Absorption of carbon dioxide by raw and treated dye-bath effluents

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Abstract

A bench-scale experimental apparatus, consisting of a glass column randomly packed with cylindrical glass rings, was utilized for the removal of carbon dioxide (CO_2) by chemical absorption. Various liquid solvents were used, in a batch mode, circulating between the column and a reservoir vessel, and contacting the gas in counter current flow. The absorptive capacity of the liquid solvents and the absorption kinetics were studied by obtaining the respective 'breakthrough curves'. Aqueous solutions of sodium hydroxide (NaOH) were initially utilized in order to demonstrate the experimental apparatus function. Dye-bath effluent proved highly effective due to its high alkalinity and the capacity of the hydrolyzed "azo-reactive" dyes to react with CO_2. Decolorized dye-bath effluent (treated with $FeSO_4$) can also be used as a chemical solvent for the absorption of CO_2; however, its absorptive capacity is much lower compared to the raw wastewater. The above technique is also a very effective method to neutralize industrial effluents.
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1. Introduction

Large quantities of carbon dioxide (CO_2) are released in the atmosphere, from several important industries around the globe, every day (e.g. electricity generation, steel manufacturing, cement manufacturing, etc.). Moreover, CO_2 is a gas that contributes, greatly, to the greenhouse effect; therefore, its removal from the industrial flue gases is very important.

Chemical absorption is an efficient technology for the removal of pollutants (e.g. CO_2 or H_2S) from industrial flue gases. In an absorption column, the pollutant is firstly transferred from the gas to the gas–liquid interface and then to the bulk of the liquid phase (chemical solvent), where a reaction or a series of reactions take place. Alkaline (NaOH or KOH) and buffering (Na_2CO_3 or $NaHCO_3$) aqueous solutions are among the most effective chemical solvents [1,2]. Furthermore, primary ($R–NH_2$) and secondary ($RR'–NH$) alkanolamines are also very popular reagents for practical applications [3–5]. Chemistry, kinetics and the mechanistic aspects of these processes have been examined in a number of publications [1–5]. In the case of CO_2 absorption, the following reactions take place:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \tag{1}$$

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- \tag{2}$$

$$CO_2 + R–NH_2 + H_2O \rightarrow R–NH_3^+ + HCO_3^- \tag{3}$$

$$CO_2 + RR'–NH \rightarrow RR'–NCOO^- + H^+ \tag{4}$$

Nowadays, there is an increasing interest of the environmental technology towards "pollution prevention" techniques rather than "end-of-pipe" solutions. Finding uses for industrial waste materials is an important pollution prevention principle [6,7]. In this respect, the potential use of raw or treated dye-bath effluent, as chemical absorption solvent, seems to be a very interesting matter for investigation.

Dye-bath effluent is characterized as highly alkaline (pH 10–11) with a great buffering capacity. Moreover, the effluent is rich in dissolved textile dyes; therefore it presents a deep color, which comprises the main environmental concern of this type of wastewaters [8,9]. Treatment with ferrous sulfate is a very common method for the decoloration of the above industrial effluent [9–11]. Furthermore, decoloration is achieved by the reductive fission of the chromophore part (azo bond, –N=N–) of the azo-reactive dye molecule. Therefore, the treated dye-

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bath effluent, although colorless, is rich in aromatic amines and requires further treatment [9–11].

In general, both raw and treated dye-bath effluents require neutralization before further treatment, which is currently achieved by sulfuric or hydrochloric acid or even liquid carbon dioxide [8]; a process that adds considerably to the total treatment cost. Thus, using an absorption process the benefit would be two-fold, i.e. removal of the gaseous pollutant and effective (economic) neutralization of the wastewater.

In this work, the absorption characteristics of a dye-bath effluent, obtained from a nearby textile industry, are examined using a packed column system, while the same is applied on the respective decolorized (by the above described technique) effluent. In order to demonstrate the system's function and to put the data in perspective, carbon dioxide absorption by various sodium hydroxide and buffering solutions is also included. Furthermore, the absorptive capacity of several aromatic amines is also investigated.

2. Experimental

2.1. Materials

The dye-bath effluent was obtained by a nearby textile industry (Komotini, Greece); its characteristics are presented in Table 1. It is evident that the above effluent was highly alkaline with a great buffering capacity. Its high COD value was exclusively due to the high content of the remaining dissolved dyes. Moreover, it was characterized by its elevated conductivity due to the high NaCl content. Also, and as expected, the effluent was highly colored (Fig. 1) and presented an absorbance maximum in the UV region due the aromatic rings content of the dye molecules (Fig. 2).

The treated dye-bath effluent resulted from a chemical coagulation process with $Fe_2SO_4 \cdot 7H_2O$ (20 g/L); due to the high alkalinity of the raw effluent, addition of lime $(Ca(OH)_2)$ was not necessary. The characteristics of this effluent are also presented in Table 1. Furthermore, as Figs. 1 and 2 depict, respectively, the effluent was colorless but rich in aromatic amines (dye by-products).

Buffer-1 solution (Table 1) simulated the alkalinity (buffering capacity) of the dye-bath effluent. Thus, Na_2CO_3 (17.81 g/L) and $NaHCO_3$ (1.01 g/L) were dissolved in deionized water in order to prepare the above aqueous solution. Conductivity was monitored by the addition of NaCl and a conductivity meter (Consort).

Buffer-2 solution (Table 1) simulated the alkalinity (buffering capacity) of the treated dye-bath effluent. In this respect,
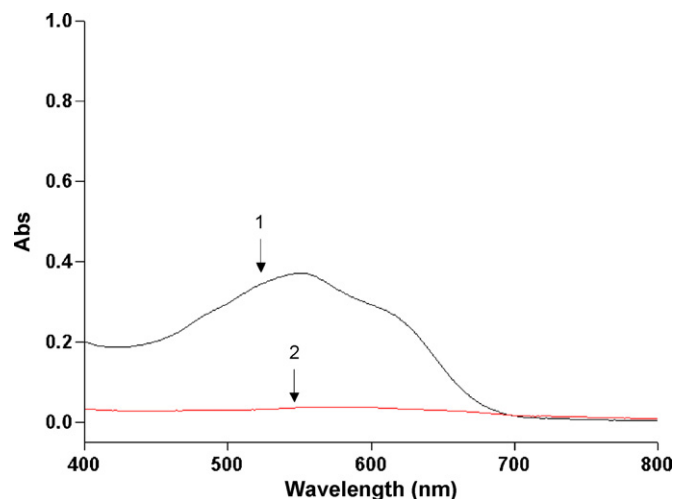

Fig. 1. Absorbance spectrum of raw and treated dye-bath effluents in the visible region (dilution ratio: 1–10): (1) raw dye-bath effluent and (2) treated dye-bath effluent. Both effluents neutralized by sulfuric acid at pH 7.
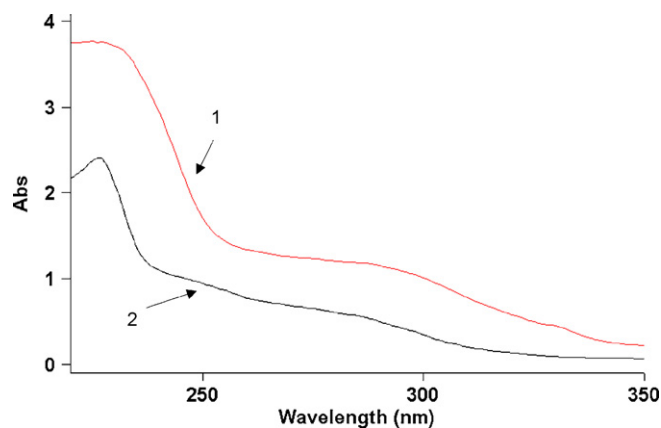

Fig. 2. Absorbance spectrum of raw and treated dye-bath effluents in the UV region (dilution ratio: 1–10): (1) raw dye-bath effluent and (2) treated dye-bath effluent. Both effluents neutralized by sulfuric acid at pH 7.

5.512 g/L of Na_2CO_3 and 6.384 g/L of $NaHCO_3$ were dissolved in deionized water in order to prepare this aqueous solution. Conductivity was monitored, as well as, with the buffer-1 solution.

The water-soluble aromatic amines, shown in Table 2, were purchased from Sigma–Aldrich. NaOH, Na_2CO_3, $NaHCO_3$, NaCl and $Fe_2SO_4 \cdot 7H_2O$ were provided by Fischer Scientific. Finally, the gases (20% CO_2 diluted in N_2 and pure nitrogen) were provided by Messer Greinsheim.

Table 1
Characteristics of different chemical solvents

	pH	Total alkalinity (CaCO$_3$, mg/L)	[CO$_3^{2-}$] (mol/L)	[HCO$_3^-$] (mol/L)	COD (mg/L)	Conductivity (mS)
Raw dye-bath effluent	10.9	17,400	0.168	0.012	1200	74
Buffer-1 (C1)	10.9	17,400	0.168	0.012	–	74
Treated dye-bath effluent	9.4	9,000	0.052	0.076	720	67
Buffer-2 (C2)	9.4	9,000	0.052	0.076	–	67

Table 2
Aromatic amines (Sigma–Aldrich)

Symbol	Compound
B1	3-Amino-2-chloropyridine
B2	4-Aminonapthalene-1-sulfonic acid sodium salt
B3	4-Amino-2-hydroxybenzoic acid sodium salt

2.2. Analytical methods

Alkalinity of the liquid samples was measured by titration with standardized sulfuric acid (H_2SO_4) solution using end-point indicators (phenolpthtalein, methyl-orange) and/or a pH-meter [12].

The COD of the raw and treated dye-bath effluents was calculated using a COD-digestion unit (VELP Scientifica) according to the Open Reflux Method. Titration with ferrous ammonium sulfate was preferred over photometric analysis [12].

A spectrophotometer (Cary 100, Varian) was utilized for color and UV absorbance analysis. All samples were filtrated (0.2 μm) prior to the analysis.

2.3. Apparatus and procedure

Chemical absorption took place in a packed column system, whereby the gas was continuously fed in the column while the liquid solvent remained in the system as in a batch mode. Thus, the liquid solvent was circulated between the column and a reservoir vessel by means of a peristaltic pump contacting the gas in counter current flow. The liquid flow rate was controlled in order to maintain a smooth liquid film, while the liquid level at the bottom of the reactor was maintained at approximately the same point where the gas was fed. The experimental apparatus is presented in Fig. 3.

The column comprises of a glass cylinder of 5 cm in diameter and 60 cm high, randomly packed with cylindrical glass rings (length, 1 cm; diameter, 1 cm) to facilitate the gas–liquid interaction. Gas flow rates were controlled by gas-flow meters, properly adjusted to obtain the desired inlet CO_2 concentration ($C_0 = 10 \pm 0.5\%$), while the total gas flow rate (1 ± 0.1 L/min) was regularly measured in the outlet stream by a gas-flow meter (Ritter, Bochum-Langendreer). The pressure was slightly higher than the atmospheric one (1.1 atm) at the inlet of the packed column and 1 atm at the outlet of the last measuring device (gas-flow
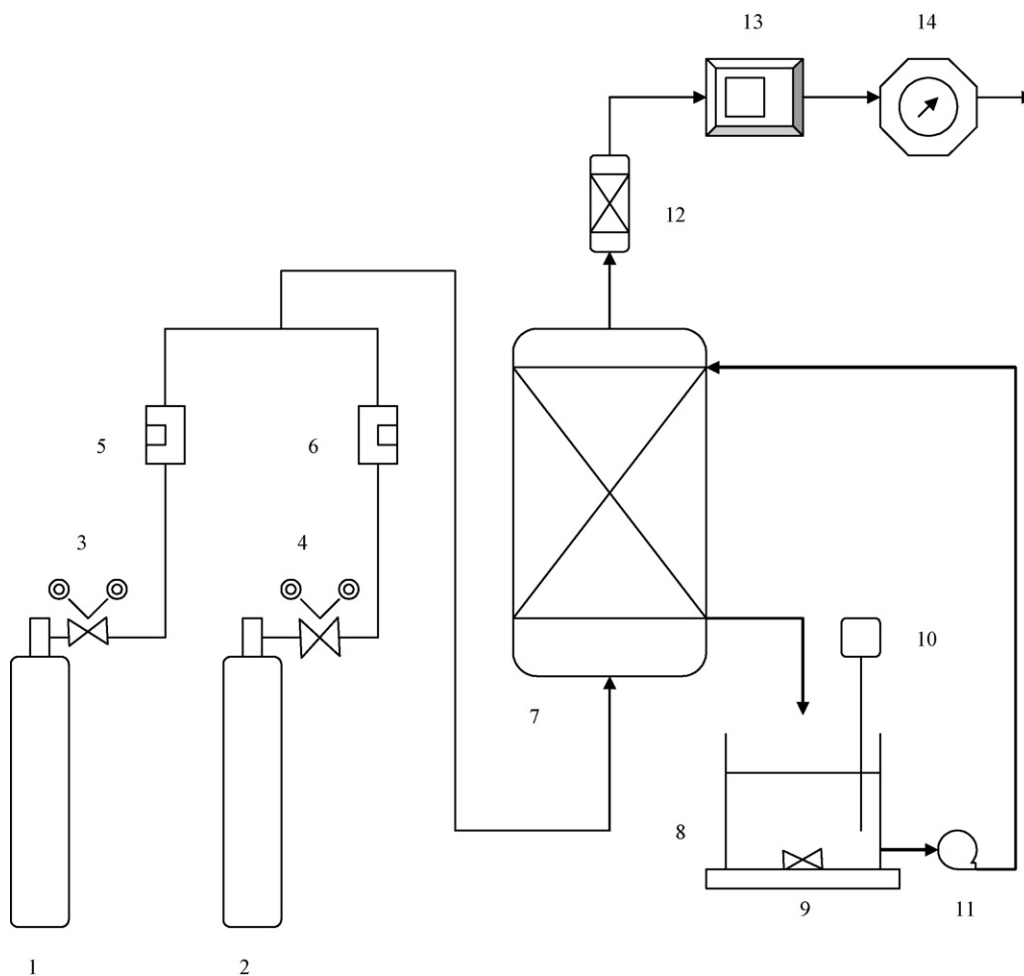

Fig. 3. Flow sheet of the experimental apparatus: (1) gas cylinder (20% CO_2, 80% N_2), (2) gas cylinder (pure N_2), (3 and 4) pressure-release valves, (5 and 6) gas-flow controllers, (7) packed-tower, (8) liquid solvent vessel, (9) magnetic stirrer, (10) pH-meter, (11) peristaltic pump, (12) silica-gel trap, (13) CO_2–IR analyzer and (14) gas-flow meter.

meter). The CO_2 concentration in the gas mixture entering or exiting the absorption column was monitored by an IR analyzer (Binos 1, Leybold-Heraeus). A silica gel trap (desiccators) was placed before the IR analyzer in order to remove humidity from the gas phase and protect the instrument (IR analyzer). The pH of the liquid solvent was measured using a pH-meter (Consort).

In a typical experiment, one liter (1 L) of the liquid solvent was placed in the reservoir vessel and recirculated to the column, while a gas mixture with a certain CO_2 concentration (C_0) was fed to the system. Recirculation of the liquid solvent started at $t = 0$ after an equilibrium of the gas flow rates and CO_2 inlet concentration (C_0) were reached. At the initial stages of a run, the liquid solvent was almost completely absorbing the pollutant and the concentration of CO_2 at the outlet stream was practically negligible ($C \approx 0$). As the absorption process was progressing, the CO_2 was continuously accumulated in the liquid solvent and after a certain point, the CO_2 started to evolve in the outlet stream ($C > 0$). At the end of each run, the liquid solvent became completely saturated and the concentration of carbon dioxide in the outlet stream was equal to the inlet ($C = C_0$). By plotting C/C_0

versus time, a 'breakthrough curve' is obtained, which is characteristic of the absorption capacity and the kinetics of the system.

3. Results and discussion

In the beginning, aqueous solutions of sodium hydroxide (NaOH) of different strength were used, as chemical solvents, in order to demonstrate the experimental apparatus (Fig. 3) function and ability to absorb carbon dioxide; the breakthrough curves obtained are presented in Fig. 4. As expected, increasing the concentration of sodium hydroxide causes an increase in the total amount of carbon dioxide absorbed, as well as, in the rate of absorbance. Initially, CO_2 reacts with hydroxyl ions (OH$^-$) according to reaction (1), while in the course of the experiment; reaction with carbonate anions (reaction (2)) takes over. The aqueous solutions are neutralized in the end of the experiments (pH 7–8).

Different types of water-soluble aromatic amines (Table 2), at their solubility saturation limit, were also examined in conjunction with NaOH. Aromatic amines are easily found in various
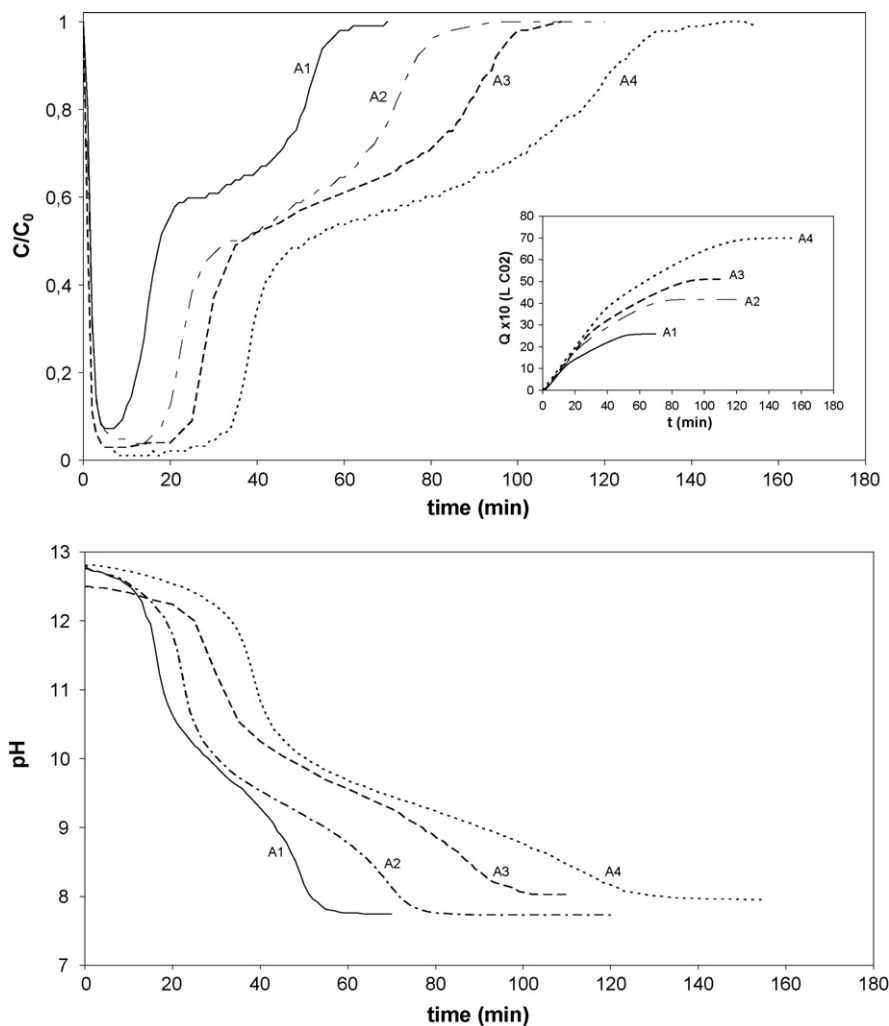

Fig. 4. Transient absorption of CO_2 by various NaOH solutions: 0.10 M (denoted as A1), 0.15 M (A2), 0.20 M (A3) and 0.25 M (A4). The upper figure shows the variation of the dimensionless CO_2 concentration (C/C_0) with time, while the inset graph shows the amount of CO_2 absorbed (Q in L) vs. time. The lower figure shows the variation of the pH of the solution with time. Experimental conditions: inlet CO_2 concentration, 10 ± 0.5 mol%; gas flow rate, 1.0 ± 0.1 L/min; ambient temperature.

raw or treated wastewaters (e.g. textile wastewaters) and might be used as absorbance reagents. As an analogous to the primary alkanolamines reaction (3), absorption of CO_2 could be described as follows:

$$CO_2 + Ar\text{–}NH_2 + H_2O \rightarrow Ar\text{–}NH_3^+ + HCO_3^- \qquad (5)$$
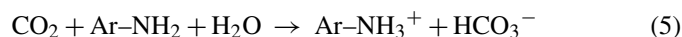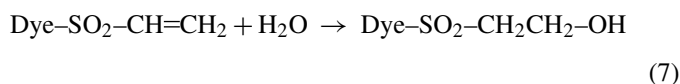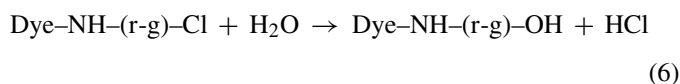
As Fig. 5 depicts, the aromatic amines used in this study showed only slight influence in the absorption of CO_2 (especially the chloropyridine type). This is due to the low basicity of this type of compounds. In the aromatic amine molecule, the electron cloud around nitrogen gets distributed over the aromatic nucleus due to the resonance effect resulting thus in lower basicity.

Dye-bath effluents are characterized as highly alkaline and with a great buffering capacity [8,9]. In this respect, dye-bath effluent (Table 1) from a nearby textile industry was utilized as chemical solvent in these experiments. Also, a synthetic aqueous solution (buffer-1, Table 1), of the same alkalinity (buffering capacity), was used for comparison. As Fig. 6 shows, the raw

dye-bath effluent demonstrated high absorptive capacity, almost 30% higher than the buffer-1 solution. Since, the only difference in composition, between the dye-bath effluent and the buffer-1 solution is the dissolved dyes ("azo-reactive") content, it becomes clear that the dyes contributed to the absorption of CO_2. This can be explained as follows:

During the dyeing process, under high temperature and an elevated pH, a certain amount of the dyes used (usually 30–50%) are hydrolyzed (e.g. reactions (6) and (7)) and remain in the aqueous phase as waste material [13,14]. Thus, the hydrolyzed azo-reactive dyes contain hydroxyl groups (−OH) that can act as functional groups during reaction with CO_2.

$$Dye\text{–}NH\text{–}(r\text{-}g)\text{–}Cl + H_2O \rightarrow Dye\text{–}NH\text{–}(r\text{-}g)\text{–}OH + HCl$$

$$(6)$$

$$Dye\text{–}SO_2\text{–}CH{=}CH_2 + H_2O \rightarrow Dye\text{–}SO_2\text{–}CH_2CH_2\text{–}OH$$
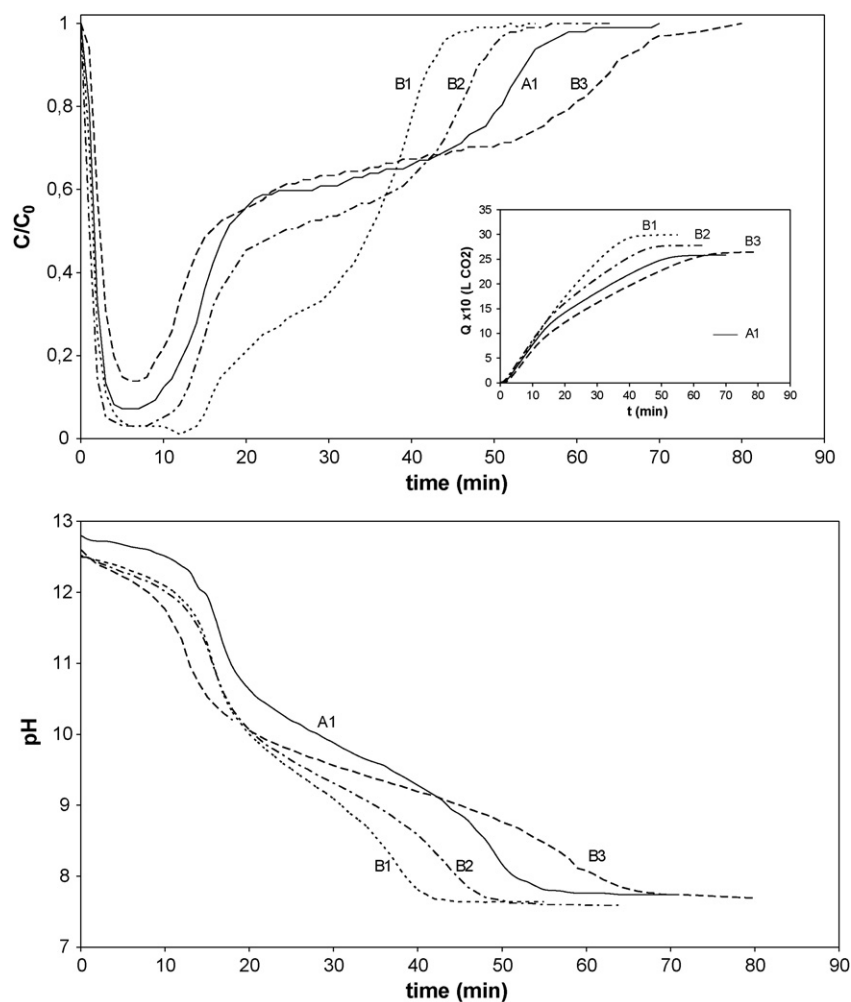
$$(7)$$

where (r-g) is reactive group.

Fig. 5. Transient absorption of CO_2 by various aromatic amines in 0.10 M NaOH solution denoted as B1, B2 and B3 (Table 2) in comparison to the 0.10 M NaOH solution (denoted as A1). The upper figure shows the variation of the dimensionless CO_2 concentration (C/C_0) with time, while the inset graph shows the amount of CO_2 absorbed (Q in L) vs. time. The lower figure shows the variation of the pH of the solution with time. Experimental conditions: inlet CO_2 concentration, 10 ± 0.5 mol%; gas flow rate, 1.0 ± 0.1 L/min; ambient temperature.
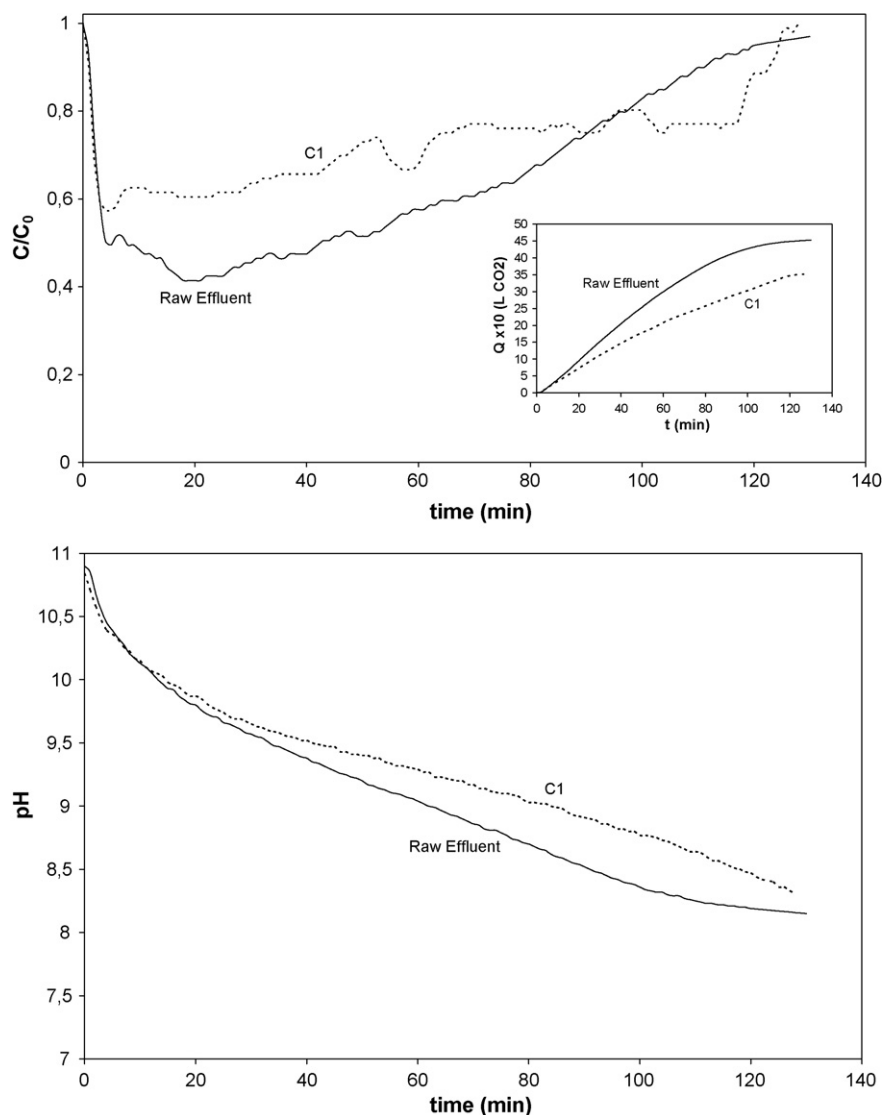
Fig. 6. Transient absorption of CO_2 by raw dye-bath effluent in comparison to the respective 'buffer-1' solution (denoted as C1, Table 1). The upper figure shows the variation of the dimensionless CO_2 concentration (C/C_0) with time, while the inset graph shows the amount of CO_2 absorbed (Q in L) vs. time. The lower figure shows the variation of the pH of the solution with time. Experimental conditions: inlet CO_2 concentration, 10 ± 0.5 mol%; gas flow rate, 1.0 ± 0.1 L/min; ambient temperature.

Finally, the treated dye-bath effluent (Table 1) – containing aromatic amines – was tested as a potential chemical solvent. For comparison, buffer-2 solution (Table 1), that has the same alkalinity with the above wastewater, was also tested. As Fig. 7 demonstrates, the treated dye-bath effluent could also be used as a chemical solvent for CO_2 absorption, even though, its absorptive capacity is much lower compared to the raw wastewater. Furthermore, it is evident that the absorptive capacity of the treated dye-bath effluent is almost exclusively due to its alkalinity, while the contribution of the aromatic amines seems negligible (Fig. 7). Table 3 summarizes the results of all the above experiments.

The above absorption process is not only useful for purifying gas emissions but also useful for neutralizing dye-bath effluents, as this is a necessary step of the treatment process of the above wastewaters.

Table 3
Absorption capacities of different chemical solvents

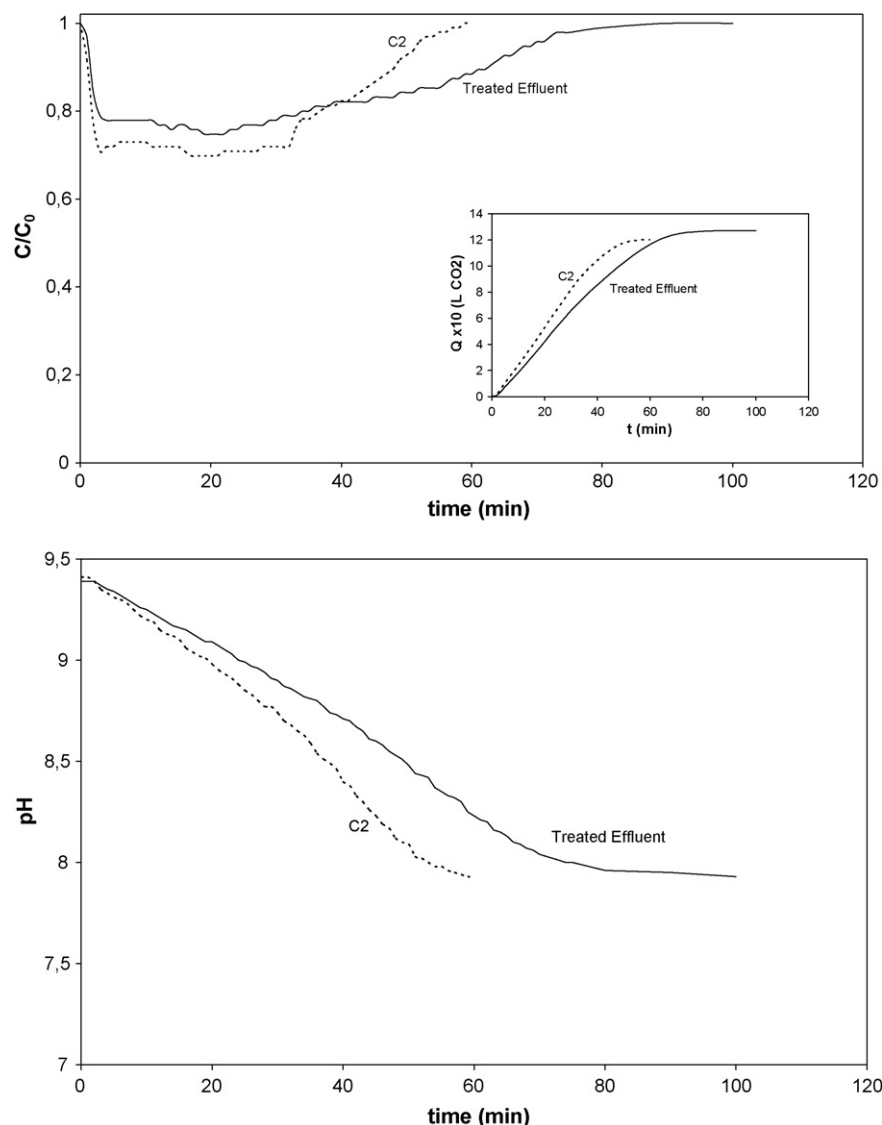| Symbol	Solvent	Q (L CO_2/L solvent)
A1	0.10 M NaOH	2.6
A2	0.15 M NaOH	4.2
A3	0.20 M NaOH	5.1
A4	0.25 M NaOH	7.0
B1	3-Amino-2-chloropyridine + NaOH 0.1 M	3.0
B2	4-Aminonapthalene-1-sulfonic acid sodium salt + NaOH 0.1 M	2.8
B3	4-Amino-2-hydroxybenzoic acid sodium salt + NaOH 0.1 M	2.6
RE	Raw dye-bath effluent	4.5
C1	Buffer solution 1	3.5
TE	Treated dye-bath effluent	1.3
C2	Buffer solution 2	1.2

Fig. 7. Transient absorption of CO_2 by treated dye-bath effluent in comparison to the respective 'buffer-2' solution (denoted as C2, Table 1). The upper figure shows the variation of the dimensionless CO_2 concentration (C/C_0) with time, while the inset graph shows the amount of CO_2 absorbed (Q in L) vs. time. The lower figure shows the variation of the pH of the solution with time. Experimental conditions: inlet CO_2 concentration, 10 ± 0.5 mol%; gas flow rate, 1.0 ± 0.1 L/min; ambient temperature.

4. Conclusions

Dye-bath effluents are very effective, as chemical solvents, for the absorption of carbon dioxide due to their high alkalinity (buffering capacity). Furthermore, the hydrolyzed azo-reactive dyes, which exist in the effluent at a high concentration, contribute to the above CO_2 absorption due to their hydroxyl ($-OH$) functional groups.

Decolorized dye-bath effluent (treated with $FeSO_4$ and containing aromatic amines) can also be used as a chemical solvent for the absorption of CO_2. However, its absorptive capacity is much lower compared to the raw effluent. Moreover, its absorptive capacity is exclusively due to its alkalinity.

Chemical absorption of CO_2 in a packed column is also a very effective technique for neutralizing industrial effluents.

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