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Production of Activated Bio-chars for Wastewater Treatment: Characterization, Activation and Evaluation of the Adsorption Capacity

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Bio-char prepared from lignocellulosic wastes is a sustainable and low-cost material with many interesting applications, such as the adsorption of contaminants from wastewaters, among others. It is obtained from the pyrolysis of biomass through a thermochemical process in the absence of oxygen. In this process, biomass hydrocarbons, volatile matter, oxygen and hydrogen are converted into a carbon-enriched material, known as Bio-char (BC). Several parameters will define the structural properties and characteristics of the BC, some of which are related to the used raw material or biomass type and others to the process conditions. In order to evaluate the potential of the BC as adsorbent of toxic compounds from wastewaters, the most relevant properties are related to the active surface area, pore size and distribution, and stability. For the use of BC as adsorbent, in order to increase the adsorption capacity, activation of the BC is typically done. In this work, cork residues from wine bottles were thermo-chemically treated under a pyrolysis process and subsequently activated with KOH. The obtained Activated Bio-Chars (ABC) were characterized in terms of proximate analysis, active surface area and pore size distribution. Furthermore, BC and ABC adsorption capacity was tested. In particular, the adsorption of the dye methylene blue, MB; was studied. The obtained results indicated that the activation process was necessary in order to reach high MB adsorption capacities, over 90%. Because of its characteristics, it is proposed that BC without activation could be used to remove lower molecular weight components, such as gaseous ones. Finally, focusing on the design of a low-impact process and following green chemistry and sustainable practices, the recycling potential of the ABC was studied in terms of number of cycles, used solvent, dye recovery and adsorption performance. Reused ABC presented good performance in terms of adsorption capacity during several batches, similar to the one of raw ABC. The performance of several solvents was studied and acetone was selected as the better one due to good results in terms of ABC regeneration capacity and low boiling point for its subsequent recuperation.

1. Introduction

The environmental impact of the industrial activities is being progressively submitted to stricter controls in order to limit their impact in soil and water environments (Elessawy et al., 2020). Many industrial processes, such as textile, pulp and paper, paint and pigments, or pharmaceutics ones, generate huge quantities of effluents and residual streams that can be potentially eco-toxic, and should be treated before their disposal (Hou et al., 2019). In particular, effluents containing dyes, have been proven to have high stability to photochemical, chemical and biological degradation, so they can affect the water ecological balance and present potential danger of bioaccumulation (Hamadi et al., 2021). A wide variety of techniques are typically used for wastewaters remediation, but most of them are ineffective and expensive, due to low selectivity and high associated costs (El Hassani et al., 2019). Adsorption technology has been identified as a convenient technique for the removal of pollutants from wastewaters as a simple, cheap and effective technology to treat effluents with dyes (Zhou et

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al., 2019). Activated carbon presents many benefits as adsorbent, such as high surface area and reactivity, high porosity given by a porous structure in the micro scale with uniform pore size distribution, which confers high adsorption capacity. The drawback of this material is its high cost, which has pushed the search for alternative options, especially to be used at large scale (Dai et al., 2018). Biomass-based materials have been studied for this purpose, as they can actively retain the toxic compounds in their porous structure while the available chemical groups in its composition offer selective reactivity to several compounds (Dias et al., 2021). Agro-forestry waste is particularly interesting for this use, as its lignocellulosic structure contains carboxyl, hydroxyl and other reactive groups, that will actively contribute in the removal of toxics from aqueous effluents (de Freitas et al., 2019) while giving a use to a residue under the philosophy of "treating waste by waste" (Huang, 2017). Available research works about the biosorption of toxic compounds by agro-forestry wastes support the potential of this feedstock for the removal of dyes, heavy metals or metallic ions, but several drawbacks have been highlighted, particularly related to its low stability and perishability (Zhou et al., 2019). To improve the performance of the adsorbent, lignocellulosic wastes have been submitted to thermochemical activation with very promising results in terms of total removal ratios of the toxic compounds (Ahmed et al., 2019). This study presents the results of the thermochemical activation of cork residues and the use of the generated BC and ABC as adsorbent of methylene blue (MB) from an aqueous stream. MB is a heterocyclic aromatic widely used in chemical textile industries, and medicine and the cationic-type dye that concerns the most researches from over the world (Nayak and Pal, 2017). The prepared ABC have been characterized (proximate analysis, BET) and tested as adsorbents for the removal of MB by UV absorbance. Moreover, the prepared ABCs were submitted to recovery and reuse cycles in order to evaluate the dye recycling potential as well as the ABC reuse capacity. Different solvents were tested (ethanol, methanol and acetone) and the adsorption-desorption behaviour was tested. Good results were achieved, particularly with acetone that allowed to a total recovery of the original dye and reuse of the ABC.

2. Materials and methods

Cork residues (CR) provided from local suppliers have been used as raw material in this work. Samples were homogenized to a particle size between 0,5 and 1mm. Proximate and ultimate analysis (TruSpec Micro LECO) were done on the raw and treated samples. Higher Heating Value (HHV) was measured using a IKA C200 Calorimeter. The rest of the values were obtained using the following UNE methods: Volatile matter (UNE- EN 15148-2010), mineral matter (UNE-EN 14775) and moisture (UNE-EN 14774-3). The results of the characterization are included in Table 1.

Table 1: Proximate and ultimate analyses, (dry basis, wt. %) and calorific value of cork residues (CR) and the obtained BC from pyrolysis (pCR).

Parameter		CR	pCR
Proximate analysis (wt.%)	Fixed carbon (%)	14,25	-
	Volatile matter (%)	84,18	-
	Inorganic matter (%)	1,57	0,02
	Moisture (%)	4,51	-
Ultimate analysis (wt.%)	C (%)	59,46	87,02
	H (%)	8,38	0,24
	N (%)	0,90	0,95
	S (%)	0,97	-
	O (%)	28,64	11,59

2.1 Pyrolysis and activation of the BCs

Pyrolysis process was conducted in a horizontal tube furnace, under the following conditions: heating rate: 10 K/min up to a temperature of 1173 K, dwelling time: 1 h in a nitrogen atmosphere, after which samples were cooled down to room temperature inside the tube furnace under 40 L/min N_2 flow. pCR samples were characterized by the following techniques: porous texture characterization was done by N_2 (ASAP2420 Micrometrics equipment at 77K) and CO_2 (BELSORP-maxII equipment at 273K) adsorption-desorption analysis. After pyrolysis, samples were chemically activated by mixing mechanically pCR and KOH (1/1 w/w ratio). The resulting mixture was carbonized in a horizontal tube furnace with a heating rate of 20 K/min up to 1173K in a 10 L/min N_2 flow. Samples were kept at 1173K for 2 h and then cooled down under N_2. Then, samples were thoroughly washed in three steps: with deionized water, with a 3.8 M HNO_3 solution and, again with deionized water until neutral pH. Finally, the activated samples (apCR) were dried at 105 ºC for 12 h.

2.2 Adsorption experiments

Adsorption tests were carried out as batch-type ones, in the following conditions: 0,15 g of the BC and ABC samples were added to 25 mL of a solution with an initial concentration of 35 mg MB/L and submitted to stirring to favour a good adsorbent-solution contact. Various contact times (1, 2, 4, 8 and 24h) were used in order to observe adsorption kinetics of the samples. After 24 h, the mixture was filtered and absorbance measurements of the resulting solution were done in a Jasco UV-VIS Spectrophotometer V-750ST, at a 665 nm wavelength. The absorbance and concentration values of MB were quantified with a calibration curve and results expressed as:

$$Q_e = \frac{(C_0 - C_{eq})}{m} \cdot V \qquad \text{Adsorption-ratio (mg}_{MB}\text{ adsorbed/g}_{BC}\text{)} \qquad \text{Eq. 1}$$

$$R = \frac{(C_0 - C_{eq})}{C_0} \cdot 100 \qquad \text{MB removal (\%)} \qquad \text{Eq. 2}$$

where: C_0: initial concentration (mg_{MB}/L); C_{eq}: final or equilibrium concentration (mg_{MB}/L); m: BC mass (g); V: solution bulk (L).

2.3 BC reuse and MB recycle

Regeneration of the adsorbent after reaching the saturation point is a crucial step of the process regarding its sustainability. A reuse of the BC in several cycles would help to reduce the accumulation of solid waste from the used adsorbent and would allow the recycle of the dye. Three different solvents, methanol, ethanol and acetone, were tested for the desorption of MB from the BC. An experimental set to study the potential recovery of the BC and its use in several cycles was asset (Figure 1).

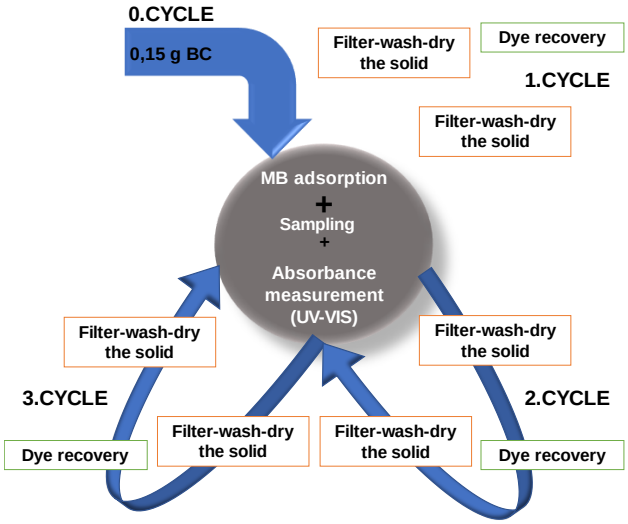

Figure 1: BC recovery and reuse experimental set.

Used adsorbents were separated by filtration and dried out at 60ºC for 24h prior to the recovery experiments. Then, samples were placed in a flask with the selected solvent and stirred continuously for 4h. Afterwards, the adsorbent was filtered, washed in distilled water and dried at 60ºC for 24 h.

3. Results

3.1 BC characterization

Porosity of BC samples was studied using adsorption-desorption N_2 isotherms at 77K. Figures 2a and 2b shows N_2 adsorption - desorption curves at 77K and Figures 3a and b the pore size distribution curves obtained using the NDFT method for pCR (a) and apCR (b). pCR samples showed very low surface areas (9,56 $m^2 \cdot g^{-1}$) and extremely low adsorption kinetics. This fact was interpreted as a presence of narrow, slit-like, micro-pores in the BC structures.

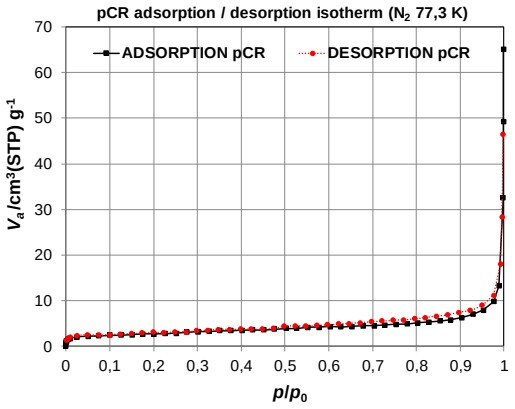

Figure 2a: pCR N_2 adsorption-desorption isotherms

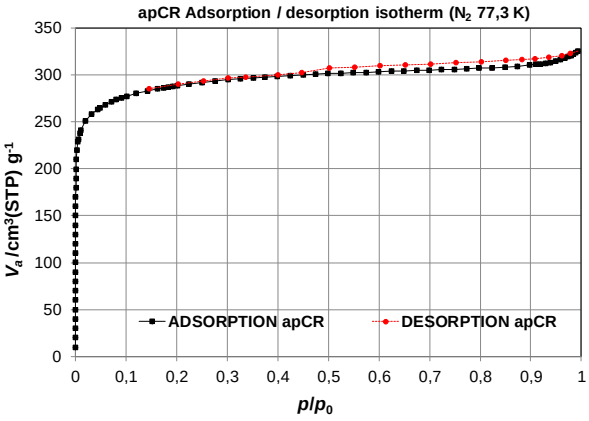

Figure 2b: apCR N_2 adsorption-desorption isotherms

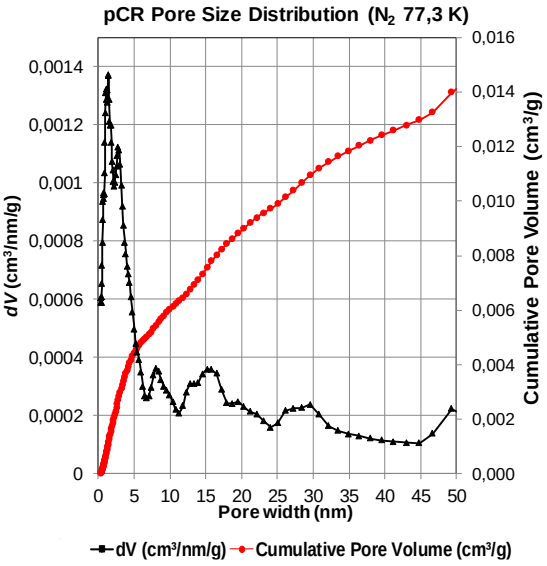

Figure 3a: pCR pore size distribution curves (NDFT)

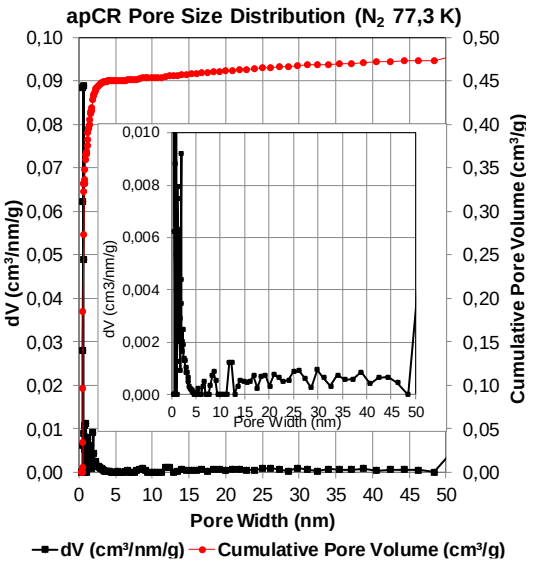

Figure 3b: apCR pore size distribution curves (NDFT)

The obtained curve met the type I adsorption isotherm, according to the IUPAC classification (Muttakin et al., 2018), with a pronounced raise at low relative pressure P/P_0, indicating micro-pore filling, followed by a stabilization. Moreover, in the isotherms an appreciable hysteresis loop could be observed, which is usually related to the presence of mesoporous structure. These results were confirmed when pore size distributions were calculated by NDFT method (Figure 3). A broad pore size distribution was found, with the highest percentage of porosity located in the micro pore region (mean pore diameter around 1.5 nm). On the other hand, apCR samples showed a totally different porosity, with a dramatically increased surface area (1227 $m^2 \cdot g^{-1}$). The apCR adsorption-desorption isotherms fitted a type I isotherm as well, and a pronounced "knee" form could be observed at low p/p_0 values, typical of highly microporous solids. A more defined pore size distribution was found for apCR, with a broader distribution in the higher micro pore and lower mesoporous region (up to 4nm), followed by three small peaks around 5.3, 6.7 and 8.6nm. Because of these results, it is reasonable to assert that activation process has contributed both to the creation of new porosity and the widening of the existing pores that, consequently, has improved the accessibility to these pores, decreasing the diffusion problems encountered previously on the non-activated samples.

3.2 Adsorption results

Figure 4 shows the results of the adsorption of MB by apCR samples, which reached a maximum MB removal rate (R) of about 100% in 2.2 h (pCR samples maximum removal rate was 45.8% in 24 h). The available functional groups on carbon surface have been reported to enhance the MB adsorption capacity of MB, via electrostatic interaction (Santoso et al., 2020). This explains the better performance of the activated samples

due to the generated improvement in the BC morphology and the increase in surface functional groups. Different mechanisms of interaction between MB and the available functional groups on carbon surface, especially phenolic groups and carboxylic acid, have been identified. MB molecule has aromatic structures, positive charges, nitrogen and sulphur in its molecule which interact with the carbon surface" (Vargas et al., 2011).

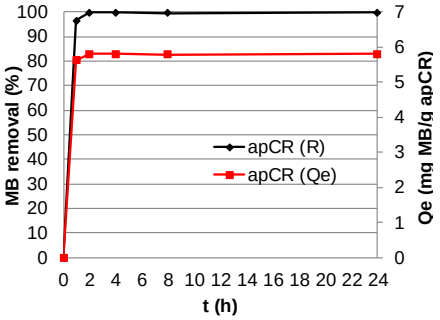

Figure 4: MB removal (R) and adsorption ratio (Qe) for apCR samples.

3.3 Adsorbent regeneration and reuse experiments

Methanol, ethanol and acetone were the used for the MB recovery experiments. They were selected due to their low boiling temperatures, which would allow an easy recovery of the dye and used solvent by evaporation. These experiments were conducted using raw CR and the MB removal rate of recovered CR samples after 24 h was compared with the removal rate of the raw CR ones and expressed as percentage (Table 2).

Table 2: Recovery of MB from CR samples, after 24 h.

Recovery solvent	Removal ratio at 24h (Recovered CR/ Raw CR)
Methanol	62,9%
Ethanol	73,3%
Acetone	93,2%

Acetone offered the best recovery results and, thus, it was selected for the recovery experimental set, in which apCR was submitted to three adsorption-desorption cycles and the adsorption ratio, Qe of each cycle was compared with the one of the fresh apCR (Table 3).

Table 3: Desorption of MB from CR samples, after 24 h.

Sample	Desorption solvent	MB removal %	Qe (mg adsorbed MB /g apCR)
Fresh apCR	None	99,89	5,8095
apCR cycle 1	Acetone	99,75	6,0874
apCR cycle 2	Acetone	99,91	6,2721
apCR cycle 3	Acetone	99,42	5,0140

The MB removal ratio was close to 100% in all the performed cycles. The fact of finding a higher MB removal ratio in the second cycle than in the fresh sample is associated with some possible removal of remaining particles that might have been left from the activation phase and could be effectively blocking some of the internal pore structure and became loose during the stirring process. Moreover, changes on the surface polarity of the apCR could improve as well the adsorption capabilities of the resulting adsorbent. The obtained results confirmed a successful recovery and reuse the BC in several cycles and the potential recycle of the MB dye to the original process.

4. Conclusions

Residual cork has been succesfully used as precursor for the generation of ABCs with good results. The pyrolysed samples, pCR a porosity type (high percentages of microporosity) not adequate for MB removal from aqueous

effluents, the chemical activation of the BC considerably improved the adsorption capabilities by enhancing the accessibility of the adsorbate to the porous structure of the ABCs. The MB adsorption results of the apCR were very promising, with removal rates close to 100% in about 2h. Finally, it was found that the used ABC could be reused in several cycles with no loss in adsorption capabilities. The performed experimental set, with three different solvents (methanol, ethanol and acetone) indicated that acetone was the most suitable one so that this was the one selected in the fnal design, which would help the minimisation of waste generation related to the treatment as well as allow the recycle of the MB dye to the original industrial process through a simple evaporation process. This finding reinforces the importance of the present research work as it is aligned with the principles of the circular economy and the life cycle engineering enhancing the sustainability of the process by using renewable sources, minimizing the inputs and effluents and allowing the recycle of a valuable compound, MB, back to its original industrial process.

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References

Ahmed M.J., Okoye P.U., Hummadi E.H., Hameed B.H., 2019, High-performance porous biochar from the pyrolysis of natural and renewable seaweed (Gelidiella acerosa) and its application for the adsorption of methylene blue, Bioresource Technology, 278, 159–164.

Dai Y., Sun Q., Wang W., Lu L., Liu M., Li J., Yang S., Sun Y., Zhang K., Xu J., Zheng W., Hu Z., Yang Y., Gao Y., Chen Y., Zhang X., Gao F., Zhang Y., 2018, Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review, Chemosphere, 211, 235-253.

de Freitas G.R., da Silva M.G.C., Vieira M.G.A., 2019, Biosorption technology for removal of toxic metals: a review of commercial biosorbents and patents, Environmental Science and Pollution Research, 26, 19, 19097–19118, 2019.

Dias M., Pinto J., Henriques B., Figueira P., Fabre E., Tavares D., Vale C., Pereira E., 2021, Nutshells as Efficient Biosorbents to Remove Cadmium, Lead, and Mercury from Contaminated Solutions, International Journal of Environmental Research and Public Health, 18, 4, 1580.

El Hassani K., Kalnina D., Turks M., Beakou B.H., Anouar A., 2019, Enhanced degradation of an azo dye by catalytic ozonation over Ni-containing layered double hydroxide nanocatalyst. Separation and Purification Technology, 210, 764-774.

Elessawy N.A., El-Sayed E.M., Ali S., Elkady M. F., Elnouby M., Hamad H. A., 2020, One-pot green synthesis of magnetic fullerene nanocomposite for adsorption characteristics, Journal of Water Process Engineering, 34, 101047.

Hamadi A., Yeddou-Mezenner N. Lounis A., Ali R.M., Hamad H., 2021, Upgrading of agro-industrial green biomass residues from chocolate industry for adsorption process: diffusion and mechanistic insights, Journal of Food Science and Technology, 58, 3, 1081–1092.

Hou N., Wang R., Geng R., Wang F., Jiao T., Zhang L., Zhou J., Bai Z., Peng Q., 2019, Facile preparation of self-assembled hydrogels constructed from poly-cyclodextrin and poly-adamantane as highly selective adsorbents for wastewater treatment, Soft Matter, 15, 6097–6106.

Huang Y.Y., 2017, Research progress of wastewater treatment by agricultural wastes as biological adsorbent, Applied Chemical Industry, 46, 2, 372-638.

Muttakin M., Mitra S., Thu K., Ito K., Saha B.B., 2018, Theoretical framework to evaluate minimum desorption temperature for IUPAC classified adsorption isotherms. Int. J. Heat and Mass Transfer, 122, 795-805.

Nayak A.K., Pal A., 2017, Green and efficient biosorptive removal of methylene blue by Abelmoschus esculentus seed: process optimization and multi-variate modelling, Journal of Environmental Management, 200, 145-159.

Santoso E., Ediati R., Kusumawati Y., Bahruji H., Sulistiono D.O., Prasetyoko D., 2020, Review on recent advances of carbon based adsorbent for methylene blue removal from waste water. Mater. Today Chem., 16, 100233.

Vargas A.M.M., Cazetta A.L., Kunita M.H., Silva T.L., Almeida V.C., 2011, Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): Study of adsorption isotherms and kinetic models, Chemical Engineering Journal, 168, 2, 722-730.

Zhou Y., Lu J., Zhou Y., Liu Y., 2019, Recent advances for dyes removal using novel adsorbents: A review, Environmental Pollution, 252, Pt A, 352-365.