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Effect of microwave radiation on the adsorption of the dye Remazol Red 198 (RR198) by O-carboxymethylchitosan-N-lauryl/F_2O_3 magnetic nanoparticles

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ABSTRACT

Nanoparticles were used to remove the anionic dye Remazol Red 198 (RR198) from aqueous solution by microwave-assisted systems. Adsorption of RR198 on OCh-ML by the microwave-assisted method was investigated with respect to pH, initial dye concentration, temperature, irradiation time, and microwave power. The microwave-assisted process decreases the time required for adsorption of the dye. Removal of the dye was optimized using a three-factor Box–Behnken design, and temperature and microwave power proved to be more influential in dye adsorption than irradiation time. Discoloration of the solution occurs by adsorption of the dye onto the surface of the OCh-ML and not by degradation of the RR198. The tests for phytotoxicity to lettuce seeds showed decreasing toxicity after adsorption of the dye for both adsorption systems. The total power consumed in microwave-assisted was the lower compared to batch method.

1. Introduction

The textile industry is a major consumer of synthetic dyes and water. Therefore, it is one of the main industries responsible for the generation and discharge of liquid effluents. The discharge of dyes from textile industry wastewater into the aquatic environment can cause serious health and environmental problems, as well as negative visual impact due to coloration of the water (Ghaly et al., 2014; Khatri et al., 2015; Ezechi et al., 2015).

Many processes have been proposed for wastewater treatment, most of them based on chemical reactions, ranging from precipitation/flocculation (Lee et al., 2014; Dasgupta et al., 2015). The adsorption process has been found to be effective for dye removal from wastewater (Yagub et al., 2014).

Recently, several researchers have reported on magnetic nanoparticles (Sayğılı et al., 2015) and magnetic nanoparticles containing chitosan derivative and their application in dye removal. The main advantage of the magnetic adsorbents containing chitosan derivatives is their higher capacity to remove dye, due to the presence of functional groups that promote specific interactions between the adsorbent and dye (Debrassi et al., 2012a,b; Zhou et al., 2014; Cho et al., 2015; Demarchi et al., 2015).

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The microwave radiation is a powerful tool in the degradation of various organic compounds, including pesticides, ammonia nitrogen and organic dyes. Recently, there have been some reports on wastewater treatment using microwave-assisted technologies (Wang and Wang, 2016; Gole and Gogate, 2014). For example, microwave-enhanced catalytic degradation of 4-nitrophenol using nickel oxide (Lai et al., 2011); degradation of methyl orange in the presence of nano TiO_2 activated carbon (Zhang et al., 2012), and granular-activated carbon and Cu/CeO_2 (Xu et al., 2014a,b); degradation of brilliant green using $CoFe_2O_4$ (Ju et al., 2013); degradation of orange acid using polyaniline (Riaz et al., 2014); degradation of crystal violet using $CaFe_2O_4$ (Shi et al., 2014); degradation of Reactive Brilliant Red X-3B by $MnFe_2O_4$ (Fang et al., 2015); microwave-assisted degradation photocatalytic of orange G by poly(1-naphthylamine) (Riaz and Ashraf, 2014); Solvent Blue and Reactive Yellow removal using microwave radiation in combination with nanoscale zero-valent iron (Mao et al., 2015); degradation of Congo red by nano-sized $CdFe_2O_4$ (Shi et al., 2015).

In this study, we report the use of *O*-carboxymethylchitosan-*N*-lauryl/F_2O_3 magnetic nanoparticles, in the removal of Remazol Red 198 (RR198) from aqueous solution. Dye adsorption was conducted by microwave-assisted systems. The toxicity of the dye before and after the adsorption process was evaluated using lettuce seeds (*Lactuca sativa*) as a bioindicator. A three-factor Box–Behnken experimental design was used to evaluate the importance of temperature, microwave power and irradiation time on the adsorption by the microwave-assisted system.

2. Experimental

2.1. Materials

O-carboxymethylchitosan-*N*-lauryl magnetic nanoparticles (OCh-ML) were synthesized and characterized as previously described (Demarchi et al., 2015).

RR198 was kindly donated by Linhas Denil Ltda (Poá, SP, Brazil). The reagents used were all of analytical grade, obtained from Vetec Química Fina (Brazil), unless stated otherwise, and all the solutions were prepared with distilled water.

2.2. Microwave adsorption of dye

OCh-ML/microwave-assisted adsorption (OCh-ML/MWA) experiments were carried out in a CEM Discovery Mod 908005 (USA) microwave apparatus. The system operated at 2450 MHz and the microwave output power ranged from 10 to 300 W. The reaction vessel was a round-bottomed flask equipped with a refluxing device. 10 mL of RR198 solution (50–250 mg L^{-1}) and OCh-ML (5–20 mg) were added to the round-bottomed flask at a controlled temperature (40–70 °C). The dye concentration was determined using a Spectrovision UV-visible DB-1880S spectrophotometer at a wavelength of 518 nm. The adsorption kinetics were carried out with RR198 concentration 250 mg L^{-1}, amount OCh-ML 15 mg and temperature 55 °C. Samples were taken at 2, 4, 6, 8 and 10 min for analysis of RR198 adsorption. The amount of dye removed was calculated by the difference between the initial concentration and the concentration of dye after the discoloration process.

The batch experiments were performed using 10 mg of OCh-ML added to 10 mL of RR198 dye 500 mg L^{-1}. The solutions were stirred with thermostating for 15 and 60 min at 70 °C. The magnetic material was then separated using an external magnetic field, and the dye concentration was calculated as described above.

RR198 solutions were analyzed by high-performance liquid chromatography (HPLC) performed with a Varian PROSTAR HPLC system equipped with a Varian 325 UV-VIS detector. The analyses were carried out under isocratic conditions (methanol:acetonitrile 75:25) using a C18 column (4.6 mm × 250 mm) packed with 5 μm diameter particles. The volume injected for analysis was 20 μL. The mobile phase used for analysis was methanol:acetonitrile 75:25 and the flow rate was 1.0 mL min^{-1}. The wavelength used was 254 nm.

The search for intermediates was performed using gas chromatography coupled to a mass spectrometer (GC–MS), using a Shimadzu QP2010S, column (RTX 30 m long, 0.25 mm i.d.). Helium was used as the carrier gas at a flow rate of 3 mL min^{-1}. The injector temperature was maintained at 290 °C, with oven temperature 80 °C kept constant for 1 min then increased up to 310 °C at a rate of 25 °C/min.

The conductivity was measured using a Digimed DM-31 conductivity meter.

2.3. Chemical oxygen demand (COD)

COD was performed according to Standard Methods for Examination of Water and Wastewater (5220). An aliquot of 15 mL of sample was added to a round bottom flask two necks containing 7.5 mL of digestion solution $K_2Cr_2O_7$ (in concentrated H_2SO_4) and 1.5 mL of sulphuric acid reagent (Ag_2SO_4 in concentrated H_2SO_4) and the mixture is heated under total reflux conditions for a period of 2 h at 140 °C. Throughout digestion chemically oxidizable organic material reduces a stoichiometrically equivalent amount of $K_2Cr_2O_7$. Ag_2SO_4 is added as a catalyst for oxidation of the low molecular mass acids. The amount of potassium dichromate reduced gives a measure of the amount of oxidizable organic material (Hunge et al., 2015). Absorbance was measured at 420 nm in a Jasco V630 spectrophotometer.

2.4. Factorial design

Factorial design is useful for studying the joint effect of different factors on a response. A Box–Behnken design of three factors at three levels was chosen based on the adsorption capacity of RR198 by OCh-ML. The design was composed of three levels (low, medium, and high, being coded as −1, 0 and +1), and a total of 15 runs were carried out to optimize the level of the chosen parameters (temperature, microwave power, and irradiation time). The factorial design matrix and the removed dye in each experiment (%) are shown in Table 1. The results were analyzed using the Statistica software version 7.0, and the main interactions between factors were determined.

2.5. Phytotoxicity assay

Seeds of lettuce (*L. sativa*) were purchased from an agricultural products store. Experiments based on seed germination were conducted according to the literature (Sancey et al., 2011). Ten seeds were placed on filter paper disks in Petri dishes (100–15 mm), and 5 mL of dye solution (500 mg L^{-1}), and either solution treated by the adsorption batch process (RR198 500 mg L^{-1}, 15 mg OCh-ML, 120 min, 70 °C) or solution treated by OCh-ML/MWA (RR198 500 mg L^{-1}, 15 mg of OCh-ML, power 300 W, temperature 70 °C, reaction time 15 min) was added. The Petri dishes were capped and the seeds were germinated in a growth chamber, in the dark, at 25 °C. After 72 h the germinated seeds were counted, and the rootlet of each germinated seed was measured with a ruler. Each experiment