

The present work report the regeneration treatment of granular activated carbon (GAC) saturated with limonene, a non-polar volatile organic compound (VOC) using electrogenerated oxidants mainly based on H_2O_2 . In this approach, limonene was adsorbed onto GAC in a fixed bed column until saturation and further treated by oxidants electrogenerated. The efficiency of regeneration treatment of GAC using oxidants in aqueous phase was evaluated by analyzing the concentration that remained in GAC desorption methanol solution after treatment. It was found that efficiency of treatment can be improved when H_2O_2 is activated by ferrocene promoting the heterogeneous Fenton reaction. However, these values are still low, and by-products generated by conversion of limonene tends to remain adsorbed onto GAC surface after treatment which limit the process. Also, it was verified that limonene in solution can be attacked by hydroxyl radicals generated by H_2O_2 activation which also indicated that difficulty of aqueous oxidants reach internal porous of GAC to oxidize limonene can also limit the applicability of this technique.

Introduction

Volatile organic compounds (VOCs) are emitted from varied sources (industrial processes, vehicle exhaust, solvents, and consumer products) [1], posing significant risks to both human health and the environment due to their harmful nature as pollutants [2]. Granular activated carbon (GAC) adsorption is widely used in treatment of VOCs polluted gas streams. During the treatment, these compounds moves from the air to the surface and pores of the GAC. As result, a subsequent regeneration step is needed to restore its adsorption capacity or, alternatively GAC saturated is sent for disposal and replaced by fresh carbon [3]. The former option is preferable, not only due to the high cost of adsorbent, but also from an environmental perspective.

In the present study, a case study of regeneration of GAC saturated with limonene (LIM), a representative non-polar hydrophobic volatile organic contaminant was conducted. The adsorption capacity of GAC to treat limonene-polluted air streams was evaluated by adsorption tests conducted in both batch and in fixed bed columns. Subsequently, GAC treatment by H_2O_2 -based AOP was investigated, where H_2O_2 electrogenerated on-demand in aqueous solutions using highly efficient electrochemical cells. Then, to promote generation of hydroxyl radicals, the effect of addition of different amounts of ferrocene as heterogeneous catalyst (heterogeneous Fenton-like) and irradiation of solution with ultraviolet-C (UVC) light (UVC/ H_2O_2) was investigated envisaging enhance the efficiency of the treatment.

Material and Methods

Fixed-bed experiments were conducted by packing GAC in two different columns as described in Fig 1. In these tests, a limonene polluted air flow (20 mL min^{-1} ; 4.5 ppmv) was controlled by a rotameter before enter the adsorption column packed with GAC. A second rotameter

was placed at the outlet of the column to ensure that no leak is occurring during the tests. GAC used in the testes are heated for 12h at $80 \text{ }^\circ\text{C}$ prior each test.

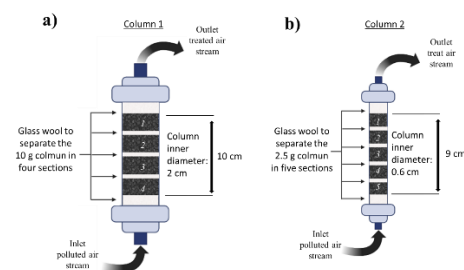


Figure 1. Diagram of the two columns packed with 10 g (a) and 2.5 g (b) of granular activated carbon.

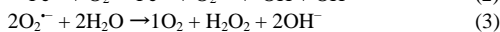
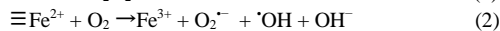
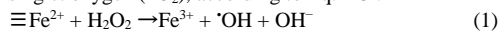
Regeneration experiments were conducted for the treatment of 2.5 g L^{-1} of GAC saturated with limonene in a batch reactor system. The effect of H_2O_2 alone was first investigated for the treatment of saturated GAC. In these experiments, GAC was put in contact with 0.15 L of H_2O_2 solutions at different concentrations ($25\text{--}200 \text{ mg L}^{-1}$) at pH 3 and room temperature ($25 \text{ }^\circ\text{C}$), under stirring for 24 h. Experiments with H_2O_2/UVC were carried out putting in contact 2.5 g L^{-1} of GAC saturated with LIM in batch reactor system with a 0.15 L of $100 \text{ mg L}^{-1} H_2O_2$ solution irradiated with a 9W UVC (placed in the center of reactor) during 6h. The experiments of heterogeneous Fenton-like were carried out using ferrocene (Fc) as heterogeneous catalyst and different Fc concentrations ($10, 100, 1000 \text{ mg L}^{-1}$) were tested by activate 100 mg L^{-1} of H_2O_2 solution during 24h.

Results and Discussion

The percentage of LIM removed from GAC as function of H_2O_2 concentration ($0, 25, 50, 100$ and 200 mg L^{-1}) is

depicted in Figure 2a. It could be observed that amount of LIM removed or eluted increases when H₂O₂ concentration increases up to 100 mg L⁻¹. It is important to note that concentration of limonene eluted to aqueous phase is < 0.2%, this is due to high hydrophobic and practically insoluble characteristics of this compound. Moreover, this result indicates that limonene removed from GAC is mostly converted to products than desorbed. The percentage of LIM removed from GAC after treatment with UVC/H₂O and UVC/H₂O₂ is depicted in Figure 2b. As can be observed under irradiation, removal was only about 15% regardless pH for UVC/H₂O₂ process, while around 1% is removed for UVC/ H₂O.

Figure.4c shows the percentage of LIM removed from GAC after treatment by heterogeneous Fenton-like reaction by Fc/H₂O₂, where the amount of Fc varied from 10 to 1000 mg L⁻¹ (ratios of Fc:H₂O₂ being 10, 1 and 0.1). Compared to other processes, heterogeneous Fenton-like system performed better achieving efficiencies up to 30.6% (acid) and 25% (neutral) for LIM removal from GAC after 24h for the higher ratio Fc:H₂O₂ (i.e 1000 mg L⁻¹ Fc and 100 mg L⁻¹ H₂O₂). The mechanism of heterogeneous Fenton-like reaction catalyzed by Fc involves generation of reactive oxygen species, mainly hydroxyl radicals (\bullet OH) and superoxide anion (O₂⁻) or singlet oxygen (O₂¹), according to Eq. 1-3 .



The percentages of LIM removed from GAC for 10 mg L⁻¹ were 21.7% (acid) and 16.2% (neutral) which are similar to values found for 100 mg L⁻¹ (20.3% - acid and 15.9% neutral). This result means that ferrocene is not the limiting agent. An interesting behavior is that increasing ferrocene to 1000 mg L⁻¹ the overall removal efficiency increased 30% (acid) and 35% (neutral), despite same amount of H₂O₂ is being activated. This indicate that an electron transfer mechanism between ferrocene and LIM can be responsible to the increase in the removal at very high concentrations of ferrocene. The amounts of LIM detected in aqueous phase was extremely low (<0.05%), indicating that limonene was quickly converted after elution to aqueous phase.

Conclusions

In this study, the chemical regeneration showed to be dependent of regenerant solution, where H₂O₂ activated by UVC and Ferrocene showed better outcomes than H₂O₂ only. Desorption studies revealed poor efficiency of use of chemical oxidants in aqueous solutions for the regeneration of GAC saturated with limonene. The poor efficiency on GAC regeneration can be explained by the properties of target VOC. Since limonene and its generated by-products are hydrophobic and practically insoluble in water, this explains why the degradation products remains on the GAC surface, which hinders the efficiency of the process. This study would provide useful information for design GAC regeneration.

Acknowledgments

The authors acknowledge the funding received by the Brazilian funding agencies including the Brazilian National Council for Scientific and Technological Development (CNPq – grant #303943/2021-1) and São Paulo Research Foundation (FAPESP – grants #2020/02743-4, #2022/03386-6, #2019/08701-4, #2022/07227-0 and #2022/12895-1). This work comprises the research project PID2019-107271RB-I00 and PDC2021-121105-I00 granted by MCIN/AEI/10.13039/501100011033/and “Unión Europea NextGenerationEU/PRTR”

References

- [1] Yu, H., Guenther, A., Gu, D., Warneke, C., Geron, C., Goldstein, A., Graus, M., Karl, T., Kaser, L., Misztal, P. Yuan, B. 595, 2017, 149-158.
- [2] Gałęzowska, G., M. Chraniuk, and L. Wolska, TrAC Trends in Analytical Chemistry, 2016. 77: p. 14-22
- [3] Larasati, A., G.D. Fowler, and N.J. Graham. Journal of Environmental Chemical Engineering, 2021. 9(4): p. 105555.

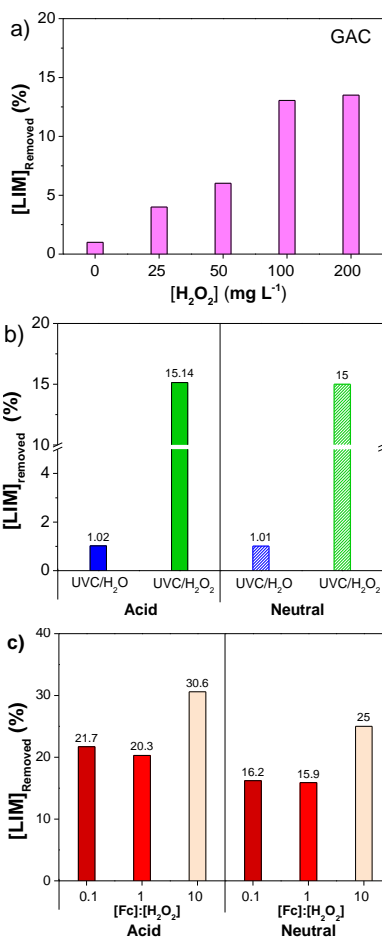


Figure 2. Relative percentage removal of LIM ([LIM]removed) as function of H₂O₂ concentration (b) UVC/ H₂O₂ and UVC only (UVC/ H₂O) at acid (pH 3) and neutral (pH 7) and (c) after 24 h contact time with Ferrocene/ H₂O₂ system at acid (pH 3) and neutral (pH 7).