# Comparative efficiency of removal/degradation of naphthenic acids using green-functionalized carbon nanotubes and peroxymonosulfate as adsorbent and catalyst

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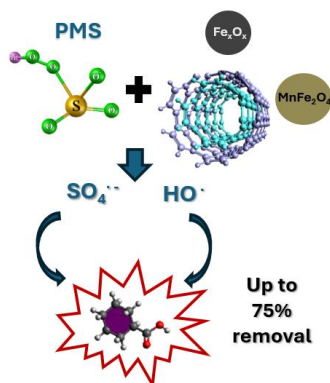
One of the most harmful substances released into "Produced Water" (PW), effluent from the oil sector, are naphthenic acids (NA). The purpose of this study was to evaluate different functionalized carbon nanotubes (CNTs) as catalysts for the activation of peroxymonosulfate and removal of cyclohexanecarboxylic acid (CHCA), a model compound of naphthenic acids. CNTs functionalized via green synthesis with Fe_2O_4 NPs and biomass extract were the most promising material among those evaluated, promoting the removal of up to 75% of the CHCA after 70 minutes of reaction. Increasing the PMS concentration above 3 mM does not produce an increase in either the reaction rate or the amount of acid degraded.

Introduction

Most petroleum sources contain naphthenic acids (NAs), which are dissolved in Produced Water (PW), a byproduct of oil extraction and refining. These compounds are considered one of the main harmful substances emitted in PW that cause environmental issues and negative impacts. In addition to the problems, these compounds are highly stable, recalcitrant, and have high resistance to biological degradation [1]. It is for this reason that advanced oxidative processes (AOP) emerge as an interesting alternative for the treatment of these molecules. Organic molecules can undergo partial or complete degradation by interactions with radicals, primarily hydroxyl and sulfate. Among the chemicals used to produce the sulfate radical is peroxymonosulfate (PMS).

In addition to AOP, a very effective treatment method for eliminating pollutants from wastewater is the adsorption process[2]. In this sense, carbon nanotubes (CNTs) functionalized with metallic nanoparticles (NPs) are a potential material to be used as a catalyst and adsorbent in PMS activation due to their unique properties. The present work aimed to evaluate the use of PMS together with several functionalized CNTs for the removal and degradation of cyclohexanecarboxylic acid (CHCA) as a model compound of naphthenic acids.

Material and Methods

Materials: Cyclohexanecarboxylic acid ($C_7H_{12}O_2$, 98%) and PMS (Oxone®) were purchased from Sigma Aldrich. Multiwall carbon nanotubes functionalized with COOH groups were purchased from NanoView, manganese chloride ($MnCl_2 \cdot 4H_2O$), Silver sulfate (Ag_2SO_4), Iron chloride (III) ($FeCl_3 \cdot 6H_2O$) and iron sulfate ($FeSO_4 \cdot 7H_2O$) from

Dinâmica. The eucalyptus leaves (E, *Corymbia citriodora*) were provided by Usina do Eucalipto (Campinas-SP/Brazil). HPLC Grade acetonitrile was acquired from Êxodo cientifica.

Methods: The functionalization of the multi-walled carbon nanotubes (CNTs) was conducted by the green and chemical route. AgFe, Fe_2O_4 and Fe_3O_4, nanoparticles were synthesized by green synthesis as described by Spaolonzi et al. [3] with minor modifications. Briefly, to prepare the extract, 5 g of eucalyptus leaves were added to 100 mL of boiling deionized water and stirred for 5 min., then the extract was filtered through 0.45 µm nylon filter. For Fe_2O_4 NPs, 10 mL of a 100 mM iron sulfate solution was added to 90 mL of the extract. For Fe_3O_4 NPs, a mixture of 25 mL of 0.2 M $FeCl_3$ and 25 mL of 0.1 M $FeSO_4$ was incorporated into 50mL of extract and then the pH was adjusted to 11 with 0.1 mM NaOH. For AgFe NPs, a mixture of 10 mL of 0.1 M Ag_2SO_4 and 10 mL of 0.1 M Fe_2SO_4 was added to 80 mL of extract, then pH was adjusted to 11 with 0.1 mM NaOH. Afterwards, 1.5 g of CNTs were individually incorporated to each synthesized NP and stirred for 24 h. Subsequently, each CNT-NP system was washed with deionized water and centrifuged for 15 min (7,000 rpm) 3 times.

Manganese-ferrite nanoparticles were synthesized by the coprecipitation method [4]. Specifically, 4 M $FeCl_2$ and 2 M $MnCl_2$ (2:1 ratio) were continuously stirred dropwise. 17 mL of 7M NaOH were introduced into the process until reaching pH 14. The procedure was carried out at 90º C. Then, 1.5 g of CNTs were incorporated and stirred for 24 h. The mixture was washed 3 times with deionized water and centrifuged for 15 min at 7,000 rpm. All resulting materials were dried in an oven at 50°C for 24 h.

Advanced Oxidation Tests: For the affinity tests, the

initial concentration of the CHCA solution was 100 mg/L. Each functionalized CNT was used at a dosage of 2 g/L, and the PMS reagent was used at 3.0 mM. The CNT-PMS system was mixed in an orbital shaker at 25 °C and 200 rpm for 24 hours. After that, the samples were filtered with PVDF 0.22 µm syringe filters and measured by HPLC (Shimadzu Serie UFLC) with a C-18 column. All tests were performed in triplicate. Equation (1) was used to calculate the amount of CHCA removed. Tests were conducted under acidic condition of pH 5.3.

$$\%Rem = \frac{(C_0 - C_f)}{C_0} x100 \tag{1}$$

Results and Discussion

Different metal nanoparticles were used to functionalize the nanotubes. As shown in Fig. 1, the amount of degraded CHCA varied depending on the type of material used. The most promising material was CNT functionalized with Fe_2O_4 nanoparticles, reaching $74.92 \pm 0.61\%$ followed by CNT-Fe_3O_4-NPs with $52.56 \pm 0.68\%$.
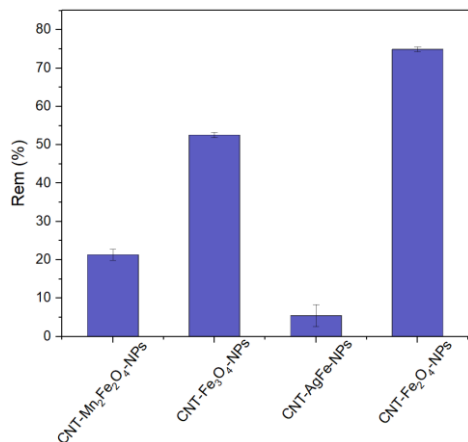

Figure 1. Degradation of ciclohexanecarboxylic acid by different CNT-NPs/PMS oxidation systems. Conditions: C_0

(CHCA) = 100 mg/L; C_0 (PMS) = 3 mM; C_0 (Catalyst) = 2.0 g/L.

These results are in line with the findings of [5], where it was demonstrated that iron nanoparticles adhered to a carbonaceous support material, as CNTs can act as catalyst in the generation of hydroxyl and sulfate radicals.

Considering the material that showed the best performance in CHCA degradation, kinetic tests were carried out. Figure 2 A shows the influence of PMS dosage on CHCA degradation. 75% of the chemical was degraded after 70 minutes of reaction. An increase in the PMS dosage did not improve the rate of CHCA degradation.
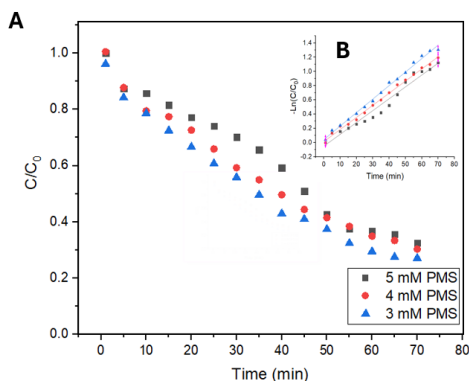

Figure 2. (A) Degradation of ciclohexanecarboxylic acid by CNT-NPs/PMS oxidation systems. Conditions: C_0 (CHCA) = 100 mg/L; Catalyst dosage = 2.0 g/L. (B) The corresponding pseudo first-order kinetic curves (R^2>0.965).

In Figure 2 B, the degradation rate decreases when the PMS concentration increases from 3 to 5 mM (k value decreased from 0.019 to 0.0167 min^{-1}). This could be caused by an excess of HSO_5 in PMS concentration, which began to quench the $SO_4^{\cdot-}$ [6].

Conclusions

Advanced oxidation tests indicated that the most promising material among those evaluated in this study for the degradation of CHCA by PMS was carbon nanotubes functionalized with Fe_2O_4 NPs. After 70 minutes of reaction, approximately 75% degradation of the compound can be reached, with the concentration of 3 mM PMS showing the most efficient degradation rate.

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