High value-added magnetic activated carbon from industrial macroalgae waste by sustainable one-step chemical activation

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Introduction

Biomass and biowaste have attracted a lot of attention as precursors of activated carbon, silica and ammonia as potential solution to reduce environmental and energy-related problems. Magnetic activated carbons (MACs) are carbonaceous adsorbents with suitable and modellable chemical and textural properties to facilitate the adsorption of contaminants. In addition, magnetic properties make them very useful and versatile adsorbents to be used in those media where conventional activated carbons are not applicable. Thanks to their magnetic properties, MACs loaded with contaminants, or chemical compounds, are easily separated from the solid or liquid medium in which they act simply by applying an external magnetic field. Therefore, this approach eliminates the need for a tedious and expensive sieving, filtration and/or centrifugation process, making the overall decontamination process more sustainable and with significant energy savings. It has been shown that these MACs can remove a variety of common environmental pollutants from solutions, including heavy metals or pharmaceutical compounds (Jyoti Sharma et al. 2023).

This research focuses on a solution that guarantees the effective management and valorisation of a solid industrial waste of the macroalgae "*Gelidium corneum*" (algae meal, AM), resulting from the production of agar-agar, transforming it into a magnetic adsorbent (MAC) for environmental applications. The waste was supplied by Roko S.A. industry, the largest producer of agar-agar in Europe, and located in Asturias, Spain. Agar-agar production generates approximately 2000-2400 kg/day of macroalgae waste (AM), and its main use is as fertilizer and fodder for farms or, in the worst case, its disposal in landfills (Ferrera-Lorenzo et al. al., 2014).

Methodology

The AM waste was ground to <3 mm. The fine particle size of the macroalgae waste facilitate the physical mixing process with different amounts of activating reagent (anhydrous $FeCl_3$) and the chemical activation process. MACs were obtained through a one-step sustainable chemical activation process; for that, the different $FeCl_3$:AM mixtures (weight ratio of 0.25:1, 0:5:1 and 1:1) were activated in a conventional tubular furnace (Carbolite CTF 12/65/550) at activation temperatures between 220 and 800ºC. The heating rate was 5ºC/min and the residence time at final temperature was 60 min; the process was carried out under a N_2 flow of 150 ml/min. After finishing the thermal process, the samples were subjected to washes with water at room temperature to remove products that could be blocking the pores. In some specific cases, and for comparison purposes, samples were washed once with a dilute HCl solution (1 M) followed by numerous washing cycles with deionized water (Milli-Q). The material washing process ends when the pH of the washing water is constant. Finally, the samples were dried in an air forced stove at 105 °C and after in a vacuum stove at 60 °C. The MACs obtained were characterized based on ash and ultimate analysis; other techniques used in the characterization of these materials were: ICP-MS, X-Ray Diffraction, FT-IR, Raman, SEM-EDX, helium picnometry, gas (N_2 and CO_2) adsorption, Mössbauer spectroscopy and the magnetic properties were analysed by means a vibrating sample magnetometry (VSM).

Results

The results of ash content, chemical composition and BET surface area of AM in the obtained MACs (activation temperature between 220 and 800ºC, and activation agent: precursor weight ratio of 0.5:1) are showed in **Table 1**. The high carbon content (44%) and low ash content (7.7%) of AM make it suitable for use as a MACs precursor. The MACs showed a carbon content up to 64% in the AMA600H0.5w (washed with water), **Table 1**. However, AMA800H0.5a1 washed with HCl 1M and water presented the highest carbon content (77%). The notable N content could enhance pollutant removal i.e. CO_2. The ash contents in these materials increased at high temperatures depending on the experimental process carried out. The iron compounds formed during the thermochemical process contributed to the increase of mineral material in the MACs. The different techniques spectroscopies confirmed the formation of magnetic compounds in the thermochemical process, especially magnetite, and also maghemite, metallic iron, iron carbides. The SEM image of an AM-based magnetic activated carbon (with a magnification of 5000x), showed some iron oxide crystals on the surface of the sample with a well-defined shape; these could be attributed to magnetite crystals, **Figure 1**.

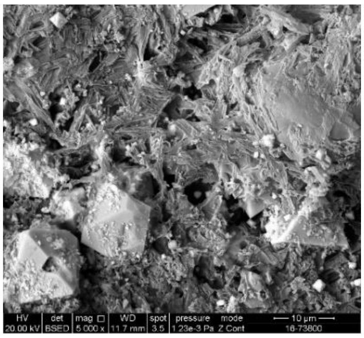
Fig 1 SEM of Macroalgae waste Magnetic Activated Carbon

Sample	T ºC	Ash (%)	C (%)	H (%)	N (%)	Fe (%)	S_{BET} (m^2/g)
AM		7.7	43.99	5.95	5.21	-	<1
AMA220H0.5w	220	-	57.36	2.47	5.13	-	13
AMA400H0.5w	400	15.00	62.77	3.18	5.16	6.87	140
AMA500H0.5w	500	22.00	63.03	2.21	4.63	10.87	494
AMA600H0.5w	600	26.00	64.22	1.5	3.67	13.34	510
AMA700H0.5w	700	36.20	54.05	1.13	3.33	7.38	528
AMA800H0.5w	800	39.70	56.11	0.86	2.96	7.94	512

The MACs of this study also developed important BET surface areas (up to 528 m^2/g) with the increase of the activation temperature and all of them are mainly microporous materials. The good chemical-textural-magnetic results of the MACs developed in this research indicated that they will be good candidates for the removal of hazardous environmental pollutants, CO_2 capture and gas storage.

Conclusion

The circular economy played an important and interesting role in the valorisation of industrial macroalgae waste (algae meal, AM) through its conversion into more useful products, such as magnetic activated carbons (MACs) for different environmental applications. The process of obtaining the magnetic adsorbents was simplified by avoiding thermal steps, the impregnation of the precursor and the activating agent and the acid washing of the materials in such a way that the one-step chemical activation process was much more sustainable. The magnetic adsorbents presented good chemical-textural-magnetic properties and the different analytical techniques confirmed the formation of magnetic species such as magnetite, maghemite, metallic iron, etc, in the MACs.

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