Carbon Dots based on Polyurethane Waste used to remove environmental contaminants

POSTER
Ph.D. Student: N
Journal: ESPR

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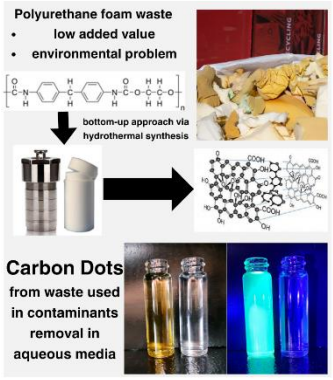

This work prepared Carbon Dots (CD) from polyurethane waste, a carbonaceous source. Quantum dots are recent nanometric materials with unique properties applicable to different science areas, such as photo sensors or catalysts. The use of polyurethane waste aligns with the sustainable development goals of the UN 2030 Agenda (goals 6, 7, 12, and 14), taking advantage of an abundant and low-cost resource discarded as upholstery waste. The synthesis was successfully carried out by the hydrothermal method at 200 °C for 14 hours, and the material was characterized by thermogravimetry, UV-vis spectroscopy, infrared spectroscopy - FTIR, Zeta potential, and N_2 adsorption/desorption. The material was tested to remove contaminants using a dye as a model molecule. The material was tested to remove contaminants using a methylene blue dye as a model molecule. Removal reached 89%, and the material was tested for five cycles, maintaining activity.

Introduction

Research into nanomaterials has gained prominence, driving significant innovations and discoveries. Carbonaceous materials versatile properties are especially interesting for nanotechnology studies. Polymers are crucial in global industry, with polyurethanes being widely used. However, recycling and reusing it is still a challenge. Considering the growing importance of sustainability, efficient recycling of polyurethanes can reduce environmental impact and promote the circular economy. In this context, carbon [1] quantum dots, derived from polyurethanes, stand out as promising materials on a nanometric scale, with potential for applications in photocatalysis for dye removal and other areas. This work developed an efficient hydrothermal synthesis route for CD, exploiting its photoluminescent and catalytic potential. Contaminant removal was tested using CD as photocatalysts. This work also aligns with the UN's sustainable development objectives, mainly in objectives 6 (Drinking water and Sanitation), 7 (Clean and Affordable Energy), 12 (Sustainable consumption and production), and 14 (Life in water).

Material and Methods

Polyurethane waste from upholstery foam was selected as the carbonaceous source. The residue was crushed in a knife mill, and the resulting powder was used to obtain carbon dots in the hydrothermal synthesis carried out in a Teflon® cup in an INOX® hydrothermal reactor. In this process, 30 mL of distilled water and approximately 2 g of polyurethane were subjected to 8 tests to obtain the best synthesis condition (Table 1).

Table 1. Entry, temperature, reaction time, and mass of polyurethane.

Entry	Temperature (°C)	Time (hour)	Poliuretane mass (g)
1	200	16	2,3014
2	160	14	2,3054
3	160	14	2,3501
4	200	14	2,3054
5	180	16	2,3092
6	200	18	2,3113
7	160	14	2,3251
8	200	7	2,3089

The best material was characterized by thermogravimetric analysis (DTG60H Shimadzu, heating from 25 °C up to 900 °C at 10 C min^{-1} under an airflow of 50 mL min^{-1}), Fourier transform infrared spectroscopy (ATR-FTIR) (Shimadzu IRPrestige-21), adsorption-desorption isotherms of N_2 (Autosorb -Quantachrome Corporation at 77 K and a degassing temperature of 150 °C for 12 h). The surface area was determined by Brunauer-Emmett-Teller (BET) method. The zero charge point was determined by measuring the variation in the pH values of the solutions. The pH was varied from 0 to 14.

The best material was applied in methylene blue (MB) oxidation reactions, using 500 μL of CD, 10 mL of MB solution (100 ppm) under the influence of a UV lamp or not. The kinetics were monitored through maximum absorbance (Mapada V-1100 D). Tests were also carried out with the addition of 300 μL of H_2O_2.

Results and Discussion

The Carbon Dots were synthesized from polyurethane waste from upholstery foam using a hydrothermal method, with eight syntheses varying temperature and reaction time. After synthesis, the resulting liquid was stored under refrigeration, showing orange. Some previous characterizations were made to define the best-obtaining route, considering the neutral medium (pH≈7), conductivity, and photoluminescence. The best test was 4, showing high conductivity, photoluminescence characteristic of carbon dots [2], and pH close to 7. The material was called 200CD14.

Figure 1(a) shows two thermogravimetry curves for polyurethane and 200CD14. Polyurethane, the precursor of the synthesized material, loses mass around 350 ºC, while 200CD14 loses mass above 380 ºC, suggesting precursor carbonization.

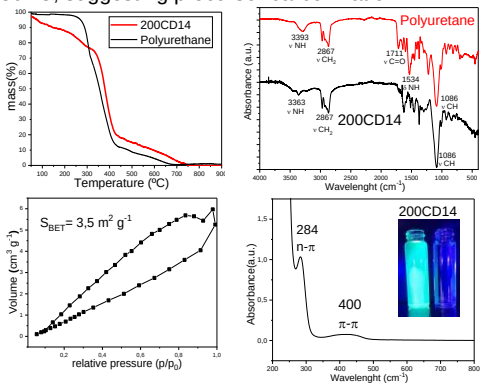

Figure 1. (a) Thermogravimetric curve and (b) FT-IR spectrum (c) Adsorption-desorption isotherms of N_2, and (d) Ultraviolet spectrum of 200CD14.

The change in loss temperature indicates a change in composition and confirms the synthesis of a new material. Figure 1(b) shows the comparison between the FTIR curves of polyurethane and 200CD14 where it can be seen that the bands[3] corresponding to the C-O bond at 1711 cm^{-1} have disappeared. There is also the disappearance of the band at 1534 cm^{-1}, related to N-H bond, reaffirming the carbonization of the starting material.

The N_2 adsorption-desorption (Figure 1(c)) for the 200CD14 material indicates a type V isotherm, typical of microporous material with low surface area. The low surface area is due to the hygroscopic nature of the material, which results in a low surface area due to equipment analysis. The UV-vis spectrum indicates two absorption bands, one at 400 nm, related to the n-π transition, characteristic of the bonds between carbon and oxygen, and at 284 nm associated with the π-π transition, characteristic of the bond between carbons.[3] The highlight of Figure 1(d) is the image of the 200CD14 solution irradiated with UV light after 30 min, showing the photoluminescence of the material.

The zeta potential was measured, and the zero charge potential was 5.3. As the pH of the 200CD14 solution is 6.3, the material's surface is negative at this pH, which favors the application of the material with positively charged substrates such as methylene blue.

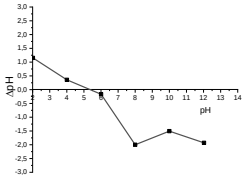

Figure 2. Zero charge point (pH_{pcz}) for 200CD14.

The material was used in MB removal (Figure 2(b)). Initially, the test with 200CD14 plus the MB solution was carried out without UV radiation, and no removal was performed. The test with 200CD14 plus the MB solution and without UV radiation also showed no removal. When the CD and the MB solution were placed under UV radiation, 41% was removed, indicating that the CD can act as a photocatalyst. To enhance the activity of the material, H_2O_2 was added as an oxidizing agent, and removal in the presence of UV light was 89%.

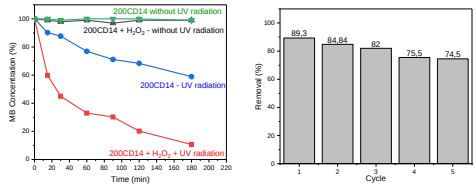

Figure 2. (a) MB solution (100 ppm) degradation kinetics in the presence of 200CD14 without UV, just H_2O_2, UV radiation, UV + H_2O_2, and (b) Reuse studies for five cycles

Reuse tests were performed (Figure 2(b)) after 180 min of reaction to evaluate the stability of the materials, and after five cycles, the system showed stability with just 17% loss. It is worth mentioning that in the literature, there are few reports of CDs being used directly as photocatalysts in removing contaminants.

Conclusions

Obtaining carbon dots at 200°C for 14 h via hydrothermal synthesis was successfully achieved. The material demonstrated photoluminescent activity and pH within the expected range. The application to remove methylene blue proved very interesting with high dye removal.

References

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