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NEUTRALIZATION OF TEXTILE WASTEWATER USING CARBON DIOXIDE

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ABSTRACT

The aim of this paper was to develop a new process for valorization of CO_2 gas into neutralization of an effluent taken from textile finishing and dyeing unit. The effect of the main operating conditions (pH of the effluent, temperature and the CO_2 gas flow) on the neutralization performance was investigated. The study showed that the decrease in the temperature and the gas flow improved the dissolution of the gas in an aqueous solution. Moreover, the optimization study showed that a gas flow of about 9mL/min bubbled during 3min at a temperature of 25°C leads to a pH decrease of 1m^3 of real effluent from 12.78 to 7. To characterize the effluent after neutralization, the variation of some pollution indicators such as pH and total suspended solids (TSS) were measured during the addition of carbon dioxide.

KEYWORDS

Textile wastewater; Carbon dioxide; Gas flow; pH; total of suspended solids.

1. INTRODUCTION

The global greenhouse gas emissions are increasing to reach a high record of about 40bn tonnes in 2014 (Brett et al, 2013). So, recently, there have been global environmental concerns for the reduction of greenhouse gas emissions from industrial sources, such as thermal power plants, to alleviate the global warming problem. In fact, greenhouse gases result from the emissions of methane, carbon dioxide, nitrous oxide and chlorofluorocarbons (Davis and Cornwell, 1991). Among these, CO_2 is considered to be the principal contributor to this problem, and thus is the main target for reductions (Khan et al, 2004). The increasing of the carbon dioxide concentration in the atmosphere and the stringent greenhouse gases (GHG) required the development of CO_2 sequestration technologies applicable for the wastewater sector (Fernández et al, 2014).

On the other hand, the concern for environmental responsibility and sustainable processes development are being more important due to the strict legislations and the frequent control of the industrial wastes. For instance, different textile finishing and dyeing treatments of Denim fabrics (mercerizing, bleaching, dyeing…) are done in basic pH solutions. Alkaline wastewater is a by-product of many textile industries. So, it needs to be neutralized before feeding it to a biological wastewater treatment plant or discharging into a sewer

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system. An adjustment of the pH is required by the addition of acid products such as HCl, H_2SO_4, HNO_3, H_3PO_4 or CO_2.

The used neutralization reagent (acid) must satisfy essentially to economic and technical characters. It must be compatible with the effluent compounds, to improve the conditions for the further treatments and not involve a non conformity to the standards. In fact, carbon dioxide is being increasingly used to neutralize alkaline process waters in many industries including beverage (McMillin et al, 1980), dairies and butcheries (King and Mabbitt, 1982), bakery and confectionery (Guynot et al, 2003), electroplating (Chang and Sone, 2011), cement and concrete (Worell et al, 2001), paper and cellulose (Zheng et al, 1998), photochemical and textile (this study).

Using carbon dioxide has many advantages: it prevents excessive accumulation of salts such as chlorides, sulphates, etc and over acidification of wastewater. Furthermore, carbon dioxide is not dangerous and don't need special precautions of use.

In this study, we are interested on neutralisation of textile wastewater by injection of carbon dioxide. The effect of the main operating conditions (pH of the effluent, temperature and the CO_2 gas flow) on the neutralization performance was investigated. The optimization of the experimental conditions was investigated using factorial design. In these optimized conditions, an economic and ecological comparison study between the neutralization of alkali wastewater using carbon dioxide and acidic chemical reagents was carried out.

2. MATERIALS AND METHODS

2.1. Materials

This study was conducted at a laboratory scale using CO_2 cylinder. The experimental installation used in this study was given in figure 1.

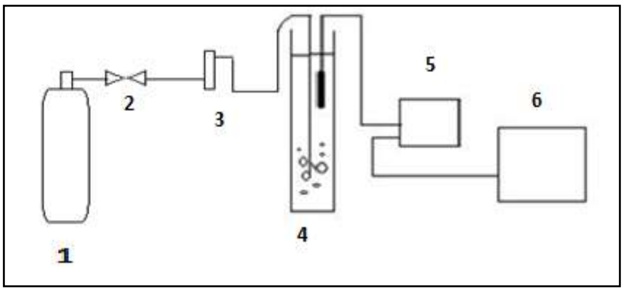


Figure 1: Experimental apparatus: (1) Gas cylinder, (2) Pressure release valve, (3) Flow meter, (4) Reactor, (5) pH-meter, (6) Computer

The wastewater used in this study was an industrial textile effluent charged with vat dyes taken from a Tunisian finishing and dyeing unit and conserved at a temperature of 5°C. The physicochemical characteristics of the studied wastewater were determined through analysis of pH, total suspended solids (TSS) (filtration through filter paper using a vacuum, drying at 105°C for 2 hours), salinity (conductivimeter Jenway 4510, UK), absorbance (by spectrophotometer CECIL2021) and Chemical Oxygen Demand (COD). The wastewater characteristics were given in Table 1. The UV–Vis spectrum of the industrial wastewater (diluted 10 times) was recorded using UV/Vis spectrophotometer and the result was represented in Figure 2.

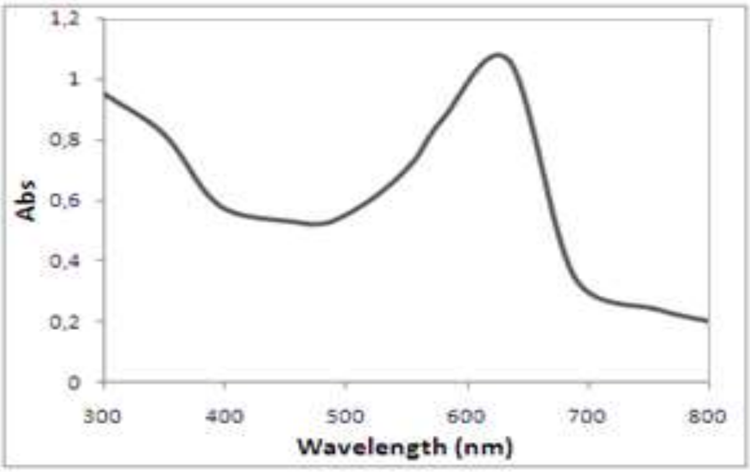


Figure 2: The UV-Vis spectrum of the studied effluent

Table 1. Textile wastewater characteristics

Parameters	Effluent
pH	12,78
Temperature (°C)	34
Maximum wavelengths λ_{max}(nm)	630
Abs	1,67*10
COD (mg O_2/l)	2350
Conductivity (mS/cm)	3,6
Turbidity (NTU)	38

2.2. Methods

The pH measurements were made using a calibrated pH meter. It was measured every 2 min after carbon dioxide bubbling in the textile wastewater. Six levels of temperature were considered: 10, 15, 20, 25, 30, 35°C, to evaluate its effect on the CO_2 dissolution. The variation of the temperature was controlled using a thermometer.

The gas flow was controlled usually using a flow-meter connected directly to the pressure release valve of the CO_2 cylinder during the experiments. The effect of the gas flow was studied through four values: 3, 5, 8 and 10 $mL.min^{-1}$. The total suspended solids (TSS ($mg.L^{-1}$)) were measured at the neutral pH. The pollution parameters of the wastewater were measured according to standards methods as described by Rodier et al, 2009.

A comparison study with the chemical acidic reagent was carried out to evaluate the neutralization process using carbon dioxide. Sulphuric acid (96%), chloric acid (36%), nitric acid (69%) and citric acid (M= 192.12 $g.mol^{-1}$) were of technical grade. Acid solutions of $0.2mol.L^{-1}$ were prepared and used in this study.

3. RESULTS AND DISCUSSIONS

3.1. Effect of time

The variation of the pH and the total suspended solids during bubbling time of CO_2 is given respectively in figures 3 and 4. The effluent temperature was about 25°C and the flow gas was fixed to $8mL.min^{-1}$.

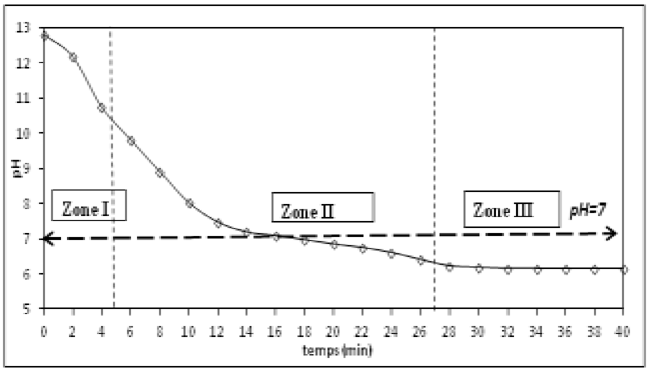


Figure 3: Effect of bubbling time on the pH of effluent

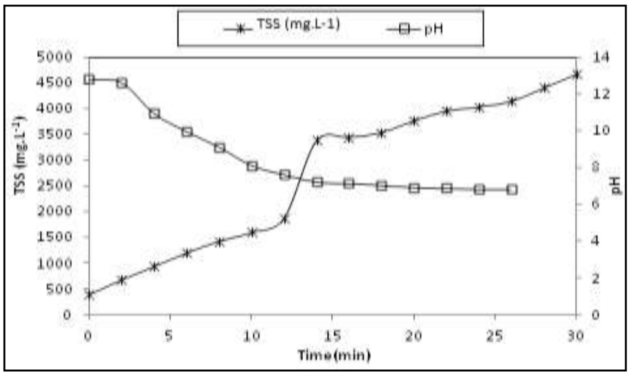


Figure 4: Effect of bubbling time on total suspended solid

The carbon dioxide in aqueous solution took the form of dissolved gas. A small proportion of the carbon dioxide is converted into carbonic acid by this reaction (1):

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

At high pH values, carbonic acid discharged two protons that participate in the neutralization process. However, only one proton was discharged at pH values below 9. The variation of the pH during time represented the neutralisation process given in figure 3. This process is continuous and could be divided in three phases:

- 1st phase (pH > 10.3):

$$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O \quad (2)$$

In this phase, carbonate ions (CO_3^{2-}) predominated.

- 2nd phase (6.3 < pH < 10.3):

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (3)$$

The percentage of hydrogen carbonates (HCO_3^-) increases as the pH decreases. The bicarbonates are more eco-compatible than the strong acid salts. Moreover, carbon dioxide is non-inflammable, non-toxic, easy to handle and safe to store. Thus, it is currently the most eco-friendly way of neutralizing alkaline wastewaters.

- 3rd phase (pH < 6.3):

In this phase, the percentage of free dissolved carbon dioxide continues to increase. Below pH=5, almost all of the bubbled carbon dioxide is in a physically dissolved state. The 3rd phase is not usually reached because the pH value required by legislation is higher than 5 (NT 106-002). In many cases, the amount of carbon dioxide required for neutralization deviates from the stoichiometric quantities. In fact, the wastewater usually contains buffer substances that make necessary the use of more acid.

$$CO_3^{2-} + 2H_3O^+ \leftrightarrow H_2CO_3 + 2H_2O \quad (4)$$

The total suspended solids (TSS) increase during the introduction of the CO_2. It is due to degradation and oxidation of vat dyes during the bubbling of the gas. In fact, the effluent used in this study contains indigo dye which is insoluble and it must be reduced with sodium dithionite to be solublized, before using. During bubbling of the CO_2, oxygen introduced oxidizes the dyes and it will be transformed on suspended solids.

3.2. Effect of temperature

The variation of the pH and the total suspended solids during the bubbling time of CO_2 at different temperatures is given in figures 5 and 6.

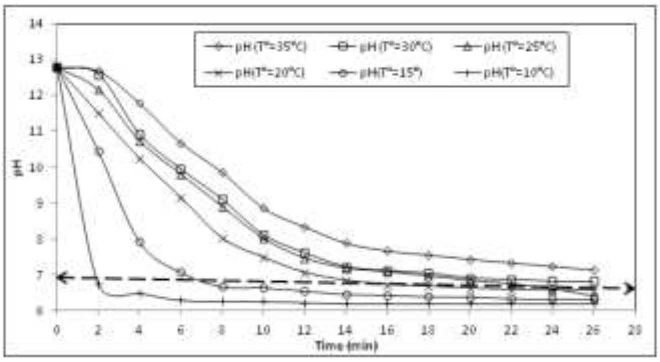


Figure 5. The effect of temperature on pH variation

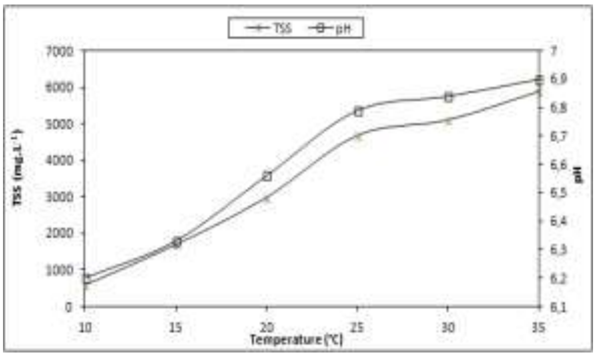


Figure 6: The effect of temperature on the variation of total suspended solids

Figures 5 and 6 showed that the variation of temperature from 10°C to 35°C presented an influence on the dissolution of the CO_2. The increase of the temperature established a decrease of the CO_2 dissolution speed and the quantity dissolved. At 10°C, the effluent was neutralized after a short bubbling time and the pH was minimum.

3.3. Effect of CO2 flow

The effect of gas flow on the variation of effluent pH during CO_2 bubbling and the total suspended solids is given in figure 7 and 8.

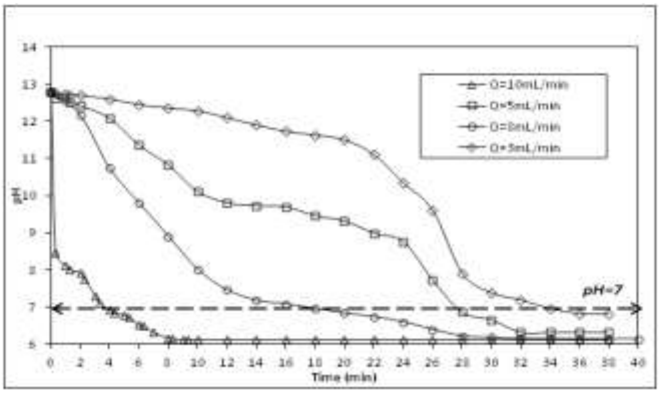


Figure 7: The effect of the gas flow on the variation of the effluent pH

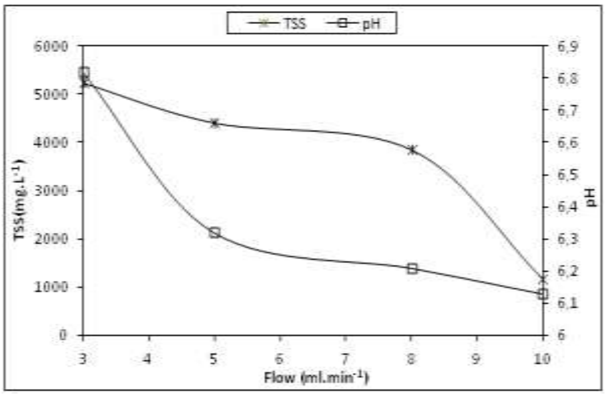


Figure 8: The effect of the CO_2 flow on the TSS

After analyzing figures 7 and 8, it is obvious that the neutral pH was reached at the minimum bubbling time for the highest flow gas value. Indeed, the flow was directly proportional to the pressure, according to the law of Darcy:

$$Q = \mu (Pe - Ps) \quad (4)$$

Where:

- Q: flow in the tube;
- µ: permeability;
- P_e : inlet pressure;
- P_s : outlet pressure (1bar).

The pressure had little influence on the solubility of the solid or liquid. The gas solubility of CO_2 increased with increasing pressure. In fact, the amount of dissolved CO_2 in water depended on the partial pressure of this gas in the gaseous phase. Therefore, according to Henry's law, the amount of gas dissolved in a solution was directly proportional to the pressure of the gas located above the solution.

$$p = k \times c : \text{Henry's Law} \quad (5)$$

- P: partial pressure of the gaseous solute located above the solution;
- k: concentration of dissolved gas;

- c: characteristic constant of a given solution.

The observation of figure 9 allowed to understand the increase of the solubility of gases with the pressure.

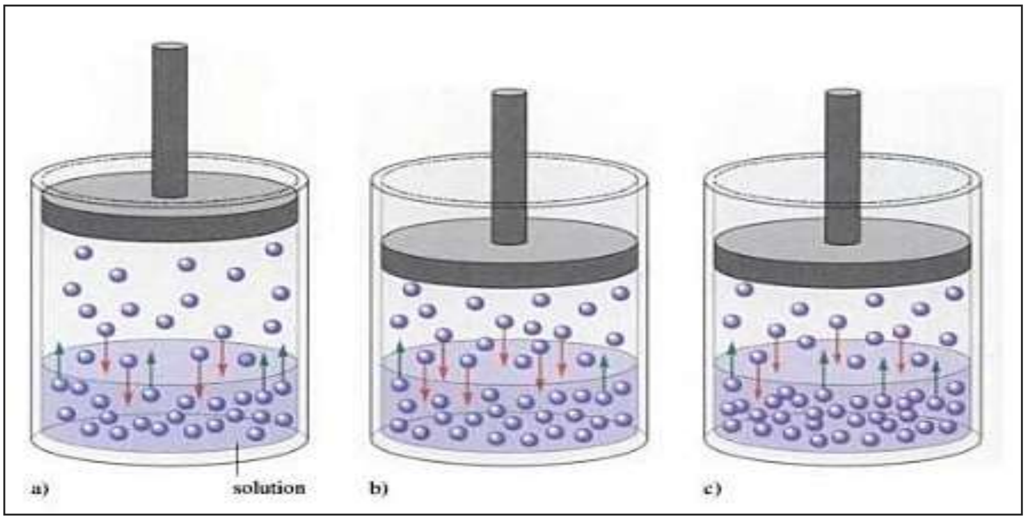


Figure 9. Effect of pressure on the solubility of CO_2 in water

The figure 9.a showed a gas in equilibrium with a solution. In this step, the speed at which gas molecules enter the solution is the same as they exit it. If the pressure rises (figure 9.b), the number of gas molecules by unit of volume will beincreased. So, the gas entered in the solution faster than it exits. Thus, since the concentration of dissolved gas increased, the rate of exhaust gas increased, until reaching a new equilibrium (figure 9.c). The solution contained more dissolved gases than previously.

On the other hand, total suspended solids increased with the increasing of the flow gas. In fact, bubbling CO_2 was accompanied with oxygen introduction when working at room pressure in an open bath. The oxidation of the effluent induced the oxidation.

3.4. Modelling and optimization of the neutralization process

The optimization of the CO_2 bubbling conditions and the evaluation of the interaction of operating parameters were carried out using Minitab 15 software. It is used for calculating basic statistics and for simple estimation and hypothesis.

In this paper, a factorial experimental design methodology was employed to estimate the influence of the neutralization process using carbon dioxide parameters. The effects of the experimental factors and the interactions between those factors were investigated.

The effect of the bubbling time of CO_2, the gas flow and the effluent temperature on the pH adjustment and TSS obtained was carried out in this section.

3.4.1. Response surface methodology regression

Response surface methods are used to examine relationship between one or more response variables and a set of quantitative experimental variables or factors. The factors considered in this study are: the bubbling time, low gas and temperature, whereas the experimental results to treat are the pH and the total suspended solids of the effluent. The factors values are chosen from the effect study of each factors developed in the previous part.

The experimental surface plan was described in Table.2, its regression analysis by a quadratic model leads to the following equations:

$$pH= 8.391 - 2.226*X_1- 0.141*X_2 + 0.006*X_3 - 0.124*X_1*X_2 + 0.014*X_1*X_3 + 0.014*X_2*X_3 + 0.006*X_1*X_2*X_3 \quad (6)$$

R^2=99.7%

$$TSS=1120.5-257.5*X_1+24.5*X_2-39.5*X_3-97.5*X_1*X_2+26.5*X_1*X_3-91.5*X_2*X_3+78.5*X_1*X_2*X_3 \quad (7)$$

R^2= 73.5%

Where X_1, X_2 and X_3 were the flow gas (mL.min^{-1}), the bubbling time (min) and the effluent temperature (°C), respectively.

For the regression equations of the effluent pH and the total suspended solids, it was found that the squared multiple correlation coefficients "R^2" were respectively 99.7% and 73.5%. So, it can be concluded that the obtained model for the pH has a good predictability (R^2=99.7%) and a moderate predictability for the total suspended solids model (100% represents the perfect predictability).

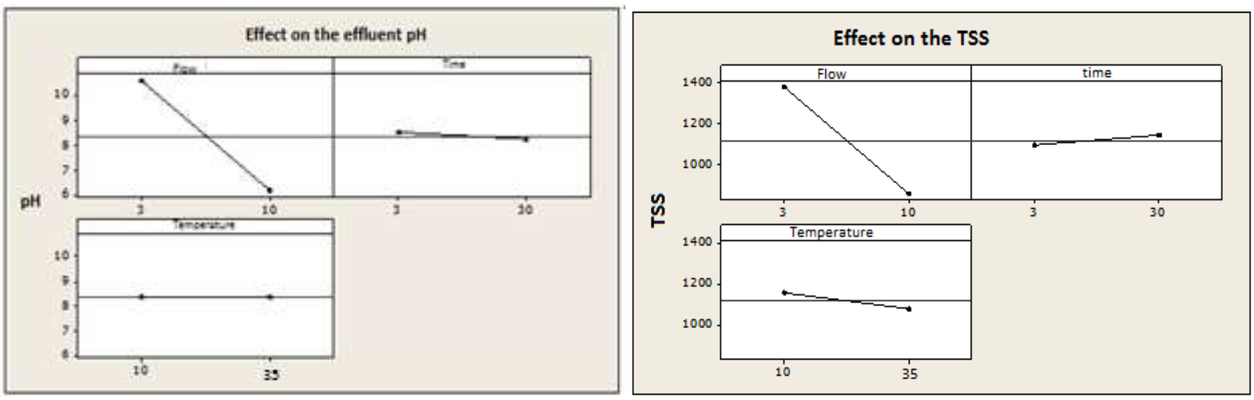
Table 2. Coded actual levels of studied variables and results obtained for a surface design

N°	Coded variables			Levels of factors			Responses	
	X_1	X_2	X_3	Flow (mL.min^{-1})	Time (min)	Temperature (°C)	pH	TSS (mg.L^{-1})
1	-1	-1	-1	3	3	10	10,65	1752
2	-1	+1	-1	3	30	10	10,6	1136
3	-1	-1	+1	3	3	35	10,62	1360
4	-1	+1	+1	3	30	35	10,6	1264
5	+1	-1	-1	10	3	10	6,43	1548
6	+1	+1	-1	10	30	10	5,86	816
7	+1	-1	+1	10	3	35	6,43	936
8	+1	+1	+1	10	30	35	5,94	764

3.4.2. Analysis of the main effects plot

The main effects of each factor (flow gas, bubbling time and effluent temperature) on the pH adjustment of the textile wastewater were shown in Figure.10.a and b. A main effect occurs when the mean response changes across the levels of a factor. It is used to compare the relative strength of the effects across factors (Bouatay and Mhenni, 2014)

After the analysis of the graphs in Figure.10, it seems that the behavior of these factors varies from ones response to another. But, it is clear that the flow of the carbon dioxide was the most important variable on the pH of the effluent. Furthermore, the effluent temperature and the CO_2 bubbling time had a low effect on the variation of the wastewater pH.

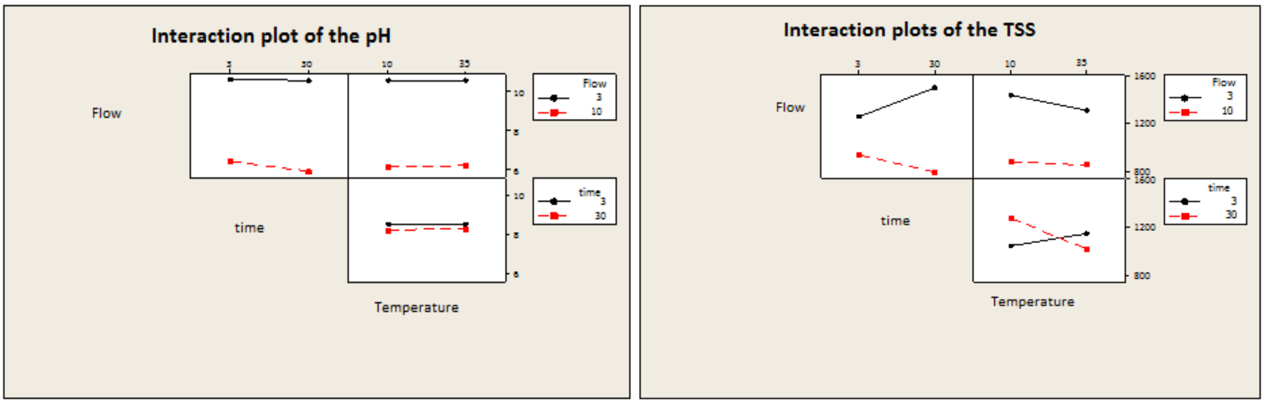


a) b)

Figure 10.The main effect plots on the pH of the effluent and the total suspended solids: a) on the pH; b) on the TSS

3.4.3. Analysis of interactions plot

The interaction effect plots are also studied and are represented in Figure 11.a and b. The interaction between factors occurs when the change in response from the low level to the high level of one factor is different from the change in response at the same two levels of a second factor. From graphs of Figure 11 and the equations (6) and (7), it can be seen that there are no significant interactions between all others factors for the pH adjustment. But, there are significant interactions between gas flow and bubbling time of CO_2 and the effluent temperature and bubbling time.



a) b)

Figure 11.The main interaction plots on the pH of the effluent and the total suspended solids: a) on the pH; b) on the TSS

3.4.4. Response optimization and model validation

The optimal conditions of the pH adjustment of the textile wastewater were predicted by response optimizer tool of Minitab 15 software for final pH equal to 7 and minimized TSS. The optimal level of the selected factors were as follows: flow gas of 8.9mL.min^{-1}, bubbling time of CO_2 of 3min and effluent temperature of 35°C leading in theory to a pH equal to 7.08 and total suspended solids of about 1000mg.L^{-1} with an overall desirability value equal to 98.6%.

The validation experiment was performed to verify the accuracy of the model. Validation tests were carried out at the optimum conditions described in the previous paragraph (flow gas of 8.9mL.min^{-1}, bubbling time of CO_2 of about 3min and effluent temperature of 35°C).

The validation experiments were conducted in triplicates and the average value was calculated. In theory, the optimum values under these optimum conditions of the effluent pH and the total suspended solids were 7.08 and 1002 mg.L^{-1} respectively, whereas, the experimental values obtained were 7.1 and 1060mg.L^{-1}, respectively. So, by the comparison of the mean values of the effluent treated obtained and the predicted values, it is obvious that the model is validated.

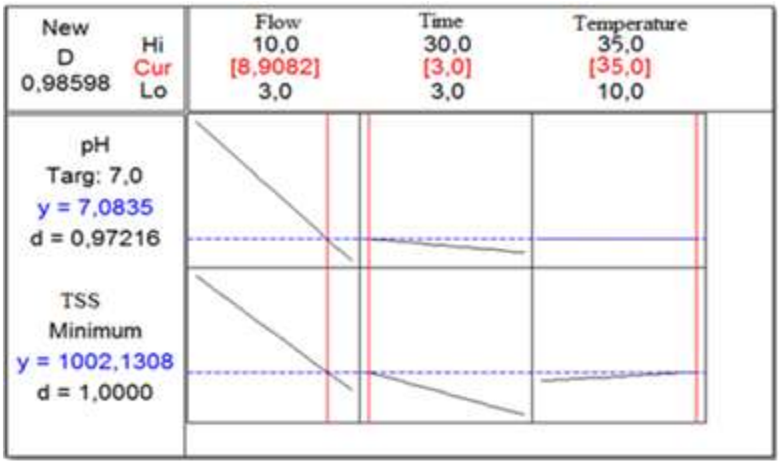
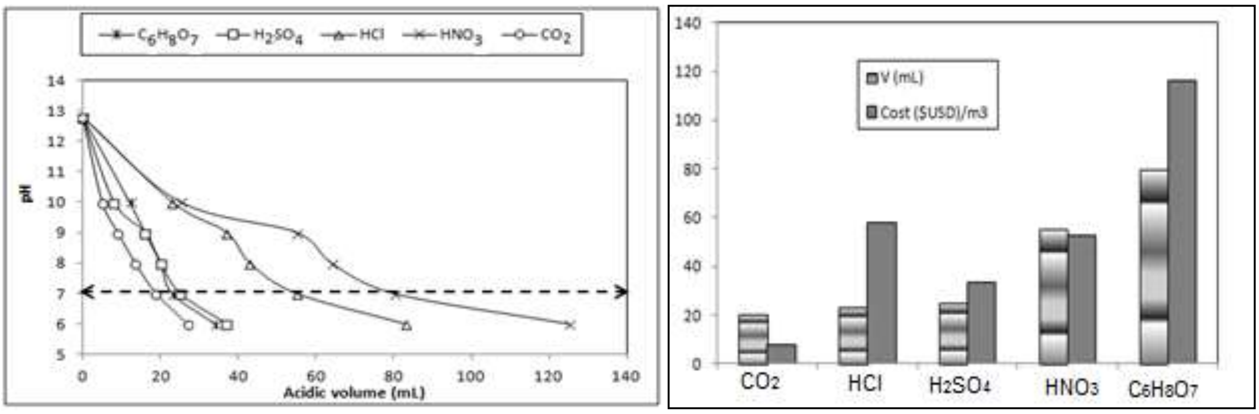


Figure 12: The response optimization

3.5. Comparison with chemical acidic reagents and marketing aspect study of the neutralization process

Using carbon dioxide gas on alkali textile wastewater neutralization was considered environmentally friendly process in comparison with inorganic and organic acids. However, a comparative study with four chemical acids (sulfuric acid, citric acid, nitric acid and chloric acid) was carried out.

As shown in Figure 13, the effluent pH achieved the neutral pH (about 7) with the minimum quantity and cost using carbon dioxide gas in comparison with other acid reagents.



a) b)

Figure 13: neutralization of alkali textile wastewater in comparison with acidic chemical reagents: a) quantity comparison; b): cost comparison

4. CONCLUSION

This study showed that CO_2 could be used as a cheap and acidifying agent for the pH adjustment of the alkaline textile wastewater before the aerobic reactor, replacing the conventional process (using acids). It revealed also that it was economical to implement this idea at full-scale plant.

The quantitative study showed that the quantity of CO_2 dissolved depends on the operating conditions such as: pH of the effluent, bubbling time of CO_2, temperature and gas flow.

In this paper, it was concluded that the total suspended solids (TSS) increase during the introduction of CO_2. Moreover, the variation of temperature from 10°C to 35°C has an influence on the dissolution of the CO_2. In fact, the increase of the temperature leads to a decrease of the CO_2 dissolution speed and the quantity dissolved. Besides, the pressure has little influence on the solubility of the solid or liquid. However, it significantly increases the gas. Injecting carbon dioxide is the best way to neutralize alkalinity while also reducing environmental stress.

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