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Oxidation of methylene blue solutions with a new catalyst Cu-activated carbon monoliths

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ABSTRACT

Activated carbon monoliths are synthesized from coconut shell and used as support for copper oxide and metallic copper catalysts. The obtained support is texturally characterized by a superficial BET area of 1427 m^2/g and because of the impregnation and activation process, this value can decrease to as low as 526 m^2/g for the catalysts. The catalysts and support are both of microporous nature. The obtained catalysts are characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), and by temperature programmed reduction (TPR). The catalytic oxidation of methylene blue solutions was performed since the application for treating wastewaters is of interest, as these can have great impacts on aqueous ecosystems. Out of all the synthesized catalysts, those with the highest concentration of metallic copper as active phase showed the highest catalytic activity.

KEYWORDS

Activated carbon;
Monoliths;
Catalysts;
Blue methylene.

1. INTRODUCTION

Over 90% of all chemical´s manufacturing processes involve catalysis in some way, due to the possibility of increasing reaction rates and controlling selectivity processes. There has been an interest and increase in the use of activated carbon as catalyst support or as a catalyst itself, because of its flexibility to be tailored to specific needs. This flexibility is reflected on the fact that activated carbon can resist both basic and acidic mediums, is stable at high temperatures, can be produced with different pore distributions, can be prepared in several physical forms, usually costs less than other supports like alumina or silica and that the active phase can be recovered burning away the carbon if it´s a precious metal[1].

Monolithic catalysts can be attractive alternatives to conventional catalysts. Currently, the most important application happens in the automotive industry, where they are used for cleaning up exhaust gases. The use of monolithic supports for other applications, especially on multi-phase or liquid phase reactions, is limited, even when a monolithic reactor offers some operational advantages over conventional reactor, such as low pressure drops, high catalyst efficiency, an easy separation from the reaction system and improved safety[2]. Among the uses for monoliths, the treatment and transport of gases and liquid purification are usually found.

Among the most common uses for copper catalysts, oxidation, reduction and desulfurization reactions are found. It has been reported that monolithic copper catalysts are adequate for catalyzing methanol steam reforming reactions and reducing nitrous oxides for nitric acid plants as well as for diesel motor emissions[3].

Copper catalysts have been frequently used for wet oxidation of organic compounds. The approach for treating wastewater depends on the content of pollutants and their resistance to oxidation. Copper catalysts have been reported to show high catalytic activities for the oxidation of organic compounds found in nonconventional wastewaters[4-6], such as those that have bactericidal properties or come from processes that involve dyes. Compared to traditional wastewater treatment methods, catalytic wet oxidation offers advantages such as high reaction rates, low production of polluting byproducts and requiring less physical space[6].

2. Methodology

Copper catalysts supported on monolithic activated carbon are prepared, some with copper oxide as the active phase and the other ones with metallic copper as the active phase. The catalysts as well as the support are texturally characterized. Then, the catalysts are used to catalyze the oxidation of methylene blue to observe their catalytic activity.

2.1. Catalyst formulation

2.1.1. Support preparation

Coconut shell is dried in an oven for 8 hours at 363K to get rid of its moisture content and for making the size reduction process easier. Then, the shell is mechanically crushed so it can be processed in a Corona® mill. The material obtained is passed through a series of sieves so the particles obtained end up with a diameter lesser than 38μm. A fine particle size provides a greater superficial contact area, favoring the monolith's final characteristics[7]. The chemical composition of coconut shell is show in the TABLE 2.

TABLE 1: Honeycomb mold specifications

Honeycomb structure	
Geometry	Cylindrical
Cell geometry	Hexagonal
Number of cells	7
Height (mm)	9,5
Total diameter (mm)	17,5
Total volume (mm3)	3645,5
Total superficial Area(mm^2)	4499,8

TABLE 2: Chemical compositon of coconut shell

Coconut shell	wt%
Cellulose	33.1
Lignin	36.6
Pentosans	29.3
Ash	0.2
Fixed carbon	43.5
Moisture	1.1
Volatile matter	53.1

The impregnation for the chemical activation is done using a 1g of coconut shell to 2ml of 32% zinc chloride ratio. This solution is placed in an oven at 368K for 7 hours, and then dried at 383K for 5 hours. After drying, the monoliths are pressed at 423K and 35 MPa. The Specifications for the mold used are shown in TABLE 1. The monoliths are kept in an oven at 773K for 2 hours using a heating ramp of 1K/min and a N2 flow of 80ml/min[8].

After leaving the oven, the monoliths are washed with HCl 0.1M, and then with hot water to remove the last traces of zinc chloride[8]. The water used for washing is qualitatively analyzed by adding a few drops of a silver nitrate solution, watching that no precipitation occurs in order to determine that the washing process is finished.

2.1.2. Copper impregnation and activation

The obtained monoliths are de-gasified at 523K for 2 hours to remove any traces of water that are adsorbed. 10% and 15% copper nitrate solutions are prepared, in which the monoliths are submerged in for 1 hour for the wet impregnation and then dried overnight at 388K. The catalysts are then calcinated at 673K, using a N2 flow of 40ml/min for 2 hours to obtain copper oxide as active phase. Later, the catalysts are reduced so metallic copper is obtained as the active phase. This reduction is done at 873K using a H2 flow of

200ml/min for 2 hours. All catalysts obtained were placed in an inert atmosphere.

2.2. Characterization of support and catalysts

The catalysts and the support are characterized through various techniques. For the catalysts and the support, points of an isotherm are taken to determine their pore volume, diameter and superficial area, which allow one to say if the structures have adequate properties for catalysis.

Through X-ray diffraction (XRD) and temperature programmed reduction (TPR), the presence of copper on the catalysts as active phase is analyzed qualitatively and quantitatively. Also, using Scanning electron microscopy (SEM), the presence of copper as the active phase is seen, by watching how it's deposited over the carbon monolith's surface.

2.3. Catalysts' tests

500ppm methylene blue aqueous solutions (300 ml) are oxidized for studying the prepared catalysts' catalytic activity. The solutions were kept at a controlled temperature of 353K. Once this temperature is reached, an O2 flow of 200 ml/min is begun and 100mg of catalysts are added to the solution. At this moment it's considered that the reaction has begun. Every 15 min samples were taken from the reacting system. The reaction's evolution was followed measuring the variation of methylene blue concentration with time by UV-visible spectophotometry following a λmax 669nm radiation absorption. The samples were diluted 100 times so their absorbance could fall in the Beer-Lambert law interval.

Figure 1 : Obtained monolith

TABLE 3: Catalysts and support textural properties

Sample	BET superficial area / m^2/g	DFT pore width mode / Å	DR pore volume/ cm3/g
Activated carbon monoliths	1427	5.47	0.795
CuO 15 wt %	839	4.17	0.453
Cu 15 wt %	526	4.17	0.284

2.4. Analysis by X-ray photoelectron

The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS), using a UHV VG Microtech MultiLab ESCA 2000 equipped with an Al Kα X-ray source (hv = 1486.6 eV) and a CLAM4 MCD detector. The surface chemical composition was determined from the orbital peak area, using the atomic sensitivity factors and corrected with the analyzer transmission function, taking CuO-mesh and Cu as reference materials. In all cases, the catalyst was etched during 2 minutes with 3.0 kV Ar^+ to eliminate contaminating carbon. The background for the high resolution and the survey spectra was that Shirley and lineal, respectively.

3. RESULTS AND DISCUSSION

3.1. Support and catalysts obtained

Figure 1 shows a picture of the obtained monoliths. The structures show good solidity and compaction. The most critical step for obtaining the monoliths is the carbonization, because for the described protocol, it lasts the longest and 69% of the mass that enters the oven is lost.

The catalysts obtained present a reddish color, which is the characteristic color of copper oxide I and metallic copper. During the impregnation process, the structures keep the monoliths' good mechanical properties obtained initially.

3.2. Structures' characterization

3.2.1. Superficial area, width and pore volume

An *Autosorb 3B Quantachrome Instruments* equipment was used for obtaining the volume of nitrogen adsorbed by the materials at relative nitrogen pressures from 0.05 to 0.35, which is the pressure range used for determining superficial area, pore volume and width.

TABLE 3 summarizes the characterization's results. The support gives a superficial area of 1427 m^2/g, which is consistent with the usual range of active carbon superficial area. The catalysts' impregnation and activation processes cause a clogging effect on the supports' pores. As a result, the catalysts' superficial area reduces

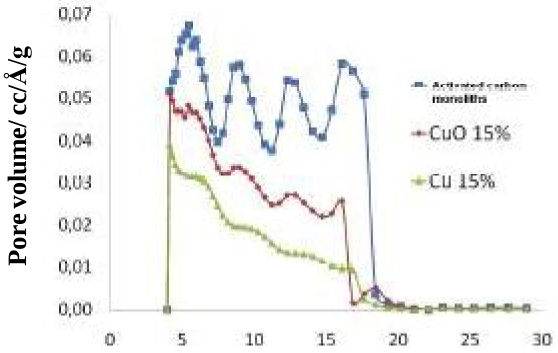

Figure 2 : DFT pore volume distribution

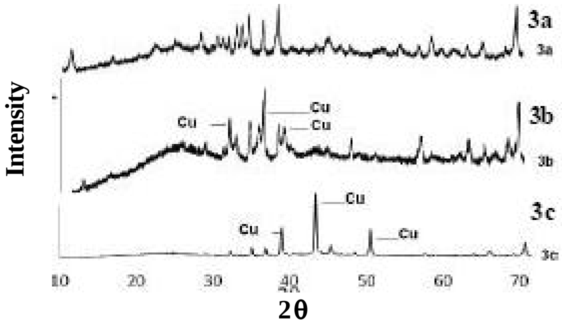

Figure 3: (a) XRD for the Activated carbon monoliths; (b) XRD for the calcinated catalyst. Impregnating solution concentration 15 wt%. (c) XRD for the hydrogenated catalyst. Impregnating solution concentration 15 wt%

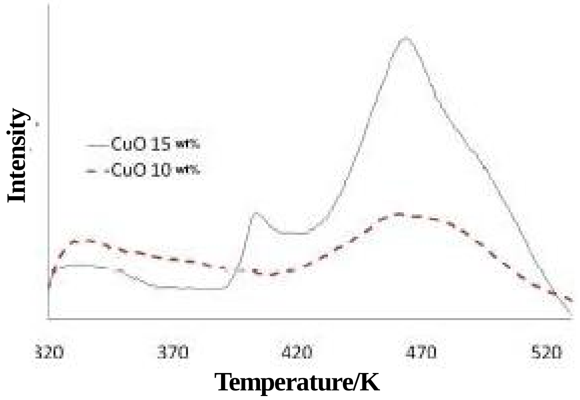

Figure 4: TPR for calcinated catalysts. Continuous line CuO 15%. Dotted line CuO 10%

significantly in comparison to the supports' area.

Figure 2 shows the DFT pore volume distribution for the support and the catalysts. Most of the pore volume occurs below 20Å for these structures, which indicates that these have a microporous nature. The pore's width mode is close to 5 Å for the support and 4 Å for the catalysts. Pore volume reduction, in addition to pore width reduction, is observed for the catalysts, which confirms pore clogging due to the impregnation and activation processes.

3.2.2. X-ray diffraction

The following difractograms are obtained using a *Miniflex Rigaku* equipment. It can be clearly seen that the monolith goes through structural changes after the impregnation and activation processes, which is shown by the appearance of new peaks in the catalysts' difractograms compared to the support's (figure 3a).

The catalysts that were activated only through calcinations, figure 3b, show peaks around 2? 39°, which indicates the presence of copper oxide II, and around 36°, which indicates de presence of copper oxide.

It's to be expected that a mixture of the oxides is obtained since the calcination does not give the same energy levels uniformly throughout the monolith, so in certain places the oxidation is not complete.

For the hydrogenated catalysts, figure 3c, the difractograms show clear sharp peaks at around 2θ 43° and 50°, the characteristic peaks for metallic copper, and that clearly show how the used catalytic process changed the valence state of the copper. The difractograms for the catalysts whose impregnation solution concentration was 10% are similar to those shown in figures 3b and 3c, showing the same peaks, so they're not presented here.

3.2.3. Temperature programmed reduction

Figure 4 is the result for the calcinated catalysts' temperature programmed reduction, which shows the existence of 2 peaks in the equipment's signal. The equipment used for this test is a Micromeritics Chemisorb 7020. The two peaks are observed around 410K and 460K, the reduction temperatures for Cu(I) and Cu(II) respectively, proving the presence of a mixture of copper oxides in the catalysts, a result consistent with that given on figure 3b.

This test shows that the catalysts impregnated with a more concentrated solution end up with a greater load of active phase, which is to be expected since starting with a more concentrated solution will make the amount of copper available to be deposited over the surface greater. For the impregnation, no agitation mechanisms are used and the solution is in excess respect to the amount of support (wet impregnation), so copper's

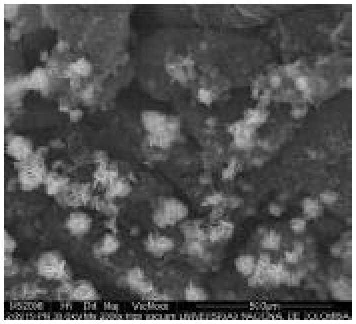

Figure 5: SEM photograph for copper oxide catalyst

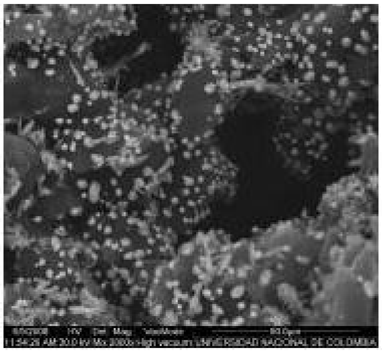

Figure 6: SEM photograph for metallic copper catalyst

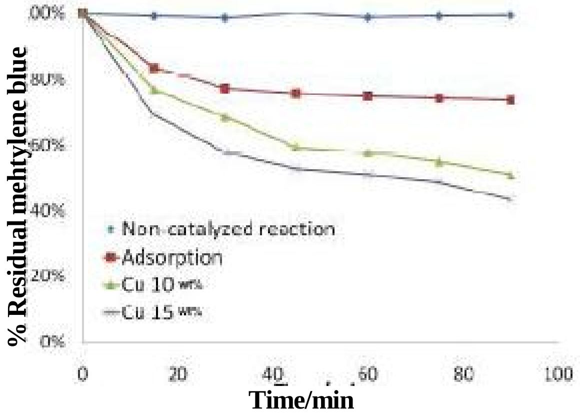

Figure 7: Residual methylene blue for metallic copper catalysts

deposition is controlled by diffusion forces[10], i.e., by mass transfer, which is favored if the impregnating solution has a greater concentration.

3.2.4. Scanning electron microscopy

This test is done in a FEI QUANTA 200 scanning microscope to observe the catalysts' shape, size, homogeneity, presence and distribution of crystalline and amorphous compounds[11]. It can be seen on figures 5 and 6 that the particles of copper are asymmetrically dispersed over the monolith's surface with different sizes and irregular shapes. Because the hydrogenation and calcinations temperatures were much below copper's fusion temperature, it was possible to obtain small particles of copper without there being agglomerates. When comparing figures 5 and 6, it's possible to see the change of state that the copper underwent during the hydrogenation process, as the shape and appearance of the material deposited on the monolith's surface are different.

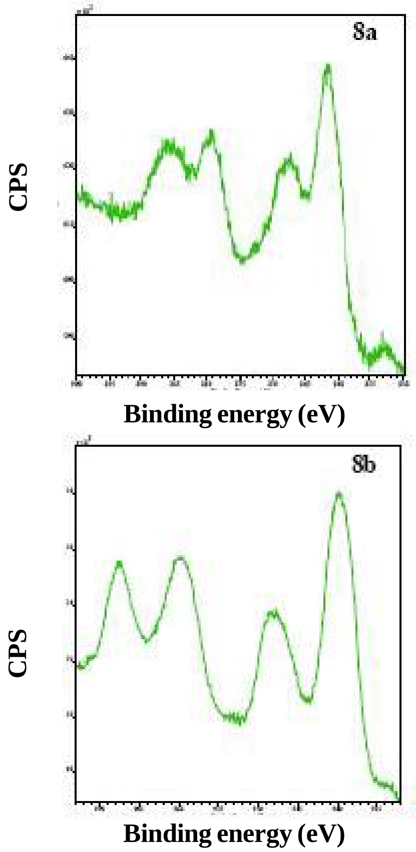

Figure 8 : (a) XPS spectrum: Catalyst Cu/C Before, (b) XPS spectrum: Catalyst Cu/C after

3.3. Catalysts' tests

While testing the catalysts, 3 processes can cause the methylene blue concentration to fall: adsorption over the support's porous surface, catalytic oxidation and non-catalytic oxidation. To determine catalytic activity, it's necessary to perform two blank tests, one to observe the degree of non-catalytic oxidation, and the other one to observe the degree of adsorption over the monolith's surface.

The results for the tests performed are given on figures 9 and 10, expressed as percent of methylene blue left in the solution in time respect to the initial concentration. Figure 9 shows the results for the hydrogenated catalysts and figure 10 for the calcinated ones.

The first blank clearly shows that the effect of non-catalytic oxidation is not significant, as the concentration of methylene blue remains practically the same throughout this test. The second blank, allows seeing the degree of adsorption over the surface. When using a temperature as high as 353 K, adsorption is not favored as this is a spontaneous exothermic process favored by using low temperatures. Even so, methylene's blue concentration diminishes about 20% when only the adsorption phenomenon is considered.

For the two types of catalysts, calcinated and hydrogenated, it's noticed that the bigger the load of active phase, the concentration of methylene blue reduces more, which is to be expected since the presence of more active phase allows the reaction to be carried out more easily as the reactants have an easier time finding copper which produces the catalytic phenomenon.

Among the synthesized catalysts, the best results were obtained for those hydrogenated whose impregnating solution´s concentration was 15%. However, the activity's difference observed was not significant, being similar for the catalysts impregnated with the same concentration of impregnating solution. For the catalysts impregnated with a 15% solution, the reduction in methylene blue concentration was around 50%, while for those impregnated with a 10% solution it was about 40%. These results show the presence of catalytic activity since the change in methylene blue concentration is significant compared to that of the two blanks see figure 7.

The figure 8a an 8b shows of XPS spectrum of the catalyst Cu/C before and after processes catalytic; in the XPS (figure 8a) show of catalyst before of process, is clear of peaks characteristic to the cooper an the figure 8b show of XPS spectrum .

4. CONCLUSIONS

Active carbon monoliths are prepared, whose characterization gives an apparent BET superficial area over 1000 m^2/g, also finding it's a microporous material. This superficial area is of great help for dispersing other materials over itself, for which it´s a feasible alternative for preparing catalysts.

Copper oxide, as well as metallic copper, catalysts were obtained, which is reflected on the textural characterization done. The superficial areas obtained show that the catalysts are adequate for catalysis, and the SEM photographs show the copper´s good distribution over the active carbon.

The obtained catalysts were tried on the wet oxidation reaction of methylene blue, showing good results for oxidizing this chemical. Among the synthesized catalysts, similar behaviors were obtained for the reacting system based on the initial concentration of the impregnating solution. The greatest catalytic activity was observed for the hydrogenated catalysts with the greatest initial concentration of the impregnating solution.

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