

Development of adsorptive and photocatalytic composites based on Biochar with titanium dioxide and zinc oxide doped with cobalt for nitrate removal from groundwater.

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Abstract

Subterranean reservoirs suffer from contamination by nitrogen compounds, such as nitrate and nitrite which are fundamental in the nitrogen cycle but harmful in excess. These compounds affect the environment and human health. The complexity of nitrification and denitrification, along with the stability and resistance of these compounds to conventional treatments, makes their removal difficult and the accumulation in environmental. Therefore, there is a need for new technologies and catalytic materials to reduce the concentration of such pollutants. Adsorption is a promising technology, especially when combined with other techniques. This study focuses on the development of adsorptive and photocatalytic composites using biochar with support from TiO₂ and ZnO₂ doped with Co, aiming at the removal of nitrate from aqueous systems. In bench-scale tests, the BC and composites were exposed to nitrate solutions at natural and acidic pH with and without UV radiation. In all studies at neutral pH, no nitrate removal was observed for either the adsorptive or photocatalytic processes. At pH 2.0, 34% and 32% nitrate removal were obtained by the adsorptive process with BC and BC/TiO₂ material. The BC/TiO₂/ZnO/CoO composition considerably reduced the adsorptive efficiency of biochar due to the blocking of the active sites. The composites studied presented little or no photocatalytic activity. Only the BC/TiO₂ showed a slight increase in the nitrate removal efficiency in the photoirradiated system.

Keywords: Adsorption; Removal Nitrate; biochar; TiO₂.

1. Introduction

Underground reservoirs are being drastically affected, causing loss of quality due to the presence of nitrogen compounds that, despite playing a fundamental role in ecosystems through the nitrogen cycle, contribute to nitrate contamination. The excessive presence of nitrogen ions can result in harmful effects on the environment, affecting both biotic and abiotic components [1, 2]. The environmental impact associated with nitrogen compounds occurs in several ways, affecting human health due to the reduction of nitrate to nitrite, which

there is evidence of correlation with the occurrence of stomach or esophageal cancer due to the formation of N-nitrosamines [1], and nitrate that can cause a disease called methemoglobinemia, especially affecting children known as blue baby syndrome [3]. The presence of nitrogen compounds is aggravated by the stability of these substances and their refractoriness to conventional treatments.

Given this scenario, there is a need to develop new technologies and new catalytic materials that enable the reduction of the concentration of these compounds in the environment.

Adsorption is a promising method for this purpose, especially when associated with other technologies [2, 4]. In the case of this study, the development of adsorbent and photocatalytic composites emerges from the synthesis of biochar (BC) and the photocatalysts TiO₂, ZnO and CoO. This approach combines the surface accumulation of pollutant ions on the surface of a material with their parallel degradation, providing a more comprehensive and sustainable strategy.

2. Methodology

2.1 Material synthesis.

2.1.1 BC/TiO₂ composite.

The synthesis was carried out using as a base the adsorbent/support material, biochar (BC), commercially acquired and produced from the shell of the palm coconut. The procedure to produce the composite consisted of the preparation of an aqueous solution of 0.5 M NaOH, together with the precursor solution containing titanium. In this precursor solution, 7.62 mL of titanium isopropoxide (0.25 M) were diluted in 100 mL of isopropyl alcohol. After preparation, the precursor solution was stirred at 200 rpm until the complete dissolution of the reagent and homogenization of the solution. Then, 5 g of biochar were added to the precursor solution, and then 50 mL of the 0.5 M NaOH solution were slowly added, keeping the system under stirring. The resulting suspension was stirred for 60 minutes at 50 °C and left to stand for 24 hours. After the aging period, the solution was filtered, and the precipitate was washed with distilled water until reaching pH ~7.0. The material was then calcined at 300 °C for 12 hours.

2.1.2 Bc/TiO₂/ZnO/CoO composite.

The development of the material consisted of the production of an aqueous solution of 0.5 M NaOH, and the precursor solutions of titanium and zinc, where 3.81 mL of titanium isopropoxide (0.125 M) were diluted in 100 mL of isopropyl alcohol, with dissolution of 1.703 g ZnCl₂ (0.125 M) and cobalt with a concentration of 0.0025 M. After preparation of the precursor solutions, they were mixed and stirred at 200 rpm until the complete dissolution of the mixture. Then, 5 g of biochar were added to the precursor solution, and while stirring, 50 mL of the 0.5 M NaOH solution were slowly added. The resulting suspension was stirred for 60 minutes at 50 °C and left to stand for 24 hours. After aging, the solution was filtered and the precipitate washed with distilled water until natural pH. Then, the material was calcined for 12 hours at 300 °C.

2.2 Adsorptive/photocatalytic system

The photocatalytic/adsorptive study was conducted in a chamber containing a mercury vapor lamp (80 W) without the protection bulb. In this configuration, a solution containing 0.1 g of biochar or composite was placed in contact with 10 mL of a nitrate standard solution (50 mg L⁻¹) under stirring under radiation for 1 hour. The temperature of the solution was kept constant at 29 °C by means of a reactor cooling system. For comparison purposes, the same procedure was performed keeping the solution under stirring outside the dark chamber, with all conditions similar to the system used with UV radiation.

After the adsorption and radiation period, the solution was centrifuged for 1 hour at 3500 rpm, followed by determination of the nitrate concentration by means of UV-Vis spectroscopy [5].

3. Results

3.1 Synthesis yield

The composites presented a satisfactory yield in relation to the proportion of components used for their production, in which a part of their mass was lost in the washing until the pH correction, Table 1.

Table 1. Yield percentage.

Composite	%
BC/TiO ₂	59.95
BC/TiO ₂ /ZnO/CoO	90.46

3.2 Adsorptive and Photocatalytic Tests

In the initial studies, it was observed that for nitrate solutions at natural pH (close to 6.0), there was no significant removal of nitrate for all the compositions studied, that is, a possible adsorptive or photocatalytic effect of the biochar or composites was not evidenced.

In acidic medium (pH~2.0), for biochar, the removal of 34.51% and 32.27% of the pollutant was obtained in the reaction in the absence of radiation and with radiation, respectively. For BC/TiO₂/ZnO/CoO, the removal was only 4.30% and 1.01%, and for BC/TiO₂, the removal was 28.98% and 30.14% for the reaction in the absence of radiation and with radiation, respectively, Table 2.

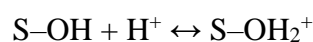
Table 2. Nitrate Removal.

Composite	Without UV	With UV
BC	34.51%	32.27%
BC/TiO ₂	28.98%	30.14%
BC/TiO ₂ /ZnO/CoO	4.30%	1.01%

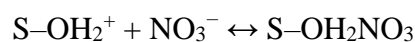
The adsorption and photocatalysis tests at natural pH showed little or no reduction in the absorbance of the nitrate solution, whether kept under UV radiation. This result indicates that the biochar and composites do not present adsorptive or photocatalytic activity for nitrate removal at pH close to neutral.

At pH 2.0, when biochar was used, a 34.51% reduction in nitrate was obtained in the absence of radiation, in just 1 hour of contact, indicating the good efficiency of the material for nitrate removal through adsorption. When photoirradiated, the removal was 32.27%, showing that the radiation did not contribute to the removal of the pollutant from the solution, and that the reduction was only due to the adsorptive process.

The greater efficiency for nitrate removal at acidic pH probably occurs due to the positive charge formed on the surface of the coal, which occurs due to the excess of protons in the solution. As a result, at acidic pH, the number of positively charged sites increases, and consequently favors the adsorption of nitrate anions due to electrostatic attraction [2, 5]:



For nitrate:



For the BC/TiO₂ and BC/TiO₂/ZnO/CoO composites, in the process without radiation, a reduction in the efficiency of the adsorptive process was observed. This result suggests that the deposition of oxides on the biochar surface inhibited the adsorptive process, due to the partial or complete blocking of the biochar active sites. This assumption was corroborated

by microscopic analyses showing the complete coverage of the BC surface by oxides.

For BC/TiO₂, photocatalysis showed a slight increase in nitrate removal, realizing the properties of TiO₂ in this material.

The BC/TiO₂/ZnO/CoO composites showed a significant reduction in efficiency compared to BC/TiO₂ for nitrate removal from solution, both for reactions with and without radiation, that is, ZnO and CoO inhibited the adsorption and photocatalytic activity of TiO₂.

Due to the photocatalytic properties of TiO₂ and ZnO, an increase in nitrate removal efficiency in the presence of photoradiation was expected, but this was not observed. The increase was quite discreet, indicating that the process would need to be improved by varying the catalyst concentration, composite synthesis method or photoradiation time. Additional studies are being conducted with the aim of mitigating the interference of titanium dioxide, TiO₂, in nitrate analysis. Such an effort aims to corroborate the photocatalytic and adsorbent efficacy of materials that include TiO₂.

4. Conclusion

In this study, the photocatalytic/adsorptive efficiency of materials, namely biochar (BC), BC/TiO₂ and BC/TiO₂/ZnO/CoO in the removal of nitrate from an aqueous solution, in acidic and near-neutral medium, was investigated. It was observed that in neutral medium, none of the materials presented adsorptive and/or photocatalytic activity for the

removal of nitrate. At pH 2.0, biochar and BC/TiO₂ presented excellent nitrate removal, reaching a reduction of 34.51% and 28.98% respectively in just one hour of reaction in the absence of radiation, indicating adsorptive activity of the materials. On the other hand, the BC/TiO₂/ZnO/CoO composition considerably reduced the adsorptive efficiency of biochar due to the blocking of the active sites. The composites studied presented little or no photocatalytic activity. Future tests will be conducted by varying the concentration and synthesis methodology with the aim of investigating whether reducing the amount of oxide deposited on the coal will increase its adsorbent potential, resulting in improvements in the photocatalytic results, as suggested by the literature.

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