Carbonaceous material production from vegetable residue and their use in the removal of textile dyes present in wastewater

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Abstract. This paper presents the adsorption results of acid, basic, direct, vat, and reactive-type dyes on carbonaceous adsorbent materials prepared starting off vegetable residue such as Opuntia ficus indica and Casimiroa edulis fruit wastes. The adsorbents prepared from Opuntia ficus indica waste were designated: TunaAsh, CarTunaT, and CarTunaQ. The materials obtained from Casimiroa edulis waste were named: CenZAP, CarZAPT, and CarZAPQ. TunaAsh and CenZAP consist of ashes obtained at 550 °C; CarTunaT and CarZAPT consist of the materials carbonized at 400 °C; lastly, CarTunaQ and CarZAPQ consist of chemically activated carbons using $\text{H}_3\text{PO}_4$ at 400 °C. Only the chemically activated materials were washed with distilled water until a neutral pH was obtained after their carbonization. All materials were ground and sieved to obtain a particle size ranging from 0.25 to 0.84 mm. The static adsorption results showed that both ashes and chemically activated carbon are more efficient at dye removal for both vegetable residues. For TunaAsh and CarTunaQ, removal rates of up to 100% in the cases of basic, acid, and direct dyes were achieved. Regarding wastewater containing reactive dyes, the efficiency ranged from 60 to 100%. For vat effluents, it ranged from 42 to 52%. In the case of CenZAP and CarZAPQ, it was possible to treat reactive effluents with rates ranging between 63 and 91%. Regarding vat effluents, it ranged from 57 to 68%. The process of characterization for all materials was done using scanning electron microscopy and infrared spectroscopy.

Keywords. Opuntia ficus indica fruit waste, Casimiroa edulis fruit waste, Carbonaceous adsorbents, Textile dyes removal.

1. Introduction

Activated carbon (AC) is one of the most commonly used adsorbents in the removal process of industrial pollutants, organic compounds, heavy metals, herbicides, and dyes, among many others toxic compounds. There are two types of activation procedures to produce AC: Physical or thermal, and chemical. In physical activation, the lignocellulosic material as such or the previously carbonized materials can undergo gasification with water vapor, carbon dioxide, or the combustion gases produced. Chemical activation consists of the impregnation with chemicals such as $\text{ZnCl}_2$ or $\text{H}_3\text{PO}_4$ on lignocellulosic or carbonaceous raw materials, later they undergo carbonization or pyrolysis, and finally, they are washed to eliminate the activating agent. The application of a gaseous stream such as air or nitrogen is a common practice during pyrolysis which generates a better development on the porosity of the material [1].

Commercially, AC is prepared by means of oxidative pyrolysis starting off soft and hardwoods, peat, lignite, mineral carbon, bones, and coconut shell [2]. AC is considered an expensive material because of the chemical and physical treatments used during its production, its low yield, its production's high energy consumption, and the thermal or solvents treatments used for its regeneration. Attempting to reduce the cost of production of AC, contemporary research is taking a turn towards industrial or agricultural wastes to be used as raw material, and, then, lessen the cost of production [3]. Besides, the use of these precursors reduces residue generation in both rural and urban areas. The objective of this research was to produce low cost AC from vegetable waste materials, Opuntia ficus indica and Casimiroa edulis carbons were used to remove different types of textile dyes. Their adsorptive properties were then analyzed to find the relationship between their different structures and chemical surfaces.
2. Experimental

**Materials.** The six ACs were carbonized in a Thermolyne 48000 muffle furnace under their combustion gases atmosphere. Three were prepared from *Opuntia ficus indica* fruit waste and were designated: TunaAsh, CarTunaT, and CarTunaQ. The three adsorbents prepared from the *Casimiroa edulis* fruit waste were: CenZAP, CarZAPT, and CarZAPQ. TunaAsh and CenZAP consist of ashes obtained from sudden heating at 550 °C for 3 h; CarTunaT and CarZAPT consist of the materials carbonized at 400 °C for 3 h with controlled heating, the heating rates were 4.7 and 3.8 °C/min respectively; lastly, CarTunaQ and CarZAPQ consist of chemically activated carbons impregnated with H$_3$PO$_4$ and pyrolyzed at 400 °C during 3 h, the heating rates were 4.3 and 2.1 °C/min respectively. Only the chemically activated materials were washed with distilled water, to eliminate the H$_3$PO$_4$ excess, until a neutral pH was obtained in the washed solution. All materials were ground and sieved to obtain a particle size ranging from 0.25 to 0.84 mm.

To explore the effects of the carbonization process over the adsorptive properties of the ACs, different types of dyes, according to the Colour Index (CI) [4] classification, were selected. Table 1 shows the selected dyes and some of their properties. With the exception of vat dyes (water insoluble) and basic dyes, which are cationic molecules. The rest of the molecules of the dyes can be considered anionic. Three of the dyes were studied as model aqueous solutions and seven were found in wastewater produced from the dyeing process of cotton fabrics.

| Dye (CI Generic Name)       | Key    | Textile Classification | $\lambda_{\text{max}}$ (nm) | Solution type | pH  | $C_i$ (ppm) |
|-----------------------------|--------|------------------------|-----------------------------|---------------|-----|-------------|
| Methylene Blue (Basic Blue 9) | BB9    | Basic                  | 665                         | Aqueous       | 6.1 | 50          |
| Crystal Violet (Basic Violet 3) | BV3    | Basic                  | 590                         | Aqueous       | 6.0 | 50          |
| Carminic Acid (Natural Red 4)     | NR4    | Acid                   | 500                         | Aqueous       | 3.2 | 50          |
| Sirius Green (Direct Green 1)     | DG1    | Direct                 | 610                         | Wastewater    | 9.8 | 20          |
| Sirius Turquoise (Direct Turquoise 86) | DT86 | Direct                 | 620                         | Wastewater    | 9.9 | 68          |
| Vat Navy Blue                  | VNB    | Vat                    | 560                         | Wastewater    | 12  | —           |
| Vat Dark Grey                  | VDGY   | Vat                    | 400                         | Wastewater    | 12  | —           |
| Reactive Blue                  | RB     | Reactive               | 610                         | Wastewater    | 11  | —           |
| Reactive Red                   | RR     | Reactive               | 515                         | Wastewater    | 11  | —           |
| Reactive Orange                | RO     | Reactive               | 495                         | Wastewater    | 11  | —           |

**Methods.** Static adsorption at 30 °C on every AC was studied using an adsorbent mass-solution volume (m/V) ratio of 0.01 g/L. The contact time was 24 h, although, in some cases, it was observed that within the first hour of contact, the dye had been completely removed from the solution. The adsorption results were compared with a commercial powder charcoal (Sigma de México) with a particle size ranging from 74 to 150 μm.

The quantification of the adsorbed dyes was done by spectrophotometry in the visible region using a HACH DR 2500 spectrophotometer at maximum wavelength absorbance. For BB9, BV3, NR4, DG1, and DT86, their respective calibration curves were constructed and used for quantification. For the rest of the dyes present in wastewater, the quantification was obtained by observing the decrease in the intensity of the main color band. Fourier transform infrared (FTIR) spectra for the ACs were acquired using a PerkinElmer Spectrum One spectrometer with attenuated total reflectance (ATR) in the 4000 to 650 cm$^{-1}$ spectral range. The microscopic surface features of AC materials were observed with a JEOL model JSM 6300 scanning electron microscope operated a 30 kV, previously the samples were coated with gold.

3. Results and discussion

The organic functional groups of the activated carbons were determined by means of FTIR spectra (Figure 1). For CarTunaT and TunaAsh (Fig. 1b), the spectra are similar. Only a slight diminishing of the intensity of certain bands is observed. However, for CarTunaQ, its functional groups do not coincide with the previous ones. Both TunaAsh and CarTunaT exhibit bands at 1400, 1100, and 1050 cm$^{-1}$ which are characteristically found in...
O-H deformation and C-O stretching vibrations in primary, secondary, and tertiary alcohols and phenols. CarTunaQ shows a band at approximately 3500 cm\(^{-1}\) which indicates the presence of primary and secondary amines because of the N-H stretching vibrations. This is confirmed by the band found at 1600 cm\(^{-1}\) which indicates N-H deformation vibration for the same kind of amines.

CarTunaQ also presents a broad band at 1200 cm\(^{-1}\) because of the O-H deformation and C-O stretching vibrations for phenols. Furthermore, a band at 999 and a shoulder at 1070 cm\(^{-1}\), characteristically found in phosphate groups [5], appear because of the H\(_3\)PO\(_4\) impregnation treatment. In CarZAPQ (Fig. 1a), the appearance of bands at 999 and 1070 cm\(^{-1}\) characteristic of phosphate groups is also observed.

The carbons obtained from Casimiroa edulis fruit waste exhibit (Fig. 1a) a greater amount of functional groups, including N-H deformation (1500 cm\(^{-1}\)), O-H deformation and C-O stretching (1400, 1100, and 1050 cm\(^{-1}\)), and C-H stretching (alquenes at 3000 cm\(^{-1}\)) vibrations. In a similar way as Opuntia ficus indica waste carbons, ash (CenZAP) and thermal carbon (CarZAPT) exhibit practically the same bands.

![Figure 1. FTIR spectra for the activated carbons prepared. (a) Casimiroa edulis and (b) Opuntia ficus indica carbons. — Ashes, —— Physical, and —— Chemical carbons.](image)

Regarding their superficial appearance, the micrographs obtained by SEM (Figure 2) for ashes and physically activated carbons (a, b, d, e) obtained from both residues show the formation of irregularly shaped and sized cavities because of the irregular structure of the raw materials and the release of volatile compounds during the thermal treatment as well as small particles deposited on the surface.

![Figure 2. SEM micrographs of carbonized materials from Opuntia ficus indica (a, b, c) and Casimiroa edulis (d, e, f) wastes. Ashes (a and d), Physical activated carbons (b and e), and Chemical activated carbons (c and f).](image)
Again, the carbons activated with $\text{H}_3\text{PO}_4$ turn out to be superficially different. CarTunaQ (c) shows superficial holes, and CarZAPQ (f) exhibits superficial cracking rather than a development in porosity as such. The adsorption capability of ACs is expressed as the dye removal percentage, and it is presented in Figure 3. Graph (a) shows that acid, basic, and direct dyes are being retained excellently in the carbons, almost as it would be the case for a commercial carbon. Graph (b) shows the removal of vat and reactive dyes in wastewater, which turned out to be acceptable, but not as good as in the previous cases. This happens because wastewater is a very complex matrix that contains diverse compounds (salts like sodium carbonate, hydroxide, hydrosulfite or sulfate, and surfactants) used during the dyeing process that surely compete for active sites, thus inhibiting the interaction of the dyes.

The high adsorption of cationic and anionic dyes is confirmed with the IR spectrums which show the presence of anionic and cationic functional groups. These give a certain polarity to the carbons and, thus, the ability to interact with the ionic dyes. Furthermore, the micrographs show a great quantity of cavities in the carbons, which favor the development of the specific surface area and, hence, a better adsorption capacity.

4. Conclusions

Both Opuntia ficus indica and Casimiroa edulis fruit wastes in their carbonized forms are effective in the removal of textile dyes, reaching removal rates superior even to commercial AC, regardless of the smaller particle size this last one has. Hence, it is possible to produce activated carbons from these two residues which are common and abundant in the region (Puebla and Hidalgo states of Mexico). The adsorptive capabilities of the ACs depend strongly of their superficial functional groups and their morphology.

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5. References

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