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A new method in the removal of Ca and Mg ions from industrial wastewater

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ABSTRACT

Wastewaters produced in sodium carbonate production industry include a high level of different mineral matters, such as calcium and magnesium salts, that cause difficulties in disposal of effluent into the environment. In this study, a new method based on chemical treatment and CO_2 gas injection in order to remove Mg^{2+} and Ca^{2+} ions from effluent of a sodium carbonate industry was presented. By employing this method, in addition to removing the calcium hardness of wastewater, CO_2 can be used as a responsible gas for global warming. Besides, the influence of some parameters, including the temperature of reaction, gas flow rate, time of gas injection, and the initial pH of wastewater, has been investigated on treatment processing. The results clarified that wastewater's initial pH was the most important factor affecting Ca^{2+} removal efficiency. The maximum removal of Ca^{2+} ions occurred when pH was above 10. At last, the proposed method manifested better performance in mineral salts' ions elimination with removal efficiency of calcium and magnesium of about 50 and 95% in optimized conditions, respectively.

Keywords: Carbonation; CO_2 reuse; Chemical treatment; Wastewater treatment

1. Introduction

An uncommon type of contaminant in some industrial wastewaters is mineral salts. Known wastewaters with high level of mineral salts are sodium carbonate manufacturing industries. Most sodium carbonate production manufactures use the Solvay method for their production process [1]. The flow diagram of the process is presented in Fig. 1.

As it is obvious in Eq. (1), a significant aspect of the Solvay process is the recovery of ammonia from filtration liquid and it was done using $Ca(OH)_2$ as a reagent material [1].

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2 \qquad (1)$$

The released ammonia is distilled in a steamed way and sent back to the adsorption towers. The material received in distillation process is commonly known as distiller waste (DW). DW is the main waste stream created in the Solvay process, which contains a large amount of $CaCl_2$ [1].

Conspicuously, only a small part of the $CaCl_2$ wastewater is concentrated to recover solid $CaCl_2$, while most of $CaCl_2$ wastewater is directly discharged to ambient such as rivers or soil. In most cases, DW suspension is directed to sedimentation ponds, where solid particles are settled. Then, the cleared overflow of DW is directed as sewage to environment, which

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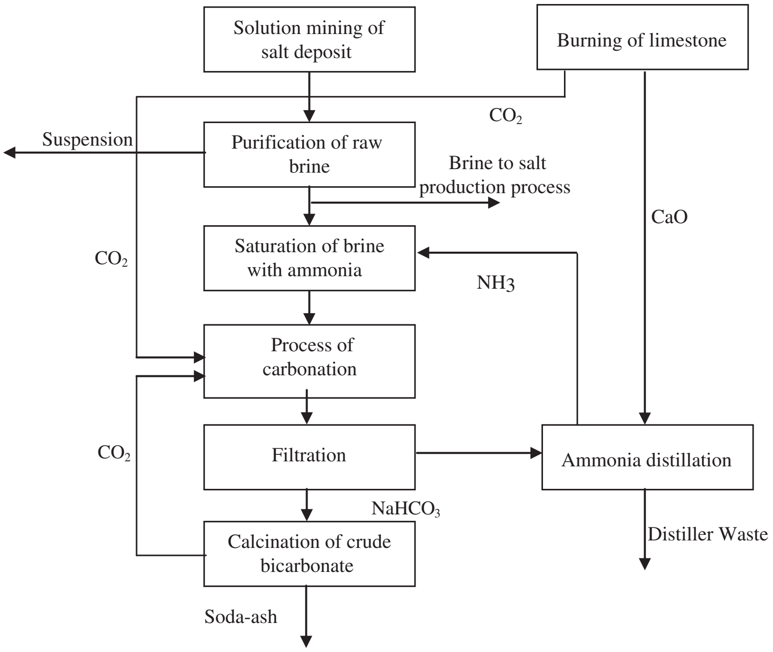

Fig. 1. Flow diagram for the production of ammonia–soda by the Solvay process [1].

causes an increase in both pH and Ca^{2+} concentration in ground waters.

Furthermore, several methods have been presented in order to remove mineral ions, including membrane distillation [2,3], chemical treatment [4], biological processes [5,6], electrodialysis [7], ion exchanging [8–10], and crystallization [11]. The sedimentation of salts by carbon dioxide injection into wastewater is another method which recently has been noticed. In this method, Ca and Mg ions were joined to carbonated forms in solution and they were removed as calcium and magnesium carbonate sediments [12]. This method is suitable and costs reasonably, especially in removing Ca^{2+} [13]. Recently, the effect of various operational conditions on the morphology and particle size of the produced calcium carbonate was investigated [14–17]. However, no significant evidence about the application of these methods in high-level content of Ca^{2+} and Mg^{2+} industrial wastewaters was presented. Besides, there are no studies showing the removal efficiency of other ions. Basically, industrial wastewaters have a wide range of ions and various components which each of them, may be, exhibiting an inhibition effect on the removal process.

In this research, a two-step procedure based on chemical treatment and carbonation was used for Ca^{2+} and Mg^{2+} removal in wastewater. The main reactions which occurred in solution are presented in Eqs. (2) and (3). According to other studies, presence of Mg^{2+} in the solution is disincentive for calcium carbonate sedimentation [18,19]; so at first, it is vital to remove Mg^{2+} ions using chemical treatment by lime (Eq. (2)). When hydrated lime is added to the solution, Mg^{2+} ions are precipitated out from solution in the form of $Mg(OH)_2$ and the chemical reaction presented in Eq. (3) occurs in solution [4]. At last, for sedimentation of Ca^{2+} ions, a mixture of carbon dioxide and nitrogen gas is injected into the solution and the precipitation of calcium ions in the form of $CaCO_3$ proceeds under the influence of lime and CO_2 gas addition, respectively.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2 \downarrow \tag{2}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \tag{3}$$

When CO_2 gas was injected into wastewater, the proposed equilibriums have the following formulas (Eqs. (4)–(6)) formed in the solution.

$$CO_2(gas) \rightleftharpoons CO_2(aq) \tag{4}$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \tag{5}$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \downarrow \tag{6}$$

where Eq. (4) indicates equilibrium at gas/liquid interface for dissolution of CO_2 gas and dissolved CO_2 is converted to carbonate ions according to equilibriums which were shown in Eq. (5). Eventually CO_3^{2-} ions react with Ca^{2+} ions and $CaCO_3$ precipitates are formed. Accordingly, when CO_2 gas bubbled into the solution, it contributes in order to increase the concentration of CO_3^{2-} and H^+ ions which achieves a decrease in pH of solution.

Table 1
Chemical analysis of selected wastewater

Ions	Unit	Amount
Calcium	mg $CaCO_3$/L	110,775
Magnesium	mg $CaCO_3$/L	5,800
Sodium	mg/L	20,050
Chloride	mg/L	99,400
Sulfate	mg/L	2,579
pH		11

2. Materials and methods

The wastewater was selected from a sodium carbonate manufacturing industry. The wastewater included several mineral ions, such as calcium, magnesium, sulfate, chloride, etc. The composition of wastewater is shown in Table 1.

To carry out the procedure, at first, 17 g of lime ($Ca(OH)_2$) was mixed with 3,650 ml of wastewater to eliminate magnesium ions and inhabitation effects of these ions on bulk precipitation of calcium carbonate. Then, the solution was mixed continuously for 30 min at 40°C and was filtered by using a filter paper with 0.2 μm average pore size. During the chemical precipitation of Mg ions, it is necessary to adjust pH and temperature at a desired level, so the pH of the solution was adjusted by adding HCl or 25% ammonia (NH_3) solution.

In the second step, a gas mixture ($CO_2 + N_2$) with desired flow rate value was introduced to the bottom of the reactor vessel via a bubbler that creates a mixed flow of gas through the solution with the small size of bubble. The experimental setup was schematically shown in Fig. 2. The reactor was made of plexiglass with a diameter of 10 cm and height 75 cm. The flow rate of CO_2 and N_2 was measured with the calibrated flow meters. The reaction process time and pH level were recorded at each 1 min intervals. At 5, 15, and 25 min after starting gas injection, samples were prepared out of solution.

To understand the effects of some reaction parameters on ion removal efficiency, the selected parameters including CO_2 flow rate, solution temperature, wastewater initial pH, and gas injection time were investigated. Table 2 lists the parameters and values.

In this study, in order to determine calcium and magnesium ions concentration, American Standard Test Methods based on titration method with Ethylenediaminetetraacetic acid agent was applied [20]. All reagents were purchased from Merck Chemical Co., and the percent of calcium removal was estimated by Eq. (7).

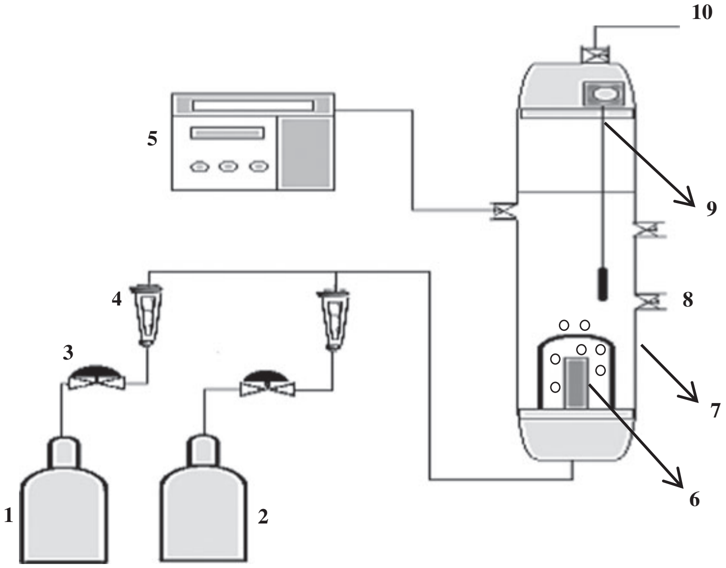

Fig. 2. Schematic of experimental setup (1. CO_2 tank; 2. N_2 tank; 3. gas valve; 4. flow meter; 5. pH meter; 6. bubbler; 7. reactor; 8. sample port; 9. thermometer; and 10. feed inlet port).

Table 2
The experimental parameters and value conditions

Parameters	Values
CO_2 flow rate	0.2, 0.3 (L/min)
Solution temperature	Ambient, 40, 60 (˚C)
Wastewater initial pH	10, 10.5, 11
Gas injection time	5, 15, 25 (min)

Table 3
Estimation of wastewater components according to bar diagram

Component	Amount (meq/L)
$CaCl_2$	1,920.67
$MgCl_2$	116.023
NaCl	871.647
$Ca(HCO_3)$	250
$CaSO_4$	53.73

$$\text{Removal percent } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{7}$$

To identify the crystalline phase of precipitates, X-ray diffraction (D-5,000 Siemens) was used to analyze produced sediment. According to bar diagram, estimation of wastewater components was shown in Table 3.

3. Results and discussion

3.1. The removal of magnesium ions

The first step of this method is based on lime addition to wastewater in order to remove magnesium ions. The lime needed for optimal refinement varies with the type of wastewater. Fig. 3 shows the effect of lime dosage on Mg^{2+} removal percent. According to the figure, the optimum amount of lime dosage is 4.6 g/L, which is equal to the value determined from stoichiometric value of lime to magnesium reaction. As seen in Fig. 3, rising the temperature from 25 to 40˚C improved the yield of Mg^{2+} elimination, but additional temperature was not effective on the removal yield.

3.2. The effect of wastewater initial pH

Fig. 4 manifests the effect of wastewater's initial pH as well as temperature on Ca^{2+} removal efficiency

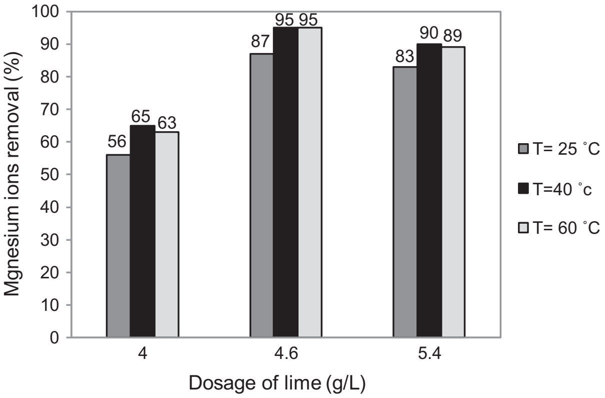

Fig. 3. Results of lime dose effect on Mg^{2+} removal percentage at different temperatures.

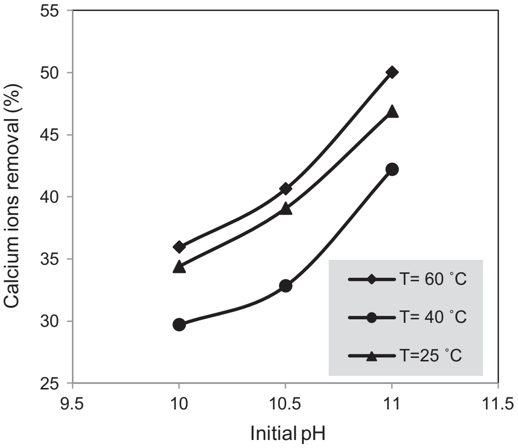

Fig. 4. The effect of wastewater's initial pH on Ca^{2+} removal efficiency (experimental conditions: Q_{CO2} = 0.3 L/min and Time = 15 min).

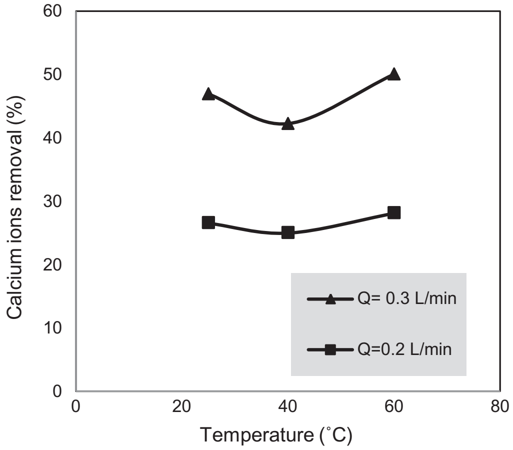

Fig. 5. The effect of temperature on Ca^{2+} removal efficiency at different gas flow rates (experimental conditions: initial pH 11 and time = 15 min).

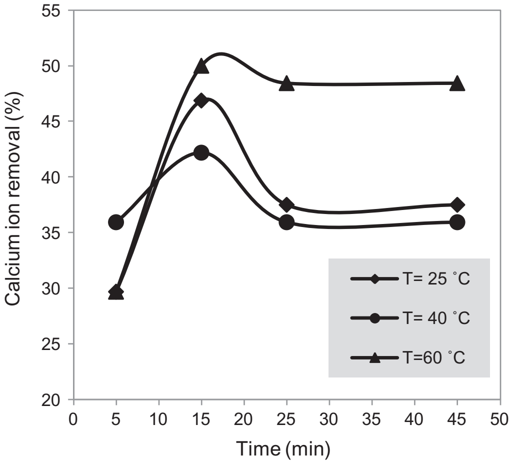

Fig. 6. The effect of gas injection time on Ca^{2+} removal efficiency at different temperatures (Q_{CO2} = 0.3 L/min and initial pH 11).

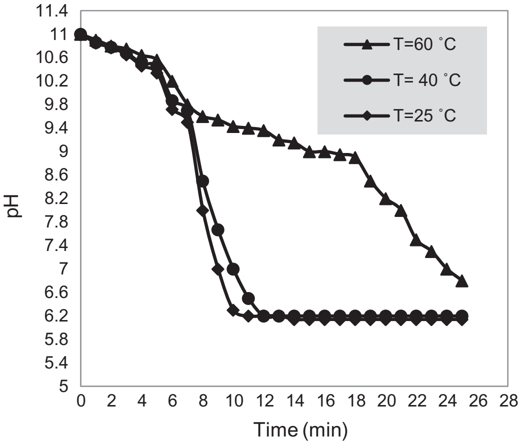

Fig. 7. Changes of pH with reaction time in various reaction temperatures (experimental conditions: Q_{CO2} = 0.3 L/min and Initial pH 11).

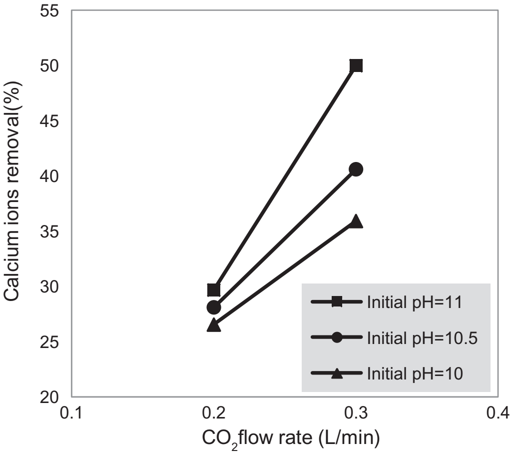

Fig. 8. The effect of CO_2 flow rate on Ca^{2+} removal efficiency.

in the experiments in terms of: Q_{CO2} = 0.3 L/min and Time = 15 min. As seen in the figure, Ca^{2+} removal efficiency enhances with increasing wastewaters initial pH.

Suitable pH for sedimentation of calcium carbonate is 9.5, which is called isoelectric pH. Since $CaCO_3$ has a much lower solubility in water (0.00012 g/ 1000 g of water) compared to $CaCl_2$, it settles down from wastewater [21]. Sedimentation begins at this pH point until pH value of 7(isoelectric point). The carbonation reaction was stopped as soon as the pH values drop to pH lower than 7. Although CO_2 gas was introduced as the source of carbonation ions, it is continuously dissolved into the solution. Moreover, the accumulation of H^+ ions caused the solution to become acidic and pH level decreased during the process. When initial pH of solution is higher than isoelectric point, to achieve the suitable pH, more CO_2 gas should be solved in solution to produce more H^+ ions and to

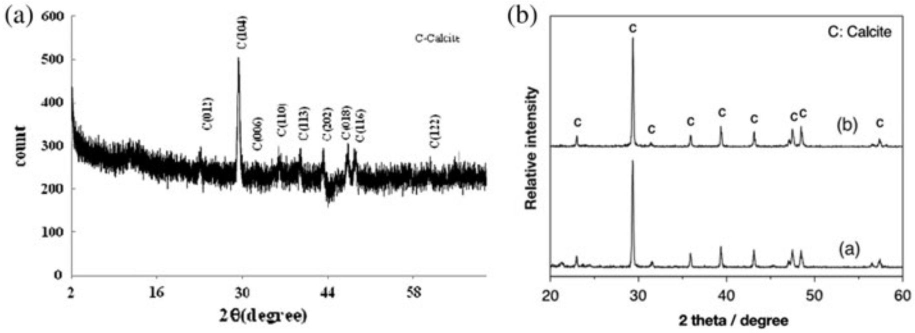

Fig. 9. (a) XRD patterns of calcium carbonate particle precipitated at $T = 60$°C, time = 15 min, initial pH 11, and Q_{CO2} = 0.3 L/min. (b) XRD patterns presented for Calcite [22].

reduce the pH level. Actually, when pH is in proper range for calcium carbonate sedimentation (7–9.5), there are more numbers of CO_3^{2-} ions in solution to react with Ca^{2+} ions. Consequently, the percent of calcium removal increases.

3.3. Effects of solution temperature

The removal percent of Ca^{2+} at different temperatures was shown in Fig. 5. As seen in Fig. 5, by increasing temperature, Ca^{2+} removal percent was decreased and then with further increase in temperature to 60°C Ca^{2+} removal percent had a sudden rising trend, so that at the temperature of 25°C the Ca^{2+} removal percent is higher than at 40°C. The basic reason for this trend is reduction of gas solubility accompanied with temperature increase. When the temperature of the solution was increased, the solubility of CO_2 was decreased and then amount of carbonate ions which are essential for precipitation process was decreased. Therefore, by growing temperature up from 25 to 40°C, calcium ions removal was decreased due to reducing CO_2 solubility.

On the other hand, it is observed that the percentage removal of Ca^{2+} at 60°C is higher than 40°C. This is because of the exothermic nature of calcium carbonate dissolution effect [21]. The comparison between the removal percentage at 60 and 25°C shows the better formation of calcium carbonate precipitates at higher temperature and it means that exothermic nature of calcium carbonate dissolution is more effective than proper CO_2 dissolving in low temperatures.

3.4. The effects of gas injection time

The removal percent of Ca^{2+} also varies with time. As shown in Fig. 6 in several experiments which were carried out at constant pH and CO_2 flow rate, by increasing the time of gas injection until 15 min the removal percentage was increased and then decreased. The reason behind this fact is that by pH reduction, precipitated calcium carbonate resolves and returns back in to the solution because of solution acidification.

As seen in Fig. 7, after 15 min of reaction time, because of pH dropping to below 7, the amount of $CaCO_3$, dissolved again and leads to an increase in Ca^{2+} ions in the solution. The increase in dissolved Ca^{2+} continues as long as the dissolution of CO_2 in wastewater occurs. After reaching the equilibrium condition, pH fixes.

3.5. The effect of CO_2 flow rate

The effect of CO_2 flow rate on the percent of Ca^{2+} removal is shown in Fig. 8. In all levels of wastewater's initial pH, Ca^{2+} removal percent in CO_2 gas flow rate of 0.3 L/min is more than CO_2 flow rate of 0.2 L/min. By increasing gas flow rate, the amount of CO_2 gas solubility increases and creates more CO_3^{2-} ions in solution, which results in more Ca^{2+} ions removal. Finally, pH drops to 5–6 ranges, which are the equilibrium pH ranges of CO_2 solution. In other words, in this condition, pH range will be constant along with increase in gas flow rate since there is no more solubility of CO_2 [21].

X-ray diffraction is the most important method to determine the nature of unknown materials. To confirm that precipitate from these processes was $CaCO_3$, powder X-ray diffraction analysis was conducted to identify the crystalline phases of the precipitates. Fig. 9(a) and (b) shows XRD patterns of the $CaCO_3$ particles synthesized at specific conditions and calcite, respectively [23]. According to these figures, the peak of calcite phase in X-ray diffraction pattern is observable. Furthermore, it is clear that under these conditions other phases of calcium carbonate, such as vaterite, cannot be formed. Category pages formed in this pattern show that the white precipitate obtained from the CO_2 gas injection process was calcium carbonate ($CaCO_3$), with calcite kind of crystal polymorphs.

4. Conclusion

Generally, a new two-step procedure based on chemical treatment employing lime and CO_2 gas injection in order to remove Mg^{2+} and Ca^{2+} ions in a sodium carbonate industry effluent was used. In this approach, two common methods were combined to treat an industrial wastewater with much unknown components that each of them may cause an inhibition for treatment process. Besides, the amount of Ca^{2+} removal was investigated by changing the operating conditions, including the temperature of reaction, gas flow rate, time of gas injection, and initial pH of wastewater in a batch experiments. The results illustrated that by increasing the wastewater's initial pH and solution temperature, the Ca^{2+} removal percentage increased. Ca^{+2} removal in wastewater was obtained about 50%, which could be achieved within 15 min, CO_2 flow rate of 0.3 L/min at 60°C, and initial wastewater's pH of 11. The analysis of the produced sediments after treating shows that they are calcium carbonate ($CaCO_3$), with calcite kind of crystal polymorphs. The proposed method can be cost-efficient and is an available process, especially in the case of applying CO_2 from combustion gasses to eliminate hardness and decreasing wastewater pH.

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