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Effect of operation conditions on alkalinity production from alkaline substances used in anaerobic wastewater treatment system

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ABSTRACT

One of the effective parameters in the anaerobic treatment process is alkalinity, which plays an important role in the performance of the process as a buffer and regulator of wastewater pH. To provide the alkalinity of anaerobic units, there are several alkaline substances, such as Na_2CO_3, $Ca(OH)_2$, MgO and NaOH, etc. Therefore, this study was conducted to determine the effect of operating conditions on the production of alkalinity from alkaline substances used in anaerobic wastewater treatment system. This descriptive cross-sectional study was performed for 4 months (from June to September 2019) in an anaerobic wastewater treatment plant in an industrial town in Hamedan, Iran. In this study, four common neutralizing agents including NaOH (1–2 g/L), Na_2CO_3 (1.5–2 g /L), $Ca(OH)_2$ (1–2 g/L) and MgO nanoparticles (0.5–1 g/L) to provide the required alkalinity was evaluated in the anaerobic process. In the present study, 224 samples were examined using the OFAT method. Alkalinity production was evaluated by each of these alkaline substances in neutralizing agents value (0.5–2 g/L), contact time (1–5 min) and mixing rate (25–150 RPM). The results showed that there is a direct relationship between alkaline substances concentration, mixing rate and contact time with alkalinity production. As the dose of alkaline substances, the contact time and the mixing rate increased, the production of alkalinity also increased. The results showed that MgO is the most suitable alkaline substance to provide the required alkalinity of the anaerobic baffle system in the range of 2,000–2,000 mg $CaCO_3$/L. In general, it can be concluded that due to the lack of alkalinity of the anaerobic baffle unit of the industrial town wastewater treatment plant, adding an alkaline substance such as MgO to regulate the alkalinity of the anaerobic baffle system, prevent pH drop and provide suitable environmental conditions for the growth and activity of microorganisms is necessary.

Keywords: Alkalinity; Anaerobic process; Anaerobic baffled reactor (ABR); Industrial wastewater treatment; Mixing rate

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1. Introduction

In recent decades, environmental and water pollution has become an issue of serious international concern [1]. In this regard, legislation requirements for discharging wastewater have recently become much stricter [2]. Meanwhile, biological wastewater treatment method due to certain advantages such as greater environmental friendliness as a safe and cost-effective treatment method is an important issue that should be considered for the treatment of various types of industrial wastewater [3], especially for industrial wastewater with impermissible discharge levels [4,5]. Also, in these methods, no chemicals harmful to the environment are used [6]. Therefore, effluent and sludge disposal from these processes have less adverse effects on receiving water sources than chemical processes [7,8]. Among the biological wastewater treatment methods, anaerobic processes are better than aerobic processes for very strong wastewater treatment such as industrial wastewater [9–12]. The anaerobic biological treatment has the potential as a low-cost and high-performance wastewater treatment system [13]. Theoretically, its benefit includes no use of fossil fuels, less space required, no or very little use of chemicals, and production of methane gas as the potential energy output [14,15]. Among the types of anaerobic systems, anaerobic baffled reactor (ABR) system is considered due to advantages such as unique hydraulic structure, resistance to toxic shocks, low hydraulic retention time (HRT), high sludge retention time (SRT), no need to sludge blanket, methane gas recovery, etc. in wastewater treatment, especially industrial wastewater [16–18]. Environmental factors such as pH, soluble oxygen, organic loading rate (OLR), temperature, concentration of organic matter, insoluble organic matter, alkalinity, nutrients, macronutrients, toxic and inorganic compounds, SRT, HRT, and sulfate affect the performance of anaerobic biological processes [19].

It has generally been proven that alkalinity is one of the most important variables to evaluate the stability of anaerobic digestion. The alkalinity of water indicates the resistance of water to pH changes. In municipal and industrial wastewater, many factors such as soluble inorganic compounds, bicarbonates, the amount of suspended organic matter and the presence of hydroxyl can lead to the production of alkalinity. Concentrations of carbon dioxide (CO_2), volatile fatty acids (VFAs) and bicarbonates are the main causes of alkalinity change in anaerobic processes [20]. Therefore, in the case of wastewater with high buffering capacity, pH measurement may not be sufficient to indicate process changes [21]. Therefore, to ensure operational stability in anaerobic digestion processes, alkalinity monitoring and control is even more important than pH or VFA [22]. The methane-producing bacteria have an optimal growth in the pH range 6.6–7.5, although the stabilization of methane production may be maintained at pH between 6.0 and 8.0 [23]. The pH values below 6.0 and above 8.3 should be avoided, so that methanogen bacteria are not inhibited [9]. However, in the case of industrial wastewater that do not have sufficient alkalinity, the addition of chemicals is required [24,25]. The need for pH neutralization increases the overall operational cost, as well as the environmental footprint of the applied process [26]. Proteins and other organic compounds, also bicarbonate, take a part in the buffering capacity and the resistance to changes in pH [27]. It's recommended that the amount of alkalinity in the wastewater entering the anaerobic system is in the range of 2,000 to 4,000 mg $CaCO_3$/L [9]. Therefore the use of alkaline supply compounds, which leads to an increase in the pH of the wastewater entering the anaerobic reactor, should be considered [28]. Neutralization of the acidic industrial wastewater by the use of commercial chemicals such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), calcium hydroxide ($Ca(OH)_2$), and magnesium oxide (MgO) is recommended [29]. The use of each of the above chemical compounds varies depending on the type and composition of the wastewater, issues of operation and maintenance, availability of compounds, cost, effective pH control and long-lasting alkalinity, etc.

The anaerobic biological treatment system of Hamedan industrial town treatment plant, which is intended to reduce the organic load of wastewater before the aerobic biological treatment system, is of ABR type, which has low efficiency in wastewater treatment. The reason for this low efficiency of wastewater treatment can be attributed to the lack of sufficient alkalinity in the inlet wastewater. In this wastewater treatment plant, in order to increase the alkalinity, NaOH is used to adjust the pH of the wastewater, which has not had much effect on the system performance. Since pH and low alkalinity effluents increase the solubility of heavy metals and inhibit anaerobic digestion, which ultimately leads to reduced performance of the wastewater treatment system [30]. Therefore, chemical treatment is required to treat this type of wastewater. Therefore, in this study, in addition to examining the parameters affecting the performance of the ABR system, the appropriate alkaline substance to ensure the proper alkalinity of the ABR unit was also examined. In order to provide optimal alkalinity, four common neutralizing agents including NaOH, Na_2CO_3, $Ca(OH)_2$, and MgO were used. Also, in order to improve the performance of each alkaline substances, optimal performance conditions such as dose, contact time and mixing rate were evaluated. Finally, according to the factors affecting the selection of alkali, the optimal alkaline substances was selected.

2. Materials and methods

2.1. Chemicals and reagents

The chemicals utilized in the present study were of analytical grade, and they were used without further purification. The total chemicals required for this study, including NaOH, Na_2CO_3, $Ca(OH)_2$, and MgO, sulfuric acid (H_2SO_4), were provided by Sigma-Aldrich (St. Louis, MO, USA).

2.2. Wastewater preparation

This research is a cross-sectional descriptive study that was sampled from ABR of an industrial town in Hamedan, Iran for 4 months (from June to September 2019). The daily fluctuations of this wastewater treatment plant were between 900–500 m^3. The constituent units of this wastewater treatment plant including screening, grit chamber, equalization basin, anaerobic reactor (2 units), aeration lagoon, sedimentation unit and chlorine injection unit. The anaerobic unit of this wastewater treatment plant was ABR anaerobic system.

The characteristics of raw wastewater used in this research are shown in Table 1. The samples were collected in two 20-L containers and immediately transferred to the chemistry laboratory of the Faculty of Health of Hamadan University of Medical Sciences for chemical tests. The sampling type in this study was composite. All sampling and testing conditions were performed according to the guidelines of the standard method [31]. All experiments were performed at ambient temperature.

The experiments were performed using the jar test. For this purpose, four common neutralizing agents including NaOH (1–2 g/L), Na_2CO_3 (1.5–2 g/L), $Ca(OH)_2$ (1–2 g/L) and MgO nanoparticles (0.5–1 g/L) to provide the required alkalinity (2,000–4,000 mg $CaCO_3$/L) was evaluated in the anaerobic process.

In order to perform the experiments, 1 L of raw wastewater was dumped in 6 jar test beaker. It should be noted that in determining the optimal amount of all variables, a beaker was considered as a control sample. Then the range of different concentrations of the studied neutralizers (NaOH, Na_2CO_3, $Ca(OH)_2$, and MgO) was prepared and for each neutralizer separately, these concentrations (according to the amount of neutralization of that substance) were added to each beaker and placed in a jar test for 1 min at mixing rate of 1,000 rpm. At the end of the contact time, the pH of the samples was measured and based on the best pH and alkalinity, the best neutralizing agent and its optimal dose were selected.

To determine the optimal contact time of each alkaline substances, the optimal concentration of each substance at the contact times (1–5 min) and the mixing rate of 50 rpm were examined, then the alkalinity and pH were measured and recorded.

In order to determine the optimal mixing speed, the dose values of each alkaline substances were tested at the optimal contact time and at a mixing rate of 25–150 rpm, then the alkalinity and pH of the samples were measured and recorded.

In order to determine the type and optimal concentration of alkaline substances, the above values were tested for 1 min at a mixing rate of 100 rpm, and finally the alkalinity and pH of each were measured and recorded.

The pH test was performed using pH meter (Sension model, Systec-Germany country) and total alkalinity test was performed using H_2SO_4 titration method (0.02 N) according to the standard method. The number of samples was calculated using one-factor-at-a-time (OFAT) method and 224 samples (4 × 56 = 224) were prepared. Data analysis was performed using Microsoft Excel version 20.

Table 1
Characteristics of raw wastewater used in research

Parameter	Sampling period			
	1	2	3	4
Alkalinity (mg $CaCO_3$/L)	620	660	760	600
pH	6.3	6.7	7	5.8

3. Results and discussion

3.1. Effect of concentration

In Figs. 1–4 has been shown the effect of concentration on the production of alkalinity by $Ca(OH)_2$, NaOH, Na_2CO_3 and MgO in the contact time of 1 min and mixing rate of 100 rpm and concentration range 1.11–1.35, 1.2–1.46, 1.59–1.93, and 0.6–0.73 g/L, respectively. The results presented in Fig. 1 show that the maximum and minimum alkalinity produced by $Ca(OH)_2$ were 2,260 and 1,100 $CaCO_3$/L at pH 9.4 and 8.7, respectively, which are related to the second sampling period with a concentration of 1.35 g/L and the third sampling period with a concentration of 1.29 g/L. The results presented in Fig. 2 show the alkaline values produced by different concentrations of NaOH

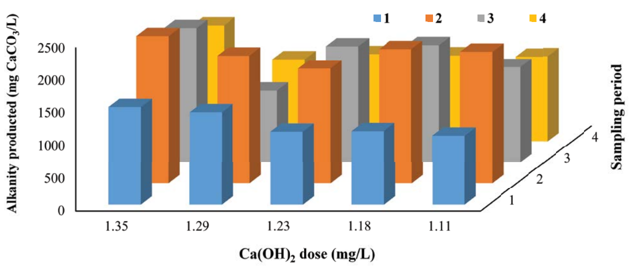

Fig. 1. Effect of various concentration of $Ca(OH)_2$ on alkalinity production.

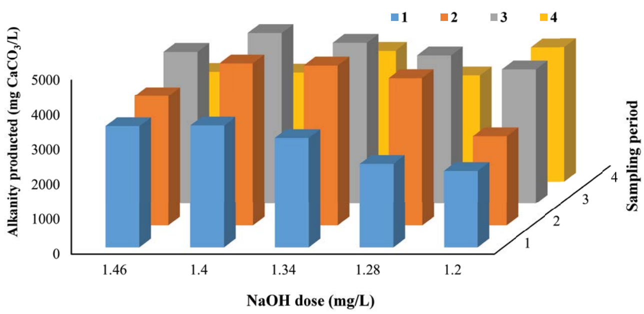

Fig. 2. Effect of various concentration of NaOH on alkalinity production.

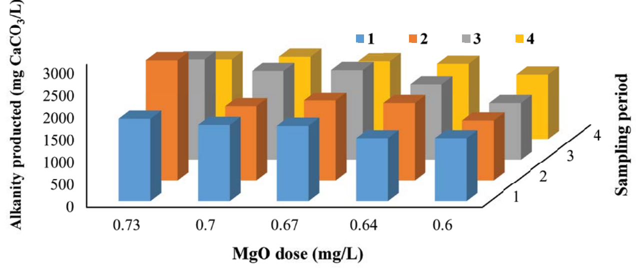

Fig. 3. Effect of various concentration of MgO on alkalinity production.

during different sampling periods. The maximum and minimum alkalinity produced by NaOH were 4,900 and 2,200 mg $CaCO_3$/L at pH 11.9 and 9.5, respectively. These values were related to the third sampling period with a concentration of 1.4 g/L and the first sampling period with a concentration of 1.2 g/L. The results for the alkalinity produced by different concentrations of MgO during different sampling periods are presented in Fig. 3. According to the results, the maximum and minimum alkalinity produced by MgO were 2,700 and 1,270 mg $CaCO_3$/L at pH 9.56 and 8.3, respectively. These values were related to the second sampling period with a concentration of 0.73 g/L and the third sampling period with a concentration of 0.6 g/L. Also, according to Fig. 4, the maximum and minimum alkalinity produced by Na_2CO_3 were 4,560 and 2,760 mg $CaCO_3$/L at pH 11.7 and 9.6, respectively, which are related to the third sampling period with a concentration of 1.93 g/L and the fourth sampling period with a concentration 1.59 g/L. The results for optimum concentration and alkalinity produced by each alkaline substances are shown in Fig. 5. The optimum concentration values for NaOH, $Ca(OH)_2$, MgO, and Na_2CO_3 were obtained as 1.4, 1.35, 0.73, and 1.93 g/L, respectively. At the above concentrations, the alkalinity values produced were obtained 4,050 ± 861.2, 1,897.5 ± 335.5, 4,060 ± 336.6, 2,150 ± 421.5 mg $CaCO_3$/L, respectively. Based on the presented results, the alkalinity produced during different sampling periods under the same conditions is variable, which can be attributed to the difference in wastewater conditions such as temperature, the presence of minerals and borate ions, phosphate and silicate [32,33]. The increase in alkalinity produced by $Ca(OH)_2$, Na_2CO_3 and MgO due to the increase in the concentration of alkali can be attributed to the increase in the number of particles and thus to the increase in the reaction between the particles and the reducing factors of alkalinity. At the extreme alkalinity, strong electrostatic repulsion of ionized groups occurred, leading to solubilization of proteins, which was reduced alkalinity [34].

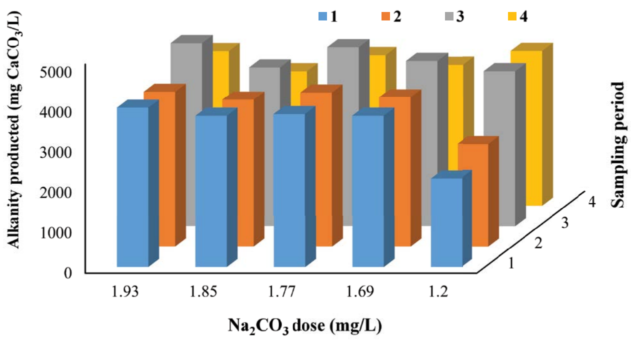

Fig. 4. Effect of various concentration of Na_2CO_3 on alkalinity production.

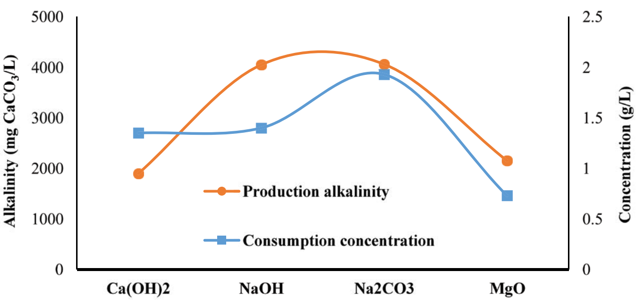

Fig. 5. Optimum concentrations and alkalinity produced by alkaline substances.

3.2. Effect of contact time

In Figs. 6–10 has been shown the effect of contact time on the production of alkalinity by $Ca(OH)_2$, NaOH, Na_2CO_3 and MgO in concentration of 1.35, 1.46, 1.93 and 0.73 g/L

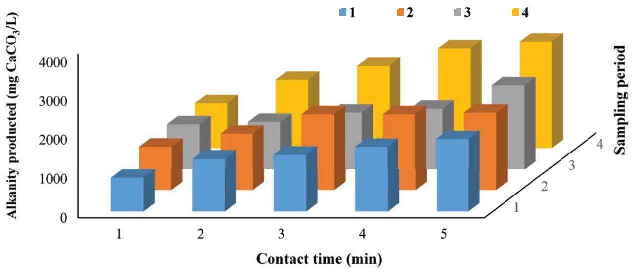

Fig. 6. Effect of various contact time of $Ca(OH)_2$ on alkalinity production.

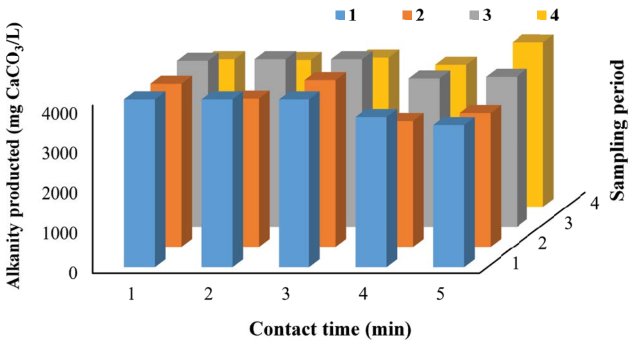

Fig. 7. Effect of various contact time of NaOH on alkalinity production.

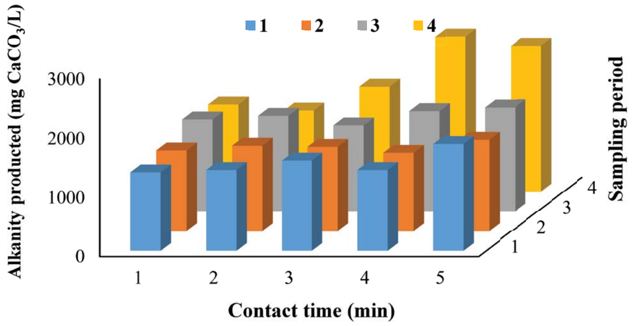

Fig. 8. Effect of various contact time of MgO on alkalinity production.

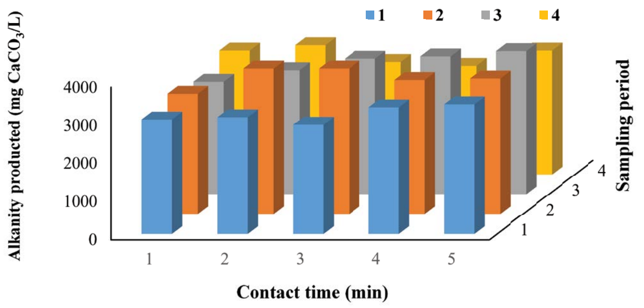

Fig. 9. Effect of various contact time of Na_2CO_3 on alkalinity production.

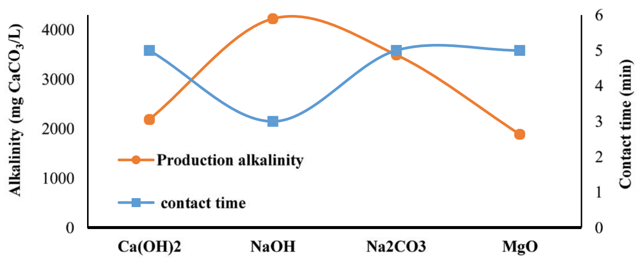

Fig. 10. Optimum contact times and alkalis produced by alkaline substances.

with the contact time of 1–5 min and mixing rate of 50 RPM, respectively. The maximum alkalinity produced by $Ca(OH)_2$, Na_2CO_3 and MgO at a contact time of 5 min was obtained 2,190 ± 386.6 mg $CaCO_3$/L at pH of 9.47, 3,495 ± 219 mg $CaCO_3$/L at pH 10.2, and 1,890 ± 396.8 mg $CaCO_3$/L at pH 8.9, respectively. So that the minimum alkalinity produced by $Ca(OH)_2$, Na_2CO_3 and MgO at a contact time of 1 min was obtained 1,075 ± 144.5 mg $CaCO_3$/L at pH of 8.36, 3,095 ± 139.8 mg $CaCO_3$/L at pH 9.9, and 1,430 ± 110.1 mg $CaCO_3$/L at pH 8.2, respectively. On the other hand, for NaOH (Fig. 7), the alkalinity produced decreased after 3 min of contact time. Thus, 3 min was considered as the optimum contact time for the NaOH, because the additional increase in the time did not increase the alkalinity produced. The maximum and minimum alkalinity produced by NaOH was obtained 4,225.5 ± 355.6 and 3,550.5 ± 273.9 mg $CaCO_3$/L with pH 11.2 and 10.1 and at contact time of 3 and 1 min.

3.3. Effect of mixing rate

Mixing is used to minimize the variability of water and wastewater flow rates and composition. Mixing must be provided in the neutralization tanks to reduce the required reaction time [35]. In Figs. 11–15 has been shown the effect of mixing rate on the production of alkalinity by 1.35 g/L $Ca(OH)_2$, 1.4 g/L NaOH, 1.93 g/L Na_2CO_3 and 0.73 g/L MgO in the contact time of 1 min and mixing rate of 25–150 rpm. The results in Fig. 11 show that the maximum and minimum alkalinity produced by $Ca(OH)_2$ were 2,960 and 1,060 mg $CaCO_3$/L with pH 8.1 and 9.2, respectively, which is related to the third sampling period with a mixing rate of 150 and 25 rpm. According to Fig. 12 maximum and

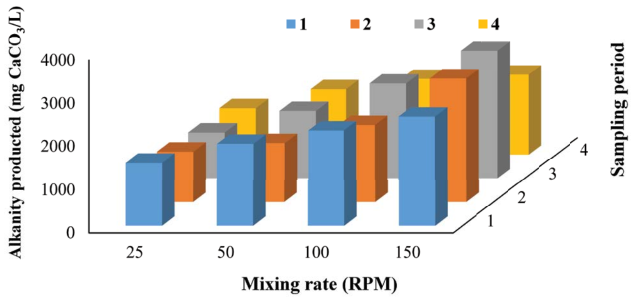

Fig. 11. Effect of various concentration on alkalinity production by $Ca(OH)_2$.

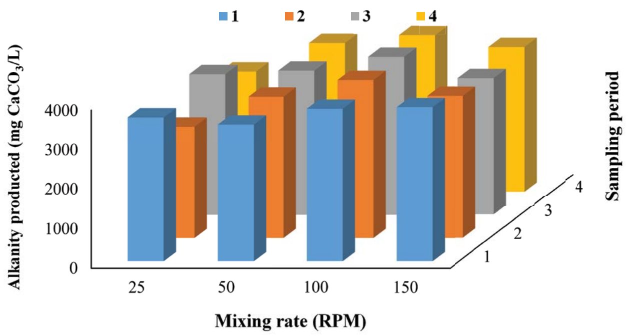

Fig. 12. Effect of various concentration on alkalinity production by NaOH.

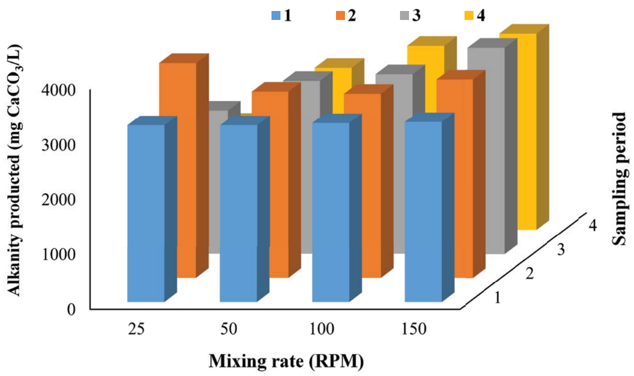

Fig. 13. Effect of various concentration on alkalinity production by Na_2CO_3.

minimum alkalinity produced by NaOH were 4,100 and 2,820 mg $CaCO_3$/L with pH 9.5 and 10.8, respectively, which is related to the third and second sampling period with a mixing rate of 100 and 25 rpm. The results obtained from the effect of mixing rate on the production of alkalinity by Na_2CO_3 and MgO showed that the maximum alkalinity produced were 3,760 and 2,700 mg $CaCO_3$/L with pH 10.4 and 9.6, respectively, which is related to the third sampling period at a mixing rate of 150 rpm. Also, the minimum alkalinity produced by Na_2CO_3 and MgO were 1,960 and 1,240 mg $CaCO_3$/L with pH 9.46 and 8.4, respectively, which is related to the fourth and second periods of sampling were obtained at a mixing rate of 25 rpm (Figs. 13 and 14). The results of Fig. 15 show the optimal mixing rate for $Ca(OH)_2$, Na_2CO_3, and MgO were 150 rpm and for NaOH of 100 rpm. The average alkalinity produced during the sampling period was obtained for $Ca(OH)_2$, NaOH, Na_2CO_3, and MgO of 2550 ± 497, 3980 ± 99.3, 3560 ± 202, and 2,370 ± 386.6 mg $CaCO_3$/L, respectively. According to Table 2, the contact time and mixing rate required to produce one unit of alkalinity by NaOH are less than other alkalines. The reason for this can be related to the solubility of each of these materials, because in the pressure of an atmosphere and temperature 20°C, the solubility of NaOH, Na_2CO_3, $Ca(OH)_2$ and MgO in aqueous solutions are 109, 21.5, and 0.173, and 0.0086 g per 100 mL, respectively. In terms of alkaline substances consumption, MgO with the lowest dose (0.3 mg/L) and Na_2CO_3 with the highest dose (0.54 mg/L)

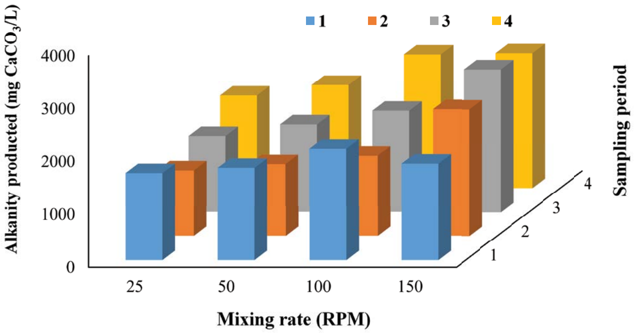

Fig. 14. Effect of various mixing rate on alkalinity production by MgO.

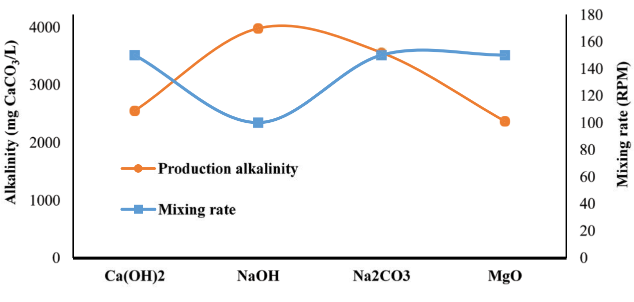

Fig. 15. Optimum mixing and alkalinity values produced by alkaline substances.

provides alkalinity equal to 1 mg $CaCO_3$/L. According to the above results it can be said that MgO, due to its ability to provide more alkalinity it can be determined as the optimum alkaline substance to provide the alkalinity required by the anaerobic unit. MgO is an excellent choice for anaerobic and aerobic biological wastewater treatment plants that require additives for pH and alkalinity control. The use of MgO in biological wastewater treatment plants can be prioritized for reasons such as lower cost and more stable alkalinity production [36]. These benefits are due to MgO high alkalinity (acid-neutralizing capacity) and pH buffering properties [37]. A major advantage that MgO has over other neutralizing agents is enhanced precipitation of heavy metals with minimal sludge production. Unlike NaOH and lime which form high volume gelatinous heavy metal sludge, MgO precipitation forms a denser more crystalline solid.

The decomposition of magnesium hydroxide sludge is easier due to its high density and therefore produces less sludge than NaOH and lime. MgO is a buffered alkalinity source, so it has less chance of spiking system pH due to over addition [38]. Even with over addition the maximum pH that can be attained with MgO is 9.0. The MgO is a good source of nutrients and alkalinity by providing magnesium (Mg) and support bacterial growth. MgO can improve secondary solids settling and dewatering due to improved biofloc formation [39]. MgO is safe for humans and the environment and does not cause toxicity and corrosion. Unlike lime, MgO does not cause scaling in equipment that necessitates frequent cleaning and maintenance [37]. Excessive consumption of NaOH can quickly increase the pH of the stream to more than 12, the dangers posed by high concentrations of NaOH provide many precautions for wastewater treatment plant operators exposed to this substance [22,40]. It is necessary to have minimal personal protective equipment and immediate washing stations in the treatment plant. Another factor that limits the use of sodium to magnesium oxide is the freezing point of 4.4°C, which requires its use in hot climates or heating tanks [41]. One of the most important aspects that limit the use of Na_2CO_3 as an alkaline substance is the production of abundant foam which is difficult to control [9,35]. The use of calcium hydroxide (lime) for reasons such as average effect time, higher consumption and increased sludge, which increases the cost of maintenance and disposal of sludge and in severe cases leads to blockage of treatment lines with more restrictions than MgO is also faced with the use of alkaline lime due to the presence of impurities such as insoluble calcium sulfate can cause problems such as excessive wear of valves and pumps, in addition to increasing the suspended solids in

Table 2
Concentration, contact time and optimal mixing rate to provide an alkalinity (mg $CaCO_3$/L)

Alkaline type	Purity (%)	Optimum concentration (mg/L)	Optimum mixing rate (RPM)	Optimum contact time (min)
$Ca(OH)_2$	95	0.53	150	5
NaOH	98	0.35	100	3
Na_2CO_3	98	0.54	150	5
MgO	97	0.3	150	5

the sewage and the production of dust in consumption time leads to intolerable irritation of the throat and nose another problem is the use of lime [42].

3.4. Study limitation and recommendation

Rainfall can change the alkalinity of the wastewater in the wastewater treatment plant. For this purpose, sampling was not done until a few days after the time of rainfall, which was one of the limitations of the present study. It is suggested that in future studies, the amounts of biogas produced and the amount of volatile fatty acids (VFA) produced by the ABR aerobic system be investigated. It is also suggested that in future studies the effect of other factors producing alkalinity and the effect of other environmental parameters on the performance of the anaerobic reactor be investigated.

4. Conclusion

The aim of this study was to investigate the effect of dose, contact time and mixing rate on the production of alkalinity in several alkaline substances in an ABR reactor. The results showed that alkaline substances concentration, mixing rate and contact time were directly related to alkalinity production. As the dose of alkaline substances, contact time and mixing rate increased, alkalinity production also increased. The optimal alkalinity of four common substances (NaOH, Na_2CO_3, $Ca(OH)_2$ and MgO) was investigated to regulate the alkalinity of the ABR biological system. According to the results of alkalinity resulting from the dissolution of Na_2CO_3, $Ca(OH)_2$ and MgO, with increasing the contact time and mixing rate increased. Thus, in these alkaline substances, the optimal contact time and mixing rate were obtained under the conditions of maximum contact time (5 min) and mixing rate (150 rpm), while NaOH at a contact time of 3 min and a mixing rate of 100 RPM produced an alkalinity of 2,000–4,000 mg $CaCO_3$/L. The results also showed that MgO, despite its low solubility at contact time of 5 min and a mixing rate of 150 rpm with a lower concentration than other alkaline substances, can produce an alkalinity unit in terms of $CaCO_3$. Therefore, MgO can be prioritized in the alkalinity production process due to its safety, easier maintenance, required dose and lower cost.

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Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this work.

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