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Successive cycles of sorption/regeneration for granular activated carbon in the removal of nitrate ions

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ABSTRACT

Granular activated carbon was used in the sorption of nitrate ions with subsequent regeneration by assessing the capacity of the sorbent in successive cycles of sorption/regeneration (S/R). Solutions of HCl, $C_6H_8O_7$, NaOH, $CaCl_2$, as well as H_2O were employed in the regeneration of activated carbon saturated with nitrate. Solution of $CaCl_2$ was the best regenerative agent. Contact times of 30 min and 400 mL of 2,000 mg L^{-1} $CaCl_2$ solution were used for regeneration. Twenty cycles of S/R, which yielded 54% nitrate removal at the end of the cycles, were possible. During regeneration, the concentration of Ca^{2+} in the solution of $CaCl_2$ was monitored to keep the initial concentration constant. After 20 S/R cycles, the sorbent was desorbed using 50 mL of 100 mg L^{-1} HCl and 50 mL H_2O (60°C). Over 20 S/R cycles were performed for the sorbent recovered with HCl and 20 S/R cycles for the sorbent desorbed with H_2O (60°C). Approximately 58% of nitrate removal was achieved at the end of 20 S/R cycles in both cases. We performed a total of 60 S/R cycles with the average removal of 55% at the end of the last cycle.

Keywords: Regeneration; Sorption; Activated carbon; Nitrate ions; Cycles

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1. Introduction

There are several established methods for the regeneration of activated carbon saturated with ions. Shende and Mahajani [1] studied the wet oxidative regeneration of activated carbon loaded with dyes, Weng and Hsu [2] investigated an electrochemical process applied to the regeneration of activated carbon saturated from a sewage wastewater while Tan and Lee [3] evaluated the efficiency of supercritical CO_2 desorption in fixed bed of activated carbon saturated with toluene. Similarly, Sabio and colleagues [4] used three techniques of thermal regeneration: pyrolysis, gasification pyrolysis, and gasification directly, using activated carbon saturated with *p*-nitrophenol. Cooney and colleagues [5] evaluated 19 solvents in batch process that involves desorption of organic adsorbate

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(phenol) from activated carbon. Liu et al. [6] studied the regeneration by microwave irradiation of activated carbon saturated with 2,4,5-trichlorobiphenyl (PCB29). Coelho and colleagues [7] studied the effect of chemical and structural properties of the surface of activated carbon in sorption process of molinate in aqueous solutions with subsequent bioregeneration using bacterial cultures. Drouiche and colleagues [8] also developed a treatment method for regenerating activated carbon saturated with H_2S using electrodialysis equipped with cationic, anionic, and a bipolar membrane.

Each of the regeneration techniques has its respective characteristics and application area. However, cost is the limiting factor for the application of these methods. At a small scale, San Miguel and colleagues [9] reported that the thermal regeneration is the most widely used technique in the recovery of activated carbon (saturated mainly with organic compounds). This technique, however, has some disadvantages such as high power demand due to the high temperatures employed in the process; considerable amount of carbon (5–15%) is lost by friction during regeneration and washing.

Usually, the regeneration processes of activated carbon using solvents are employed in reversible sorption methods such as treatment of effluents with high concentrations of ions and effluents containing high commercial values. According to Guo and colleagues [10], the advantages of solvent regeneration technique include: (i) the process can recover useful substances from the regeneration liquid; (ii) sorbent reactivation can be operated in a sorption tower; (iii) the technical process is easy to implement in practical production processes; and (iv) loss of activated carbon is lesser. On the other hand, the disadvantages of solvent regeneration method include: (i) solvents that can constitute pollutants are desorbed; (ii) regeneration is not always complete because the pores in the activated carbon can easily become air logged, which affects the recovery rate; and (iii) it is necessary to find a method for recovery of solvents free of pollutants.

This study aimed to evaluate different solvents for the regeneration of activated carbon used in the removal of ions in aqueous solutions.

2. Materials and methods

2.1. Specifications of the reagents and sorbent

For this work, granular activated carbon (GAC) (Synth®, Diadema, São Paulo, Brazil) of particle size between 1 and 2 mm was used as a solid sorbent. Sodium nitrate (NO^{-3}) was used as adsorbate. Calcium chloride ($CaCl_2$) was used for surface modification of the activated carbon. The regeneration agents used are citric acid ($C_6H_8O_7$), water (H_2O at 60°C), hydrochloric acid (HCl), calcium chloride ($CaCl_2$), and sodium hydroxide (NaOH). Supply: NO^{-3}, NaOH, $CaCl_2$, HCl and $C_6H_8O_7$ (Sigma-Aldrich®, São Paulo, Brazil).

2.2. Chemical modification of GAC

A 2,000 mg L^{-1} of $CaCl_2$ (1,000 mL) was prepared. The solution was transferred into a 1,000 mL beaker, where a 10 g of GAC was added and stirred for 1 h. Subsequently, the solution was filtered and the residue (GAC) was dried 24 h at 25°C.

2.3. Sorption experiments and regeneration

A 20 mg L^{-1} of NO^{-3} solution was used; a 4 g of GAC was added to 200 mL of NO^{-3} solution at pH 6 and agitated for 30 min (optimum conditions [11]). The process began by treating the GAC with $CaCl_2$ as described in Section 2.2. The solution of NO^{-3} was put in 200 mL bottles and was subjected to pH adjustment and then placed in stirrer (Shaker Wagner–Marconi, Brazil) for a specified time. At the end of the agitation, the suspension was filtered, and aliquot was quantified using Win Cary–UV spectrophotometer (Model 1-E) to determine the concentration of NO^{-3} in the solution after the sorption process. Knowing the initial concentration and final concentration of NO^{-3}, it was possible to calculate the percentage of removal with the aid of Eq. (1).

$$\text{Removal}\,(\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (1)$$

where C_i is the initial concentration of NO^{-3} in the solution; C_f is the final concentration of NO^{-3}.

The regeneration of GAC saturated with NO^{-3} was carried out using 400 mL of regenerating solution at concentrations predetermined in accordance with the regenerating agent used. In this process, a 4 g of NO^{-3}-saturated GAC was added to 400 mL of regenerating agent's solution, and stirred for 30 min on the shaker. Subsequently, the regenerating solution was decanted and the carbon was washed with 50 mL of water (25°C) to complete the regeneration cycle. The regenerated GAC was used for another sorption step (without treatment with $CaCl_2$). The percentage efficiency of the regeneration process was evaluated using Eq. (2). Sorption–regeneration process was carried out for seven consecutive cycles using $C_6H_8O_7$,

H_2O (60˚C), HCl and $CaCl_2$. However, five cycles of sorption–regeneration process were possible for NaOH due to low efficiency.

For H_2O at 60˚C as regenerative agent, desorption was carried out in a beaker of 1,000 mL placed in a thermostatic bath coupled with a mechanical stirrer. The temperature was controlled by the equipment and a thermometer placed adjacent to the beaker. The efficiency was calculated using Eq. (2).

$$\text{Efficiency}\,(\%) = \frac{\text{Removal}\,(\%)\,\text{in the test}}{(\text{Removal}\,(\%)\,\text{initial}/100)} \tag{2}$$

2.4. Regeneration time dependence

The saturated GAC (4 g) was subjected to the process of regeneration using a 400 mL of HCl (10 mg L^{-1}) or H_2O (60˚C), varying the contact time of 5, 10, 15, 20, 30, 40, 50, and 60 min. The GAC was subjected to sorption process to determine the percentage of removal for the various time-dependence experiments (regeneration).

2.5. Sorption/regeneration (S/R) tests

In this step, the sorption process followed the same procedures described in Section 2.3.

For the regeneration step, solutions of $CaCl_2$ (regenerating agent) were used due to its performance in the preliminary tests. The GAC (4 g) saturated with NO^{-3} was subjected to the regeneration process using 400 mL of 2,000 mg L^{-1} $CaCl_2$ solution (equivalent to 544 mg L^{-1} of Ca^{2+}). The mixture was placed in a 1,000 mL beaker and stirred for 30 min. The same regenerative solution was used for all cycles. During the process, the Ca^{2+} in the regeneration solution was replaced to ensure that the concentration was always close to the initial concentration, an amount determined to be the best in the present process. After 20 cycles of sorption/regeneration, the GAC was subjected to desorption using (A) 50 mL of 100 mg L^{-1} HCl or (B) 50 mL H_2O (60˚C). After this process, the GAC was added to $CaCl_2$ solution and another sorption/regeneration cycles were carried out. After each step, the removal efficiency and the percentage were determined as described in the previous section. Fig. 1 shows a schematic diagram used for the sorption/regeneration.

2.6. Calcium analysis

For the quantitative determination of calcium (Ca^{2+}) in the process of sorption/regeneration, EDTA titration method was used [12].

3. Results and discussion

3.1. Influence of regeneration time

Fig. 2 shows the influence of the regeneration time using 10 mg L^{-1} HCl and H_2O (60˚C). It is noted that as the regeneration time increases, the removal capacity increases up to a point for both solvents, after which stabilization in the process occurred. It can be inferred that sorbate migrates to the regenerant solution up to certain concentration. When an equilibrium is reached, the sorbate migration is practically stopped or the sorption takes place in the same intensity as desorption. The results also showed that when the regeneration time for the 10 mg L^{-1} HCl was 30 min, the removal capacity was constant, and showed the best results (65%). For H_2O at 60˚C, 30 min was also suitable, and showed 60% removal.

It is observed that desorption promotes more pronounced removal until 10 min. However, when the process reached 30 min, there was no apparent change in the percentage removal. Thus, to study cycles of sorption/regeneration, 30 min was used as regeneration time.

3.2. Studies of different regenerative agents

Table 1 shows the results of efficiency in regeneration percentage. The sorption capacity before the first cycle of the modified GAC was considered to have 100% regenerative efficiency, therefore, other values were calculated based on the initial sorption capacity. The conditions for sorption in all cases were: pH 6.0, contact time 30 min, concentration of sorbent solid (C_{ss}) 20 g L^{-1}, and 200 mL of solution with initial

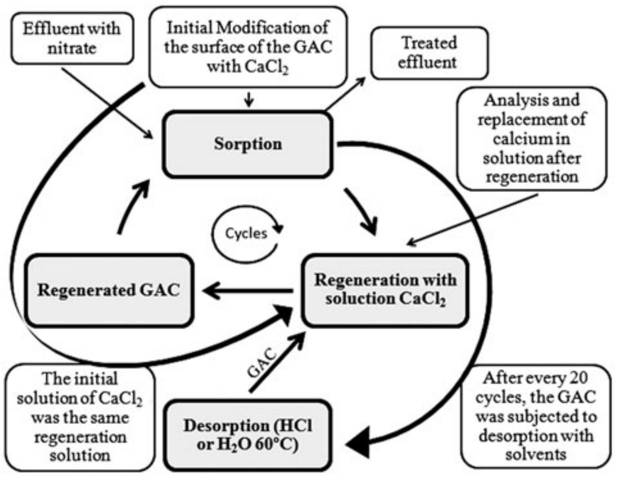

Fig. 1. Schematic diagram of the system used in the sorption/regeneration tests.

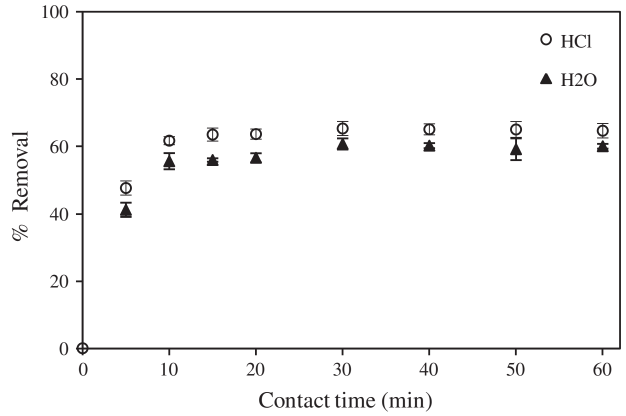

Fig. 2. Effect of desorption time on the percentage of removal.

concentration (C_i) of 20 mg L^{-1} of nitrate. Conditions for desorption: time 30 min and 400 mL of regeneration solution.

The results of the regenerative cycles in which desorption was carried out with solution of 100 mg L^{-1} NaOH (only five cycles S/R were completed). It is observed that after the first desorption cycle the efficiency was not satisfactory, probably due to the deprotonation of the surface of the functional groups that are important for the sorption process, leaving GAC with negative charge.

For desorption process utilizing citric acid ($C_6H_8O_7$), the behavior was similar to the desorption process in which NaOH was used as a regenerating agent. In the first cycle of S/R for $C_6H_8O_7$ efficiency was 25.33%, which makes the process unviable for use in successive cycles.

With desorption using H_2O at 60°C, seven cycles of S/R could be performed with efficiency of 32.42% at the end. Until fourth cycle, the process was efficient above 50%.

For 10 mg L^{-1} HCl, process shows attractive results in the first five cycles (efficiency above 50%). Similarly, 20 mg L^{-1} HCl shows the process efficiency above 50% in all cycles.

The decrease in efficiency can be explained based on the following reasons: (i) incomplete desorption of nitrate in the solid phase (ii) reduction of the calcium in the surface of GAC (calcium from the initial modification), and (iii) desorption of substances of nature or structure of GAC.

Using $CaCl_2$ (20 mg L^{-1}), after seven cycles S/R, the efficiency was 53.19%. Based on this result, we chose to increase the concentration of the regeneration solution to 2,000 mg L^{-1}, the same concentration of solution was used for surface modification of the GAC.

With 2,000 mg L^{-1} of $CaCl_2$, and reusing the same regeneration solution (AS) in all cycles, the process was made more effective. It can be seen from Table 1 that efficiencies of the first and second cycles were more effective (higher percentage) compared with the sorption made with new GAC. It is noteworthy that in all cycles, S/R efficiencies were greater than 80% for 2,000 mg L^{-1} of $CaCl_2$ as regenerative solution.

Due to the good results obtained with 2,000 mg L^{-1} of $CaCl_2$ as regenerative agent and when same solution was reused, experiments were performed in which a new solution of 2,000 mg L^{-1} $CaCl_2$ was used in each cycle. The results showed that removal efficiency in this case, unlike the others, grew at each cycle, reaching efficiency of 108.09% at the end of the seventh cycle of S/R. In other words, more nitrate ions were removed in the seventh cycle than in the initial sorption. This result shows that the treated GAC (regenerated with 2,000 mg L^{-1} of $CaCl_2$) exhibits an increase in sorption capacity, which makes the process efficient and economically attractive from the standpoint of industrial applications or in the

Table 1
Efficiency in the regeneration of GAC modified with $CaCl_2$ for different regenerative agents.

		% Efficiency of regeneration							
Cycles		0	1	2	3	4	5	6	7
Regenerative agents	NaOH 100 mg L^{-1}	100.00	7.30	7.84	5.88	5.43	7.49	*	*
	$C_6H_8O_7$ 100 mg L^{-1}	100.00	25.33	24.97	17.50	14.12	13.84	11.65	10.52
	H_2O 60°C	100.00	81.11	57.03	55.03	53.80	48.99	45.96	32.42
	HCl 10 mg L^{-1}	100.00	85.48	70.30	61.94	59.82	54.93	49.34	46.46
	HCl 20 mg L^{-1}	100.00	93.99	81.16	72.89	69.86	65.60	58.80	56.32
	$CaCl_2$ 20 mg L^{-1}	100.00	84.59	85.25	69.01	68.14	65.16	63.03	53.19
	$CaCl_2$ 2,000 mg L¯1 AS	100.00	106.37	104.73	97.95	96.72	90.71	84.19	80.31
	$CaCl_2$ 2,000 mg L^{-1}	100.00	104.59	105.43	105.56	106.47	107.34	108.02	108.09

*AS—same solution for all stages of desorption.

treatment of water that is polluted with nitrate ions for human consumption.

3.3. Cycles of sorption/regeneration (S/R)

In this study, the same regeneration solution was reused for each cycle of S/R, i.e. the solution was not changed, only the calcium concentration was maintained, which was always equal to the initial concentration. Fig. 3 shows the percentage of removal of nitrate in the aqueous phase in every regenerative cycle.

It is observed that the sorption capacity of regenerated GAC in the first four cycles increased, i.e. removed more nitrate in the fourth cycle (82.2%) than in the first (71.1%). However, a gradual decrease in the percentage of removal began from the fifth cycle until the twentieth cycle, where the removal was 54.3%.

The removal of nitrate increased in the first cycle because calcium ions were added to the regenerating solution, which increases the number of positively charged active sites. When all the sites were filled by Ca^{2+}, the removal capacity of the sorbent began to decrease.

After the completion of 20 S/R cycles, with about 55% removal, the process was no more efficient. At this time, there was a need for renewal of the sorbent. Therefore, nitrate sorbed on GAC was desorbed with two different solutions: (A) 50 mL of 100 mg L^{-1} HCl and (B) 50 mL H_2O 60°C for 4 g of saturated sorbent.

Two batches of solvent-regenerated GAC were used to evaluate the sorption capacity and regeneration of GAC modified with $CaCl_2$ for more 20 S/R cycles (21st–40th). Fig. 3 shows the results. The GAC after the desorption process, was treated with $CaCl_2$ solution (regenerative solution), before the second stage of 20 cycles.

For desorption using both solvents, the GAC has excellent capacity for nitrate removal. More than 85% of percentage removal was achieved in the 21st S/R cycle for the two cases and this value is higher than those values observed in the first 20 cycles. There was no increase in the regeneration after the 21st cycle (from 21st to 40th cycles of S/R) unlike the first stage where we had an increase in the first four cycles. At the end of the 41st cycle of S/R, however, removal of nitrate was possible in both cases; approximately 58% or above the value obtained at the end of 20th cycle of S/R that was approximately 55%.

Based on the results obtained after GAC passed through 20 S/R cycles and after the 40th cycle, the removal was still above 50%. More stages of 20 S/R cycles were made.

Similarly, steps of desorption were carried out with 50 mL of 100 mg L^{-1} HCl and 50 mL of H_2O at 60°C. Immediately after the sorbent was treated with $CaCl_2$, more stages of 20 S/R cycles (41st–60th) were initiated. Fig. 3 shows the results for this study.

We observed a pattern similar to the results presented for the second stage (21st–40th). In the third step, the initial removal was above 85%, and after the 60th S/R cycle, more than 55% of the anion present in solution was removed. Desorption carried out every 20 S/R cycles, renewed removal capacity of GAC giving the possibility of new applications. This result is confirmed by the sequence of tests performed in this study.

The variation in the concentration of calcium for each regenerative cycle can be seen in Fig. 4. It is observed that there was calcium intake in the first two cycles. After the second cycle, there is a slight

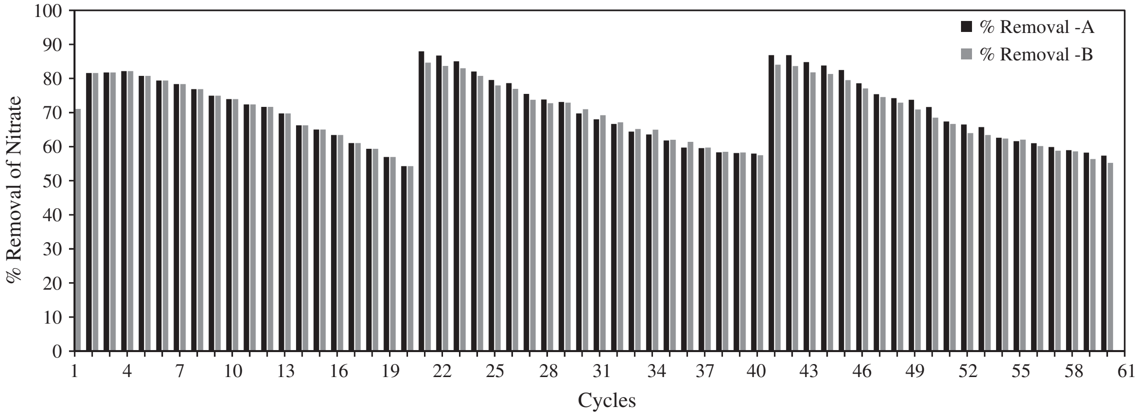

Fig. 3. Percentage removal of nitrate in the aqueous phase in each cycle of regeneration with a solution of $CaCl_2$ 2,000 mg L^{-1}. Desorption: (A) 50 mL of 100 mg L^{-1} HCl and (B) 50 mL of H_2O 60°C.

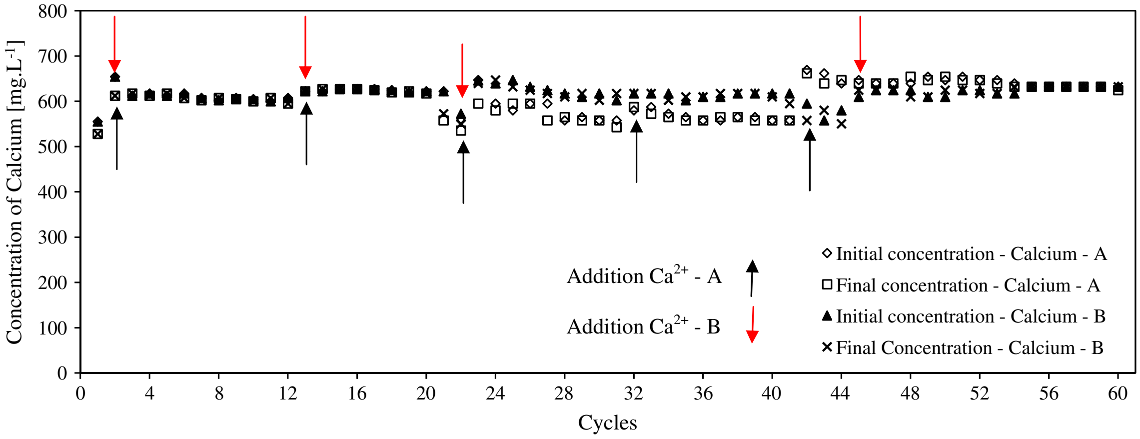

Fig. 4. Calcium concentration in solution during the regeneration cycles. Desorption: (A) 50 mL of 100 mg L^{-1} HCl and (B) 50 mL of H_2O 60°C.

reduction in calcium concentration in solution, but this consumption was not significantly different. After the first cycle, it was necessary to add 40 mg of $CaCl_2$ to replace the calcium consumed, however, 100 mg (60 mg excess) was added. However, it was necessary to add calcium again after the 12th cycle, and from this there was no need to add calcium up the 20th S/R cycles.

For the second step, as seen in Fig. 4, the consumption of calcium in the 21st cycle was greater than the consumption of calcium in the previous steps (1st–20th). In the first cycle, a 4 g of GAC consumed approximately 10 mg of calcium. From the 21st cycle in the case of carbon desorbed with HCl, 46 mg was consumed by the same quantity of GAC but 4 g of corresponding carbon desorbed with H_2O consumed 40 mg calcium. The concentration of calcium in this phase remained practically constant in both cases. A 32 mg of $CaCl_2$ was added to keep the concentration of calcium constant in both cases after the 21st cycle. For the case in which desorption was made with HCl, in the 31st cycle, 21 mg of $CaCl_2$ was added as the concentration was below the required concentration.

The calcium consumption in the third stage (41st–60th) was similar to that of the second stage (21st–40th) for desorption carried out with 50 mL of 100 mg L^{-1} HCl, with a high consumption of calcium after the 41st cycle and consumption of calcium for the process was not relevant for subsequent cycles. Then, it was necessary to add calcium after the 41st cycle, after this, addition of calcium was no longer necessary because the concentration has remained constant.

During desorption with 50 mL of H_2O at 60°C, the behavior of calcium in the solution of regeneration was different from the results obtained so far. It can be seen in Fig. 4 that the use of calcium in the 41st cycle was not high, and there was no need to add calcium in this cycle, $CaCl_2$ was only added at the 45th cycle to supply calcium concentration to the solution for regeneration. Based on this result, it can be concluded that the desorption performed with H_2O at 60°C did not remove all calcium from the surface of the sorbent, this result is considered an attractive and promising because there is less consumption of calcium in the process.

4. Conclusion

The regeneration of the saturated GAC with nitrate using solutions of $C_6H_8O_7$, HCl, NaOH, and H_2O (60°C) improved sorption capacity of carbon. This sorption capacity decreases as S/R cycle increases. The best regenerating agent was 20 mg L^{-1} HCl. The results of $CaCl_2$ as a regenerating agent were surprising. The sorption capacity of regenerated GAC with $CaCl_2$ showed better sorption capacity in the first cycle compared with unregenerated GAC. The optimum contact time for desorption process was 30 min. Sixty (60) cycles of S/R were performed and the GAC was very efficient during the 60 cycles. It was possible to remove 55% of the nitrate from solution at the end of 60th cycle. Both HCl and H_2O (60°C) showed similar results. Twenty (20) cycles of S/R were possible when $CaCl_2$ was used as regenerating agent with percentage of removal > 50% at the end of 20th cycle.

Desorption carried out every 20 cycles of S/R, renewed removal capacity of GAC giving the possibility of new applications. This result is confirmed by the sequence of tests performed in this study. There was no need to change the regenerating solution for 60 cycles of S/R, only the concentration of Ca^{2+} was kept constant. The process can be considered economical because it was not necessary to change the regeneration solution, and always using the same solid sorbents (without loss of sorbent). The amount of $CaCl_2$ added to the process, accounted for 42% (mass) of the total nitrate removed for 60 cycles. This process can be applied to sorption mechanisms involving ion exchange or physical adsorption involving electrostatic attraction.

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