

Article

Photocatalytic Reduction of Cr(VI) with Titanium Dioxide Supported on SiO₂-Coated Magnetite Particles

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ABSTRACT: Hexavalent chromium compounds are considered carcinogenic to humans. Its reduction to Cr(III), which is relatively non-toxic and an essential nutrient for humans, is a critical process. Heterogeneous photocatalysis with TiO₂ is a promising remediation method with satisfactory results. However, this semiconductor cannot be released into an aqueous media because it is dangerous to multiple forms of life. The removal of TiO₂ requires laborious and costly methods, so a practical method is needed. One of these alternatives is to immobilise TiO₂ on magnetic particles to facilitate its extraction. In this work, the photocatalytic reduction of Cr(VI) is carried out with TiO₂ immobilised on SiO₂-coated magnetite particles, called FST-5. As a sacrificial reduction agent, EDTA (Ethylenediaminetetraacetic acid) was used with satisfactory results. When both are combined, a significant decrease in the aqueous Cr(VI) amount is observed. It indicates its potential application for the remediation of water courses contaminated with this heavy metal.

Keywords: Cr(VI); Environmental pollution; Remediation; Photocatalytic reduction; Magnetite; Immobilised TiO₂; SiO₂-coated particles

1. Introduction

Contamination of natural watercourses with wastewater is a serious problem. Many anthropogenic pollutants are dumped into rivers, lakes, and streams, affecting their aquatic flora and fauna. Between them, heavy metals aggravate the problem.

These elements are found naturally in the environment, but their industrial, domestic, agricultural, medical, and technological applications promote their presence in amounts that can be toxic [1]. For example, if the isolation of urban garbage dumps is ineffective, leachate from waste containing these metals can reach watercourses, making them extremely dangerous for the flora, fauna, and populations near them. Many of these heavy metals (mercury, cadmium, chromium, thallium, lead, *etc.*) have toxic effects even at very low concentrations [2–4]. In particular, hexavalent chromium, Cr(VI), is a known carcinogen that can

cause multiple damages to human health, either by inhalation or ingestion through mains water [5–7]. It is present mainly in industrial environments such as tanneries, foundries, welding, and chrome plating. Smoke from traditional and electronic cigarettes and automobile exhaust gases also contains it [5]. The elimination of this heavy metal (and others) becomes a priority activity that deserves immediate attention.

The removal of Cr(VI) anions in aqueous media can be carried out by different methods [8–12]. However, photocatalytic reduction with a semiconductor (mainly TiO₂) is one of the most used processes [13–16], due to its efficiency to reduce small amounts of this anion [17]. In this redox process, hexavalent chromium is converted to Cr(III) species, which are significantly less toxic at low concentrations; on the other hand, Cr(III) is considered an essential trace element for human life [18]. Furthermore, if the redox process is carried out in neutral aqueous media, Cr(III) can precipitate as insoluble Cr(OH)₃, which greatly facilitates its separation. However, the subsequent removal of bulk TiO₂ is not considered, which could cause serious damage to the environment [19–22]. To prevent it, TiO₂ was immobilized on magnetite particles, Fe₃O₄, coated with SiO₂ (to prevent the reduction of its photocatalytic properties) [23]. This support makes it easy to remove with a magnetic field. This catalyst, called FST-5, has been successfully tested in the degradation of a herbicide present in a commercial formulation [23]. To extend its use as a remediation method, its activity in the photocatalytic reduction of Cr(VI) to Cr(III) was evaluated under varying conditions. To the best of our knowledge, the photocatalytic reduction of Cr(VI) by TiO₂ immobilized on magnetic support has not yet been reported by other researchers.

2. Experimental

2.1. Catalyst Synthesis and Characterization

All catalysts were synthesized and characterized by previously reported methods [23]. Briefly, TiO₂ was obtained by the sol-gel method. Magnetite particles encapsulated in SiO₂ were called FS. The immobilization of TiO₂ on the FS support (FST-5 catalyst) was carried out by evaporation of solvents at reduced pressure. Finally, these solids were oven-dried.

2.2. Reagents

Potassium Chromate (K₂CrO₄) and Ethylenediaminetetraacetic acid (EDTA) were supplied by Timper (La Plata, Argentina) and BDH Chemicals Ltd., (Poole, UK), respectively, and used as received.

2.3. Evaluation of Photocatalytic Activity

The experiments were carried out in duplicate in an open glass reactor, with a 300 W lamp as the irradiation source [23].

25 mg·L^{−1} K₂CrO₄ solutions were obtained from a stock solution of 400 mg·L^{−1}, with adequate dilutions with distilled or mains water. The initial pH of these solutions was adjusted to 5 in all experiments with dilute nitric acid, unless otherwise indicated, due to the isoelectric point of FST-5, 5.4 [23]. Under these conditions, the catalyst surface, positively charged, strongly attracts Cr(VI) anions. 2.5 g·L^{−1} of FST-5 was added to the reactor; at this amount, this solid showed higher photocatalytic activity [23]. Bulk TiO₂, either commercial Degussa P25 (Evonik, Rheinfelden, Alemania) or synthesized according to the sol-gel technique described above (s-TiO₂), was used for comparative experiments at 1.185 g·L^{−1}, which corresponds to 47.4% of the FST-5 catalyst [23]. Also, FS support was employed at 1.32 g·L^{−1}, according to 52.3% of FST-5 [23].

Before illumination, the suspensions with Cr(VI) anions and different catalysts or FS support were mechanically stirred to establish the adsorption equilibrium. 20 min was enough according to dark absorption experiments (previous equilibrium time). At the end of each experiment, the solids were removed from the samples by magnetic attraction (FST-5 or FS) or 0.20 µm filters (P25 or s-TiO₂).

The reuse of FST-5 and s-TiO₂ was evaluated over five cycles, each lasting 200 min. Both catalysts were washed with distilled water and immediately reused with a fresh 25 mg·L⁻¹ K₂CrO₄ solution containing EDTA.

The variation in CrO₄²⁻ concentration was evaluated by UV spectrometry at $\lambda = 370$ nm in a GBC Scientific Equipment (Melbourne, Australia) Cintra 10e double-beam spectrometer.

3. Results and Discussion

3.1. Cr(VI) Reduction-Effect of Adding EDTA

Figure 1 shows the photocatalytic reduction of Cr(VI) on FST-5 and FS catalysts. At the previous equilibrium time, 43% of these anions were adsorbed on this catalyst, as can be seen in this Figure ($t = 0$ min). The negligible adsorption of Cr(VI) on the magnetic support FS indicates that this compound is mainly deposited on the TiO₂ surface immobilised on FST-5. This semiconductor has a positive surface charge due to the acidic aqueous medium.

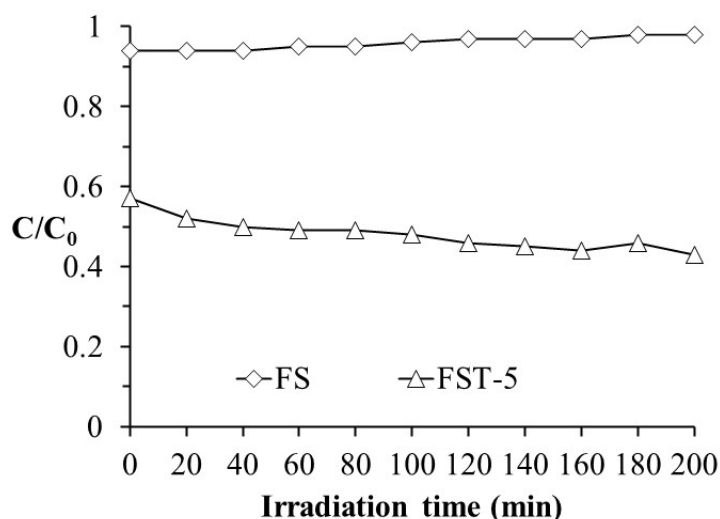


Figure 1. Photocatalytic reduction of Cr(VI) with magnetically separable FST-5 or FS composites. [FS] = 1.32 g·L⁻¹. [FST-5] = 2.5 g·L⁻¹. [Cr(VI)] = 25 mg·L⁻¹. Initial pH = 5 in all experiments.

Also, FS does not possess photocatalytic activity due to its SiO₂ shell. This compound has a band gap value between 7.62–9.70 eV [24], which requires wavelengths close to 130 nm to photogenerate electron/hole pairs (e⁻/h⁺). These wavelengths are not emitted by the lamp used in these experiments.

At the end of the irradiation time, 43% of the initial Cr(VI) amount remains in the aqueous medium containing FST-5. The incomplete elimination of Cr(VI) is due to the reoxidation of Cr(III) species, obtained by the reduction of this pollutant. On the surface of supported TiO₂, the photogenerated h⁺, or the OH[•] radicals that they generate, are responsible for this detrimental process [25]. Recombination of e⁻/h⁺ pairs is also an unproductive reaction.

To improve the reduction of Cr(VI), a sacrificial agent is needed. These compounds prevent the recombination of e⁻/h⁺ pairs, and they can act as electron donors to the reaction system [26]. Among them, EDTA is a very useful sacrificial agent because it has both properties. When h⁺/OH[•] react with EDTA molecules, strongly reducing species EDTA[•] are generated. Thus, photogenerated electrons or EDTA[•] radicals reduce Cr(VI) to Cr(III) using sequential one-electron reactions [14].

With the FST-5 catalyst, three EDTA/Cr(VI) molar ratios were evaluated (Figure 2). All tested molar ratios significantly reduce the presence of Cr(VI) anions at the end of the reaction time. However, EDTA/Cr(VI) equal to 3:1 is the optimum ratio for the catalyst activity due to the higher initial rate,

decreasing more than 99% of the Cr(VI) amount within 60 min. On the other hand, the pH value of these experiments is optimal for EDTA activity [27].

The initial decrease in the Cr(VI) amount (ca. 50%) is due to two combined effects: the adsorption of these anions on FST-5 (previously mentioned), and the spontaneous oxidation of EDTA by Cr(VI) anions in acidic conditions.

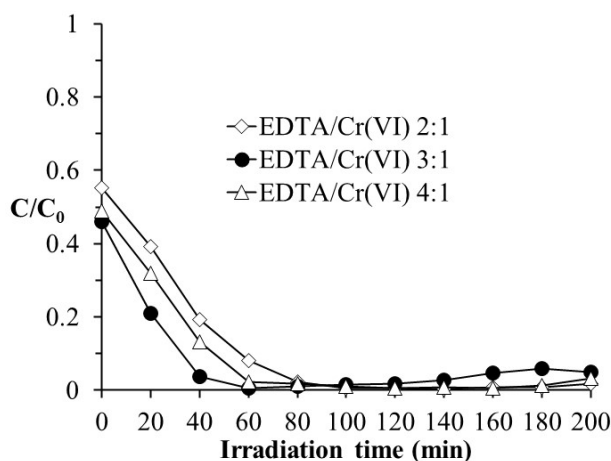


Figure 2. Effect of three EDTA/Cr(VI) molar ratios on the photocatalytic reduction of Cr(VI) with FST-5. [FST-5] = 2.5 g·L⁻¹. [Cr(VI)] = 25 mg·L⁻¹. Initial pH = 5 in all experiments.

Once the optimum EDTA/Cr(VI) molar ratio was determined, it was used to evaluate its influence on the photoactivity of EDTA and FS support to reduce Cr(VI) anions. These results are shown in Figure 3.

Without FST-5, EDTA shows no photoreducing activity on Cr(VI), even when it is combined with FS. FS does not generate e⁻/h⁺ pairs because it does not receive the appropriate wavelengths (as mentioned above), and EDTA does not form additional reduction species under irradiation. In dark conditions without FST-5, EDTA shows similar reducing activity (Figure 4).

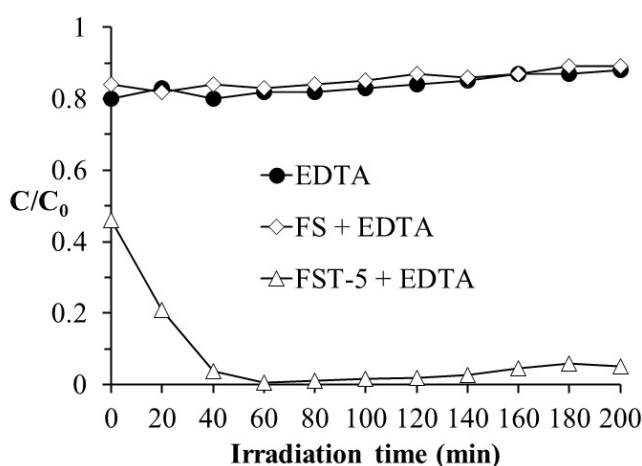


Figure 3. Photoreduction of Cr(VI) with EDTA (without FST-5) or FS + EDTA. Photoactivity of FST-5 (white triangles) was added for comparative purposes. EDTA/Cr(VI) = 3:1. [Cr(VI)] = 25 mg·L⁻¹. [FS] = 1.32 g·L⁻¹. [FST-5] = 2.5 g·L⁻¹. Initial pH = 5 in all experiments.

Six days later, aliquots from photostimulated reactions were analyzed again (Figure 4). In all of them, the Cr(VI) amount additionally decreased by ca. 20%. It indicates that the spontaneous reduction of Cr(VI) by EDTA was active under dark conditions during this period, an effect observed by Boyd-Boland [28].

This fact is very important because it indicates that EDTA can be used as a pretreatment method for watercourses contaminated with Cr(VI) species.

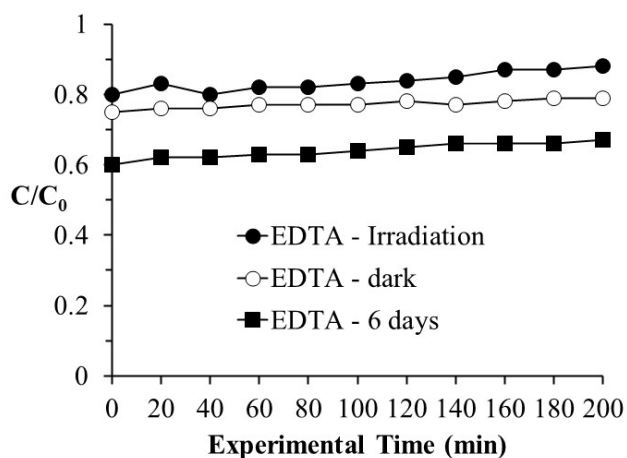


Figure 4. Spontaneous reduction of Cr(VI) by EDTA at different experimental conditions. Photoactivity of EDTA (black circles) was added for comparative purposes. EDTA/Cr(VI) = 3:1. [Cr(VI)] = 25 mg·L⁻¹. Initial pH = 5 in all experiments.

3.2. Reduction of Cr(VI) Anions with Bulk TiO₂

Figure 5 shows the activity of the supported TiO₂ (in FST-5) in comparison with that corresponding to its equivalent amount of bulk TiO₂ (s-TiO₂ and P25). The initial reduction of Cr(VI) anions on P25 was lower than that of other catalysts. Due to that, the spontaneous reduction of EDTA is present in all cases, and all TiO₂ surfaces are positively charged, the difference lies in the amount of Cr(VI) anions adsorbed on each catalyst. This fact depends on the specific surface of TiO₂ particles, mostly in the anatase phase, which is inversely proportional to the average particle size: 15.8 nm for P25 [29], 8.9 and 5.40 nm for s-TiO₂ and supported TiO₂, respectively [23]. The latter can be more evenly distributed across the entire surface of the FS support, thereby avoiding agglomeration. Therefore, this order explains the observed adsorption effect.

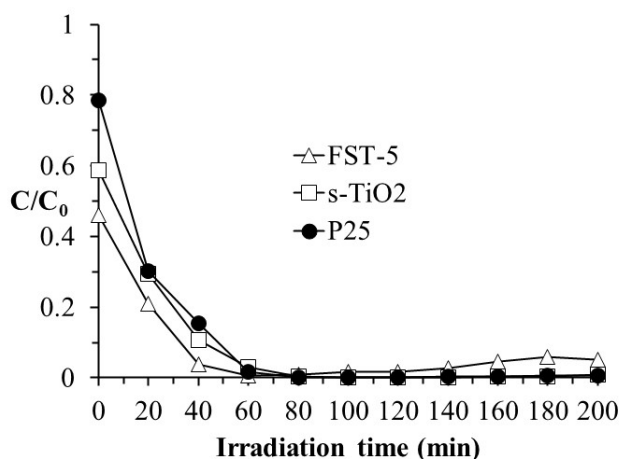


Figure 5. Photocatalytic reduction of Cr(VI) with bulk TiO₂ (s-TiO₂ and P25). Photoactivity of FST-5 was added for comparative purposes. [s-TiO₂] = 1.18 g·L⁻¹ = [P25]; EDTA/Cr(VI) = 3:1 in all experiments. [FST-5] = 2.5 g·L⁻¹. [Cr(VI)] = 25 mg·L⁻¹. Initial pH = 5 in all experiments.

All catalysts showed the same rate of reduction and reached the same final values of Cr(VI) in the solution. However, the magnetic support facilitates the removal of the supported TiO₂, which is an advantage over the other two solids.

3.3. Reduction of Cr(VI) Anions in Mains Water

The optimized conditions were applied to reduce these anions in mains water. Initially, its original pH value (6.60) was not modified. The photostimulated reactions were carried out under two conditions: with and without the addition of FST-5 during the adsorption/desorption equilibrium time (Figure 6). In this last condition, the catalyst was added at the start of irradiation to evaluate the effect of EDTA at the equilibrium time, with a pH close to neutrality. At these conditions, the EDTA species HY^{3-} (the triply-deprotonated form of EDTA) predominates, repels Cr(VI) anions, and prevents their reduction, as can be seen in Figure 6. On the other hand, the presence of FST-5 in the equilibrium time slightly decreases the initial concentration of Cr(VI) due to adsorption on the catalyst surface, despite its electrostatic repulsion. In both experiences, only 41% of these anions were reduced at the end of the reaction time.

At pH = 5, the reduction of Cr(VI) in mains water became more efficient. At the beginning of the reaction time, its initial concentration was reduced by 60% due to the aforementioned effects of spontaneous reduction by EDTA and adsorption on the catalyst surface. Also, the oxidation of aqueous organic matter by Cr(VI) anions under acidic conditions should be considered. These three factors could be responsible for the significant decrease in the amount of Cr(VI) at low irradiation times compared to distilled water samples. Consequently, as there are fewer Cr(VI) anions, their reduction occurs at a faster rate, reaching minimum values in solution before 40 min of irradiation.

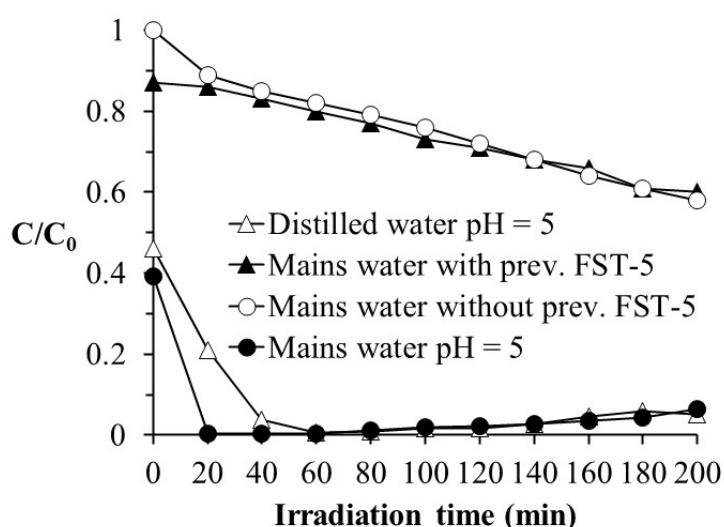


Figure 6. Photoreduction of Cr(VI) in mains water. FST-5 was added in the previous equilibrium time (black triangles) or at the beginning of the irradiation time (white circles). Initial pH = 6.6 in both experiments. In mains water at pH = 5 (black circles), FST-5 was added at the beginning of the previous equilibrium time. Photoactivity of this catalyst in distilled water (white triangles) was added for comparative purposes. EDTA/Cr(VI) = 3:1 in all experiments. $[\text{Cr(VI)}] = 25 \text{ mg}\cdot\text{L}^{-1}$. $[\text{FST-5}] = 2.5 \text{ g}\cdot\text{L}^{-1}$.

FST-5 may be composed of a fraction of magnetite particles that have not been efficiently coated by SiO_2 . On these bare particles, the Cr(III) species may be adsorbed [30].

3.4. Catalyst Reuse

Recovery and reuse of catalysts are very important processes because they extend their useful life and save costs [31]. Both factors influence the choice of a catalyst for remediating contaminated watercourses.

Figure 7 shows the photocatalytic reduction of Cr(VI) by FST-5 or bulk s-TiO₂ over five cycles in distilled water or mains water.

The activity of FST-5 depends on the aqueous medium. In distilled water samples, FST-5 is more active than in mains water samples. This difference may be due to anions present in the latter samples, capable of

adsorbing on the surface of supported TiO_2 , thus decreasing its activity. This fact decreases the electrostatic attraction among Cr(VI) anions or EDTA and supported TiO_2 . In mains water, EDTA is partially used as a sacrificial agent, and it can form complexes with Cr(III) . For this reason, a purple aqueous compound was observed in the supernatant once the fifth cycle had ended. This compound is a Cr(III) -EDTA complex, determined by UV-visible spectrometry at 545 nm; this wavelength was reported by Meichtry et al. (2014) [25]. This complex is formed at pH values between 5 and 6, with a temperature close to 20 °C [32]. These conditions are met in this reaction medium. On the other hand, in distilled water samples with Cr(VI) anions, the aforementioned factors do not occur. EDTA acts as a sacrificial reduction agent, and the Cr(III) species may be deposited on uncoated magnetite particles, as mentioned above.

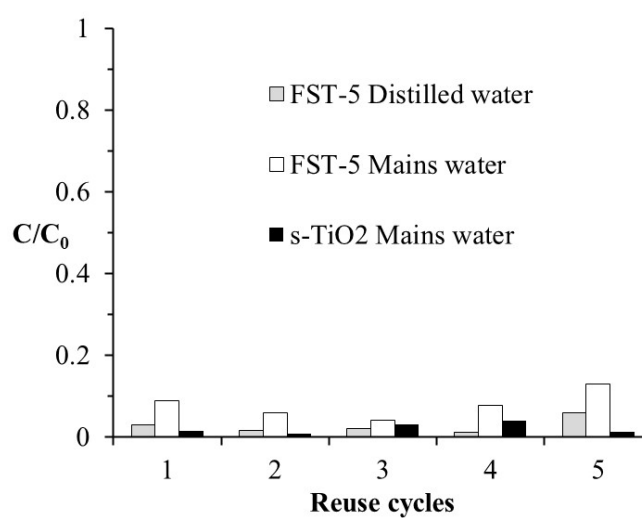


Figure 7. Residual concentration of Cr(VI) after photoreduction process with FST-5 or s-TiO_2 at consecutive cycles. pH = 5, $\text{EDTA/Cr(VI)} = 3:1$ in all experiments. $[\text{FST-5}] = 2.5 \text{ g} \cdot \text{L}^{-1}$, $[\text{s-TiO}_2] = 1.18 \text{ g} \cdot \text{L}^{-1}$ only in the first cycle.

Finally, Figure 7 shows the reuse cycles of bulk s-TiO_2 in mains water. It should be noted that, in all cycles, it has better reduction activity than FST-5, decreasing the initial concentration of Cr(VI) anions by 99% in the last one. Also, a weak purple color of the Cr(III) -EDTA complex was observed in the solution, along with green Cr_2O_3 on the catalyst surface, as was previously observed by Meichtry et al. (2025) [33]. This last compound intensified its color through successive cycles, which was observed on P25 by Meichtry et al. (2014) [25]. This fact indicates that EDTA significantly participates in the redox reaction, unlike what happens with FST-5. On the other hand, Cr_2O_3 does not interfere with s-TiO_2 activity. Further studies are required to understand these questions.

4. Conclusions

Reduction of Cr(VI) anions by supported TiO_2 on magnetite particles coated with SiO_2 (FST-5 catalyst), with or without added EDTA, has been evaluated. Both FST-5 and EDTA can reduce these anions, but their individual activity is low. When both are combined in a photostimulated reaction medium, the reduction of Cr(VI) is significantly increased, and the Cr(III) species generated can be deposited on the catalyst support or surface, or form purple complexes with EDTA, depending on the catalyst used.

FST-5 or s-TiO_2 can also be reused in successive cycles with mains water, maintaining its activity at significant values. However, only FST-5 can be easily removed from the treated aqueous medium, indicating its suitability for application in watercourses contaminated with Cr(VI) anions.

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Author Contributions

Conceptualization, E.L.S. and E.M.F.T.; Methodology, J.P.M. and C.L.H.; Validation, J.P.M.; Formal Analysis, J.P.M. and C.L.H.; Investigation, J.P.M. and C.L.H.; Resources, E.L.S.; Writing—Original Draft Preparation, J.P.M.; Writing—Review & Editing, J.P.M.; Visualization, J.P.M. and E.M.F.T.; Supervision, E.L.S. and E.M.F.T.; Project Administration, E.L.S. and E.M.F.T.; Funding Acquisition, E.L.S. and E.M.F.T.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Not applicable.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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