon in the column

$C^e_{O_3}$ (mg/Nl)	P_{CA}	The specific consumption of ozone (g of O_3/g of sulfides)
30	−	1.36
30	+	1.19
23	+	1.05
9.6	+	0.59
2.4	+	0.16

As shown in Table 3 the specific amount of ozone needed for the removal of 100% dissolved sulfides in about 16 min in the presence of activated carbon (paked bed 16 cm in height) was 1.19 g of O_3/g of sulfides. To achieve this conversion rate in the OZAC process we needed 972 g of activated carbon/m^3 of treated water.

Furthermore, the presence of activated carbon reduced the consumption of ozone during the process by about 12.5% and increased the conversion rate by 25% when we compared the addition of 30 mg/Nl of ozone both in the presence and in the absence of activated carbon.

For investigating the oxidized product of dissolved sulfides in water, we measured the production of sulfate ions for different ozone concentrations in the inlet gas.

Fig. 9 shows that when the ozone concentration increased the production of sulfate contained also increased. The presence of activated carbon reduced the production of sulfate ions when comparing the produced sulfates for an inlet concentration of ozone equal to 30 mg/Nl in the presence and in the absence of activated carbon.

3.4.3. The effect of the recycled water flow rate on the OZAC process

For all the previous experiments, the solution flow was controlled by the peristaltic pump (750 ml/min). The experimental apparatus operated by fixing the height of the activated carbon bed at 16 cm and the ozone concentration at 30 mg/Nl in the oxygen gas (40Nl/h). Different water flow rates ranging from 20 ml/min to 750 ml/min were tested.

As shown in Fig. 10 the removal of sulfides was improved by increasing the solution flow rate. The high flow rates up to 500 ml/min had similar effects on the OZAC process, external mass transfer kinetics

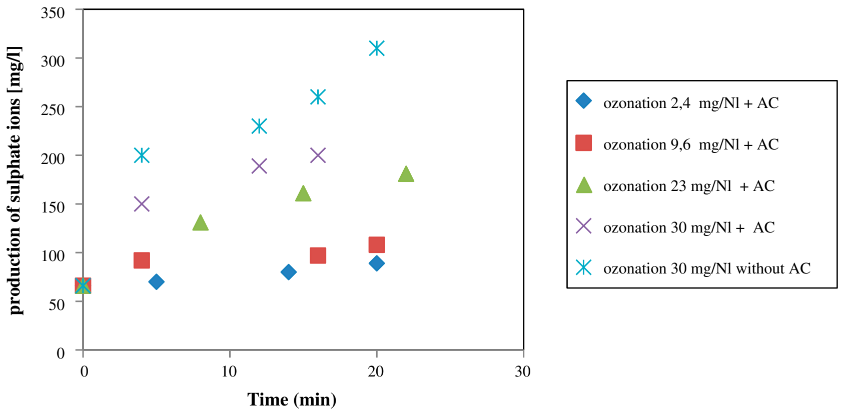


Fig. 9. Production of sulphate ions under different combinations of ozone/activated carbon $C^{e}_{SO_4^{2-}}$ = 60 mg/l, C_e = 123 mg/l, H_l = 16 cm, G = 40 Nl/h and L = 750 ml/min.

at the fixed bed could be the origin of this observation. These flows achieved the fastest and most effective results.

3.4.4. The effect of the carbon bed height on the process

In order to study the effect of changing the bed height on the process, we kept the same experimental apparatus. The sulfide solution was operating continuously in a closed system at 500 ml/min. An ozone concentration equal to 30 mg/Nl was continuous fed to the reactor. Different bed heights 3, 7, 11 and 16 cm were tested; the results were compared with those of an empty column.

It can be seen from Fig. 11 that when the bed height increased, the elimination of sulfides improved. The combination of ozone with activated carbon at a bed height of 16 cm ensures a better conversion rate of sulfides compared to the other heights tested.

3.5. Ozonation kinetics

The ozonation kinetics was carried out in the OZAC process operating with an empty column with only ozone supplied to the reactor. Indeed, the depletion of dissolved sulfides (123 mg/l) by ozone (30 mg/Nl of O_2) over time was analyzed. The oxidation of sulfides followed a first- order kinetics (straight line with $R^2 = 0.977$). The kinetic constant (k) was determined from the slope of $-\ln(C/C_e)$ vs. t.

From Fig. 12, the experimental data revealed that the first-order kinetics constant was $k = 0, 0.568\ \text{min}^{-1}$.

The experimental kinetics constant would be used in the modeling section.

3.6. Kinetic modeling the ozonation/adsorption of sulfides by the OZAC process

The molar balance which represented the consumption of dissolved sulfides in water by the OZAC

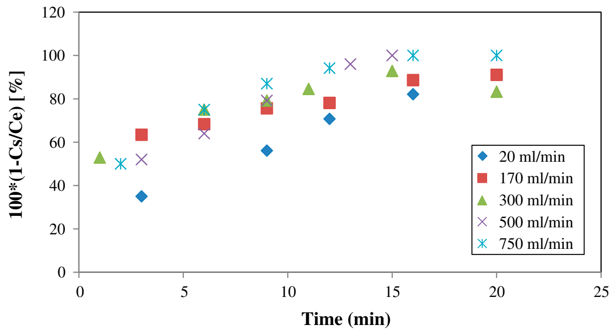


Fig. 10. The effect of recycled water flow rate on the OZAC process.

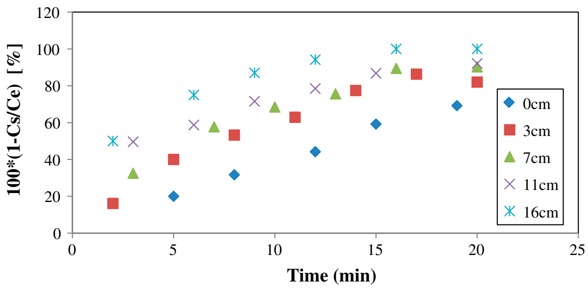


Fig. 11. The effect of the activated carbon bed height on the OZAC process.

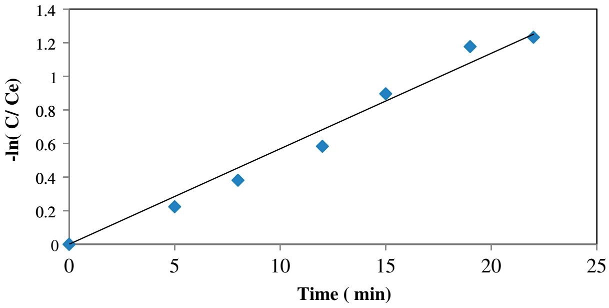


Fig. 12. First-order kinetic regression of ozone sulfides reaction for $C^{e}_{O_3}$ = 30 mg/Nl, C_e = 123 mg/l.

process in isotherm conditions can be represented by the following equation

$$-W\frac{dq}{dt} - r \times V = \frac{dn}{dt} \tag{4}$$

We found from the experimental data that the adsorption of sulfides on AC follows first- order kinetics:

$$\frac{dq}{dt} = K(q_e - q_t) \tag{5}$$

The rate of the ozonation equation was reduced to Eq. (6) based on the experimental data:

$$r = kC \tag{6}$$

A substitution of Eqs. (5) and (6) in (4) with an appropriate arrangement gave Eq. (7):

$$-\frac{WKq_e \times e^{(-Kt)}}{V} = \frac{dc}{dt} + kC \tag{7}$$

At $t = t_0$, $C = C_e$.

The integration of Eq. (7) led to Eq. (8) that predicted the degradation of dissolved sulfides through the OZAC process by adsorption-ozonation over time:

$$C(t) = -\frac{WKq_e}{V \times (k-k)}e^{((-k)t)} + \left(C_e + \frac{WKq_e}{V \times (k-k)}\right)e^{(-kt)} \tag{8}$$

Table 4
Summarizes experimental data from the OZAC process $C^{e}_{O_3}$ = 30 mg/Nl, G = 40 Nl/h, H_1 = 16 cm, L = 750 ml/min

C_e (mmol/l)	q_e (mmol/g)	k (min^{-1})	K (min^{-1})	W(g)
3.84	0.49	0.057	0.088	11.664

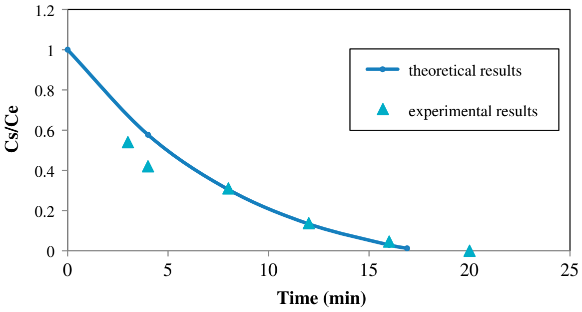


Fig. 13. Comparison between the experimental data and the process theoretical modeling $C^{e}_{O_3}$= 30 mg/Nl, G = 40 N l/h, H_1 = 16 cm, L = 750 ml/min and C_e = 123 mg/l.

The comparison between the theoretical and the experimental profile of sulfides concentration over time was represented in Fig. 13. Table 4 shows the experimental data used to solve Eq. (7).

Fig. 13 shows that the calculated results using the suggested model, agree with the experimental results obtained by the OZAC process at a laboratory scale.

4. Conclusion

From experimental investigations conducted at laboratory scale, we concluded that the OZAC process coupling the action of ozone and activated carbon proved its efficiency for removing dissolved sulfides. The process consumed 1.19 g of ozone/g of dissolved sulfides and 972 g of granulated activated carbon/m^3 of contaminated water to treat 123 mg/l of dissolved sulfides. The simple kinetic model developed agreed with the experimental results obtained. The OZAC process will have to be verified in a full scale with real contaminated water in a further research.

Nomenclature

GAC — granular activated carbon
$C^{e}_{O_3}$ — initial concentration of ozone (mg/Nl of O_2)
G — oxygen flow rate (Nl/h)
H_1 — bed height of activated carbon (cm)
L — water flow rate (ml/min)
C_e — initial concentration of sulfide (mg/l)
C_s — concentration of sulfide (mg/l)
K — adsorption rate constant (min^{-1})
k — ozonation kinetic constant (min^{-1})
W — mass of activated carbon (g)
V — volume of treated solution (l)
q_e — capacity of adsorption at equilibrium (mg/g) or (mmol/g)
r — ozonation reaction of sulfide (mmol/l min)

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