

Removal of gaseous ammonia released from odorous composting leachate employing carbonaceous adsorbents prepared from agro-industrial wastes

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Abstract. Biological and composting processes used in the treatment of municipal solid waste typically are sources of odour pollution (gaseous pollutants include SO₂, NH₃, H₂S and other toxic air pollutants). In this work, the removal of NH₃ present in odorous composting leachate was assessed for the first time in a fixed-bed column loaded with carbonaceous adsorbents prepared by hydrothermal carbonization (HTC) assisted with sulphuric acid and by pyrolysis of carbon precursors (olive stone and malt bagasse). The resultant adsorbents were characterized to study their surface chemistry and textural properties. Scarce work studying the HTC in presence of additives, but H₂SO₄-assisted HTC allow to obtain acid hydrochars with accuracy properties for NH₃ adsorption. In this work, the hydrochar prepared from olive stone by H₂SO₄-assisted HTC shows the highest NH₃ adsorption capacity (11.4 mg g⁻¹), evidencing that acidity contributes more significantly to the removal of NH₃ than the specific surface area of the adsorbents. The NH₃-saturated hydrochar was regenerated by washing with distilled water and subsequently re-used in the adsorption of NH₃, obtaining satisfactory performance (68% of the mean NH₃ adsorption capacity of its respective first use).

Keywords: adsorption, biomass waste, waste valorisation, hydrochar, carbon-based materials.

1. Introduction

Industrial and agricultural activities, coupling with waste and wastewater treatment facilities account for 78% of odour sources across European countries (Balestrini et al., 2018). Odour pollution can cause adverse effects in humans, including various undesirable reactions, ranging from annoyance to documented health effects (Nicell, 2009). Odorous pollutants may result directly or indirectly from human activities, such as waste treatment plants. Despite contributing to proper waste management, landfill

facilities and compost plants typically are sources of odour pollution (Rincón et al., 2019). A study carried out by Cheng et al. (2019) showed that both types of waste treatment facilities mentioned previously have NH₃ as one of the most critical offensive odorants that should be considered on health risk assessment. Its removal has been successfully reached by adsorption (Dai et al., 2018). For this purpose, the presence of an acidic surface could be the decisive factor of the adsorption capacity of NH₃ (Zheng et al., 2016), as well as a regular and interlinked pore system (Yeom & Kim, 2017).

Adequate adsorbents could be obtained from various agro-industrial residues converting these abundant, accessible, renewable, inexhaustible and low-cost biomass resources into carbon-based materials (Javidi Alsadi & Esfandiari, 2019). The valorisation of biomass as precursors of carbon adsorbents is a practical strategy to increase resource-use efficiency by simultaneously reducing the environmental waste burden and achieving the effect of “treating pollution with waste” (Y. Y. Huang, 2017). Among the available carbonization processes, hydrothermal carbonization (HTC) have receive growing attention, since operates at mild conditions using subcritical water (150–350 °C) (Jain et al., 2016) under autogenous pressure. However, there are scarce studies on HTC of biomass in the presence of chemical agents to improve the physico-chemical properties of the resultant hydrochars, enabling a high development for specific applications (Diaz de Tuesta et al., 2021).

This work aims at the preparation of adsorbent materials and further evaluation of its performance and effectiveness in the adsorption of the odorous pollutant NH₃ by using a fixed-bed column. Hydrochar from olive stone and bagasse of malt will be prepared for first time by H₂SO₄-assisted HTC at mild conditions and their performance compared to porous pyrochars prepared from the same carbon precursors.

2. Methods

2.1. Preparation of the adsorbents

Three types of adsorbents were prepared pyrochars and hydrochars. Each sample was labelled following its respective feedstock (OS – olive stone; MB – bagasse of malt) and preparation process (M for milling; P for pyrolysis; HTC for hydrothermal carbonization (HTC) assisted with sulphuric acid (H₂SO₄)), resulting in the four samples shown in Table 1.

Table 1. Types of adsorbent, process of preparation, feedstock and sample label of the adsorbents prepared.

Type	Process of preparation	Feedstock	Sample
Pyrochar	milling, drying, pyrolysis	OS	OS-M-P
	drying, pyrolysis	MB	MB-P
Hydrochar	milling, drying, H ₂ SO ₄ -assisted HTC	OS	OS-M-HTC
	drying, H ₂ SO ₄ -assisted HTC	MB	MB-HTC

The pyrochars were prepared as described elsewhere (Díaz de Tuesta et al., 2018). Briefly, the carbonization occurred under N₂ continuous flow with a rate of 100 Ncm³ min⁻¹, a heat rate of 10 °C min⁻¹, at 800 °C for 4 h.

Hydrochars were prepared by HTC assisted by H₂SO₄. A mass of 2.5 g of the precursor and 25 mL of 2.5 mol L⁻¹ H₂SO₄ solution was added into a 125 mL high-pressure batch reactor to operate under autogenous pressure at 200 °C for 3 h. After cooling, the solids were recovered by filtration and washed with distilled water until the rinsing waters reach the pH of the distilled water. The solid material was dried in a drying chamber at 100 °C for 24 h.

2.2. Adsorption runs

Before the adsorption runs, the mean NH₃ inlet concentration was determined. Then, three adsorption experiments were performed using each adsorbent. The fixed-bed column was designed based on ASTM D5160-95(19) – Standard Guide for Gas-phase Adsorption Testing of Activated Carbon (ASTM, 2019). It consists of a vertically supported cylindrical acetate sample tube (inner diameter = 1.2 cm, height = 8.5 cm) filled with adsorbent and supported by a fine flat mesh stainless steel screen to ensure fixed packing of the bed. Another mesh was placed at its upper end to ensure uniformity of flow profile across the adsorbent bed. NH₃ concentration downstream from the adsorption column was measured every 3 minutes until the saturation of the bed. The dynamic adsorption capacity (q_a , milligrams of adsorbate per grams of adsorbent) of the adsorbents were estimated as elsewhere (Ang et al., 2020; Balsamo et al., 2013; Gonçalves et al., 2011) by using Equation 1.

$$q_a = \frac{Q}{m} \cdot \int_0^{t_{sat}} (C_0 - C_t) dt \quad (1)$$

where Q is the gas flow rate (L min⁻¹), m is the adsorbent mass (g), t_{sat} is the time (min) when the adsorption bed reaches saturation ($C_t = C_0$).

2.3. Characterization of the adsorbents

The acidity and basicity of the adsorbents' surface were determined by titration of 0.02 mol L⁻¹ HCl and NaOH solution after 48 h of contact time with the materials.

The adsorbents' textural properties were determined by analysis of nitrogen adsorption-desorption isotherms at 77 K using a gas adsorption analyzer, following the procedure reported elsewhere (Díaz de Tuesta et al., 2018). Briefly, the Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) was determined using BET methods. The micropore volume (V_{mic}) was obtained by the t-method in which the thickness is calculated by using ASTM D-6556-01 - Standard Test Method for Carbon Black — Total and External Surface Area by Nitrogen (ASTM, 2001). The total pore volume (V_{total}) was calculated in a p/p₀ of 0.98. Calculations of those methods were all done with TouchWin™ software v 1.21. Micropore surface area (S_{mic}) was estimated by the approximations shown in Equation 2.

$$S_{mic} = S_{BET} - S_{ext} \quad (2)$$

2.4. Regeneration of saturated hydrochar

The hydrochar OS-M-HTC was selected to be regenerated based on the method presented by Ro et al. (2015), which aims to regenerate adsorbents saturated with NH₃ using water. In this sense, 0.5 g of the saturated sample was placed in a round-bottom flask containing 100 mL of ultrapure water and a magnetic stir. The flask containing the sample mixed with water was placed on a magnetic stirrer to stir at 1220 rpm and 25 °C for 4 h.

3. Results and discussion

3.1. NH₃ adsorption

Table 2 presents the values of m , and the results of C_0 , t_{sat} , and q_a .

Table 2. Parameters and results of the adsorption runs

Sample	m (g)	C_0 estimated (ppm)	t_{sat} (min)	q_a (mg g ⁻¹)
OS-M-P	1.2	8.10	93 - 99	0.07 - 0.08
MB-P	0.5	6.5 - 6.7	81 - 90	0.20 - 0.22
OS-M-HTC	0.2	8.8 - 10.6	456 - 552	9.45 - 11.42
MB-HTC	0.2	7.6 - 8.5	384 - 411	6.24 - 8.15

The hydrochar prepared from olive stones (OS-M-HTC) were the best adsorbent produced in this work for removal of NH₃, showing the greater q_a , ranging from 9.45 to 11.42 mg g⁻¹, with values similar to those found by C. Huang et

al. (2008) (7.49 – 11.25 mg g⁻¹), followed by the hydrochar prepared from bagasse of malt (MB-HTC), ranging from 6.24 to 8.15 mg g⁻¹. It is worth mentioning that both pyrochars showed a q_a greater than the commercial adsorbents derived from biomass presented by Rodrigues et al. (2007) (0.6 to 1.8 mg g⁻¹), Gonçalves et al. (2011) (4.7 – 5.3 mg g⁻¹), and C. Huang et al. (2008) (2.3 mg g⁻¹). On the other hand, pyrochars showed very limited q_a , ranging from 0.07 to 0.22 mg g⁻¹.

3.2. Surface chemistry characteristics and textural properties

Acidity and basicity of the surface of fresh and saturated first-generated adsorbents were determined. Table 3 presents the values of basicity and acidity in mmol g⁻¹.

Table 3. Acidity and basicity of the surface of adsorbents

Sample	Basicity (mmol g ⁻¹)	Acidity (mmol g ⁻¹)
OS-M-P	1.10	0.32
MB-P	0.59	0.34
OS-M-HTC	0.11	2.34
MB-HTC	0.14	2.37

As summarized in Table 3, the hydrochars show similar acidity results, 2.34 and 2.37 mmol g⁻¹, respectively. Besides increasing the adsorbents' surface acidity due to the use of H₂SO₄, the HTC process is expected to produce a material with high concentrations of oxygen functional groups, including the acid ones (Jain et al., 2016; Ok et al., 2016). The presence of acidic groups gives a polar character to the adsorbent's surface, affecting the preferential adsorption of polar alkaline adsorbates, being such groups considered the key factor on the values of q_a obtained (Foo et al., 2013; Gonçalves et al., 2011). The correlation between the amount of NH₃ adsorbed and the total amount of acidic groups on the surface of the adsorbent is approximately linear (Gonçalves et al., 2011; C. Huang et al., 2008; Mochizuki et al., 2016; Wang et al., 2016; Zheng et al., 2016). The higher q_a values were obtained with samples OS-M-HTC and MB-HTC, which also present higher surface acidity.

The textural properties of the adsorbents are summarized in Table 4.

Table 4. Textural properties of the adsorbents: specific surface area (S_{BET}), micropore surface area (S_{mic}), micropore volume (V_{mic}) and total pore volume (V_{total}).

Sample	S_{BET} (m ² g ⁻¹)	S_{mic} (m ² g ⁻¹)	V_{mic} (mm ³ g ⁻¹)	V_{total} (mm ³ g ⁻¹)
OS-M-P	172	158	83	109
MB-P	50	39	20	34
OS-M-HTC	4	0	0	16
MB-HTC	12	1	0	25

Table 4 shows that pyrochars present the highest values of all textural properties, likely due to the removal of volatile matter through the pyrolysis process, that enriched the carbon composition, forming the porosity on these adsorbents (Yek et al., 2019). These samples are

predominately microporous, as observed when comparing V_{mic} values with V_{total} .

It is also noticed that sample OS-M-P shows a S_{BET} value three times higher and a S_{mic} value four times higher than those of sample MB-P. Even the same pyrolysis process was considered in the preparation of both samples, the precursor of MB-P was not subjected to milling before preparation to reduce the precursors' particle size. Since particle size affects the structure of pyrochars (Asadullah et al., 2010), the smaller particle size of biomass OS leads to a higher available surface area subjected to pyrolysis, which may explain the higher values found for S_{BET} and S_{mic} of sample OS-M-P.

On the other hand, the hydrochars, that presents higher NH₃ adsorption capacity show very low values for all textural parameters, some of them even zero (**Error! Reference source not found.**4). That may be explained by the fact that the specific surface area and pore volume do not directly influence the adsorbing amount of NH₃ (C. Huang et al., 2008).

3.3. Adsorption capacity of the regenerated hydrochar

After the first NH₃ desorption-sorption cycle, the regenerated sample OS-M-HTC has shown a q_a value of approximately 7.08 mg g⁻¹, which is 68% of the mean q_a value obtained in the first-generation OS-M-HTC.

4. Conclusions

In this work, hydrochars and pyrochars were prepared using agro-industrial residues as carbon precursors: bagasse of malt and olive stone. They were tested for removal of NH₃ in a fixed-bed column, showing that biomass waste can be valorised into high-added-value products with environmental applications.

The samples prepared by H₂SO₄-assisted HTC revealed higher content of acid groups and NH₃ adsorption capacities. On the other hand, samples subjected to pyrolysis show good textural properties and minimal NH₃ adsorption capacity. The results obtained confirm the crucial role of acidic functional groups in NH₃ adsorption and that surface area and pore volume, independently, do not directly influence the adsorption of NH₃.

Lastly, the regeneration process using water delivered an adsorbent capable of being used in one NH₃ sorption-desorption cycle with satisfactory performance, leading to the increase of the materials' resource-use efficiency. Keeping the adsorbents in use longer by reusing them makes the process potentially more sustainable, promoting a circular economy.

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