Optimization of the synthesis of TiO_2/AC composites for removal of Sulfamethoxazole in water

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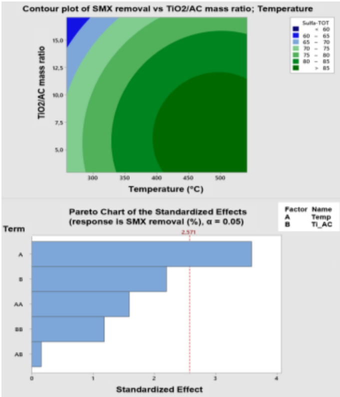

Despite the persistence of Sulfamethoxazole (SMX) in water and wastewater after conventional treatment, there is a lack of innovative approaches for removal of this antibiotic from aqueous media. The aim of this study was to assess the applicability of heterogeneous photocatalysis using titanium dioxide and activated carbon (TiO_2/AC) composites, for adsorption/photocatalysis of Sulfamethoxazole found in low concentrations in aqueous media. Design of Experiments (DoE) for process optimization was used and different ratios and calcination temperatures were tested for the synthesis. The composite with the best SMX removal efficiency was the one formed by TiO_2 and 6.5% AC calcined at 489 °C. This composite was applied to remove SMX at environmentally relevant concentrations (100 µg L^{-1}). The composite was characterized by SEM. Under optimized feasible conditions, the efficiency of TiO_2/AC6.5% to remove SMX from water was 95.6%.

Introduction

Sulfamethoxazole (SMX), a sulfonamide antibiotic ($C_{10}H_{11}N_3O_3S$; CAS: 723-46-6), is commonly found in wastewater and surface water. This antibiotic, utilized in both human and veterinary applications to treat respiratory, urinary, and gastrointestinal infections has been detected in surface water at levels from 96 µg L^{-1} to 142 µg L^{-1} in Africa [1]. It means that conventional water treatment does not remove completely SMX from water.

Utilization of highly adsorbent materials for water treatment has proven to an effective approach, with SMX removal rates ranging from 80% to 95% [2]. Photocatalysis has also garnered attention due to its environmentally friendly nature, reaching high degradation efficiency, cost-effectiveness, and ease of implementation [3].

Recent investigations have explored the synthesis of composites containing TiO_2 in combination with highly adsorbent materials. Its properties include large surface area, micropollutant adsorption capacity, generation of superoxide and hydroxyl radicals, and the presence of C-O-semiconductor ligands that reduce the bandgap. These mechanisms lead to greater absorption of visible solar energy and the possible adsorption of intermediate products during photocatalysis, whether or not followed by oxidation [4].

TiO_2 in combination with highly adsorbent materials, has been a promising and effective strategy to degrade SMX into less harmful products [5].

The aim of this study was to optimize the synthesis of TiO_2/AC composites using Design of Experiments (DoE) for process optimization with response surface methodoly (RSM) and to assess the applicability of composites with both sorption and photocatalyst properties to remove Sulfamethoxazole present in environmentally relevant concentrations in aqueous media.

Material and Methods

Commercial Titanium Dioxide Aeroxide® P25 (TiO_2-P25) was purchased from Evonik, Brazil. Nitric acid (65%), ethanol, and 2-propanol were supplied by Sigma-Aldrich and Polyethylene glycol PEG-600 (MW: 560–640) by Merck. Activated carbon (AC) was supplied by Vetec (Brazil). Sulfamethoxazole European Pharmacopoeia (EP) reference standard from Sigma-aldrich (99,8%). Ultrapure water was obtained using a Milli-Q® purification system (Merck-Millipore).

The synthesis of TiO_2/AC composites followed a conventional response surface methodology (RSM) employing a central composite rotatable design (CCRD). This approach is useful to reduce the number of experiments, optimizing the relevant variables and to evaluate the variables interaction. The CCRD was based on a 2n factorial run with 2n axial runs and nc center runs (three replicates) (Table 1).

The effect of two independent variables (mass ratios of TiO_2:AC components and calcination temperature) were evaluated. TiO_2/AC composites were synthesized using the alcohol impregnation method [4].

Experiments were carried out in an orbital shaker with 10 mg of composite (100 mg L^{-1}) in 100 mL of solution containing 100 µg L^{-1} of SMX. For adsorption, the samples were kept on the orbital shaker at room temperature for 120 min (without light). Samples of 2 mL were collected and filtered using a 0.20 µm syringe filter made of hydrophilic PTFE. To promote photocatalysis, the samples were exposed sunlight simulation spectrum lamp (adjusted for ~20 W m^{-2} of UV-A irradiance) provided by an Ultra Vitaluz OSRAM 300W. The solution was kept under stirring at room temperature for 120 min. After that, 2 mL samples were collected and filtered. To produce the optimized composite (TiO_2/AC6.5%), a mass ratio of 6.5% AC (m/m) and a post-annealing treatment temperature of 489 °C were used. To validate the results, experiments with TiO_2/AC6.5% were performed in triplicate under the same conditions as previously described. All the samples were analized using ultra-performance liquid chromatography (Acquity, Waters) coupled with a tandem mass spectrometer (Xevo TQD® Waters) (UPLC-MS/MS). The UPLC column employed for this analysis was a BEH C18, 1.7 µm, 2.1 × 50 mm (Waters).

Results and Discussion

The SMX removal, in the applied range of parameters, using TiO_2/AC composites, varied from 65.7% to 89.1%. The maximum removal occurred in run 8 (Table 1) with TiO_2/AC mass ratio of 10 (AC concentration of 10%) and calcination temperature of 500 °C. Using the experimental results, the regression model equation relating the responses and variables was developed in Equation 1 below:

SMX removal (%) = 14,3 + 0,29 (Temp) + 0,81 (Ti_AC) **Eq.1**

At a confidence level of 95%, in the range chosen, the only term statistically significant was the linear term of calcination temperature. The statistical significance of the model was evaluated by ANOVA (Table 2). The results showed that the regression was statistically significant ($p<0.05$) and the determination coefficient (R^2) was 80.6%. Thus, the requirements necessary to the models were obtained and the models can be visualised through the response surface methodology (Fig. 1).

The prediction test was applied to sinthesize the optimized composite (i.e. AC concentration of 6.5% and calcination temperature of 489 °C). The SMX adsorption and adsorption+photocatalysis removal was carried out for evaluating the validity of the predictive model. The RSM revealed that the maximum SMX removal efficiency of 95.6% ± (1.7) were obtained by the optimized TiO_2/AC6.5% composite.

According to the findings, the RSM-CCRD approach resulted in very good SMX removal efficiency. This implies that the method used were efficient.

Table 2. Analysis of variance for the SMX model removal obtained by TiO_2/AC6.5% under sunlight simulation conditions.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	**5**	415	83	4.15	0.072
Linear	**2**	**353**	**177**	**8.83**	**0.023**
Temp	**1**	**257**	**257**	**12.85**	**0.016**
Ratio	1	96	96	4.82	0.080
Square	2	62	31	1.54	0.301
Temp*Temp	1	50	50	2.52	0.173
Ratio*Ratio	1	28	28	1.40	0.291
2-Way inter.	1	0.5	0.5	0.02	0.883
Temp*Ratio	1	0.5	0.5	0.02	0.883
Error	5	99.9	19.9		
Lack-of-Fit	3	90.3	30.1	6.20	0.142
Pure Error	2	9.7	4.9	*	*
Total	10	515.5			

Note: 2-Way interact.: 2-Way interaction**. In bold**: variables with statistical significance.

Table 1. DCCR planning matrix with the values of the real and coded variables (in parentheses).

Nº of Run	TiO_2:AC mass ratio	Calcination temperature (°C)	Adsorption removal (%)	Adsorption + Photocatalysis removal (%)
1	5 (-1)	300 (-1)	26.6	81.9
2	5 (-1)	500 (+1)	48.1	88.0
3	15 (+1)	300 (-1)	14.7	69.4
4	15 (+1)	500 (+1)	35.2	76.9
5	2.95 (-1.41)	400 (0)	17.0	80.9
6	17.05 (+1.41)	400 (0)	20.3	78.1
7	10 (0)	259 (-1.41)	1.1	65.7
8	**10 (0)**	**541 (+1.41)**	**50.2**	**89.1**
9	10 (0)	400 (0)	22.4	84.2
10	10 (0)	400 (0)	18.4	85.4
11	10 (0)	400 (0)	16.9	81.6

Conclusions

The best results in terms of SMX removal from water was 95.6%, obtained with TiO_2/AC6.5% under sunlight simulation conditions. The results demonstrate that heterogeneous photocatalysis using TiO_2/AC6.5% composite as catalyst under sunlight activation is a potential alternative for purification of water and polishing treated wastewaters containing SMX. Now these results must be confirmed using real matrices.

References

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