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Biochars application for ibuprofen removal by adsorption: Trends in production, operating conditions and mechanisms

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ABSTRACT
The presence of drugs in the environment, such as ibuprofen, has raised concern due to their persistence and high-risk potential to local biota and health of exposed population. Thus, removal methods, such as biochars adsorption, gained notoriety for their high efficiencies and reduced production cost. Therefore, the present study developed a systematic literature review regarding the advance of low-cost adsorbents for ibuprofen removal from aqueous media. It was possible to observe certain increase in the production of studies within this subject, with preference of agricultural residues as precursor materials. Pyrolysis temperatures on literature ranged from 200 to 900 °C, depending on the process. Note that two substances (H_3PO_4 and NaOH) are used with more frequency, for chemical activation and superheated vapors in physical activation processes. Regarding chemical adsorption process, the pH was one of the most relevant factors for adsorption process and, also, most of the authors reported better fit to the pseudo-second order kinetic model; that is, adsorption process generally happening by chemisorption.

KEYWORDS: Adsorption. Biochar. Ibuprofen.

1. INTRODUCTION

Pharmaceutical and personal care products (PPCPs) constitute large class of everyday chemical substances and byproducts, linked directly to anthropization processes. These emerging contaminants — along with dyes, steroid hormones, surfactants and fuel additives — form entrance routes into the environment, mainly through human and animal excretions, as well as untreated industrial and hospital effluents (BARCELÒ, 2003; AQUINO; BRANDT; CHERNICHARO, 2013).

Nonsteroidal analgesic and anti-inflammatory drugs (NSAIDs), a portion of aforementioned compounds, gained greater attention due to their high incidence in water bodies (PATEL *et al.*, 2019), standing out from substances with high consumption and easy access, without needing medical prescription, in particular ibuprofen (2-(4-isobutylphenyl)propanoic acid), the third most consumed drug worldwide (IOVINO *et al.*, 2015). It is noteworthy that the metabolites toxicity of these drugs may be higher than the original molecule (CHOPRA; KUMAR, 2020).

With increased sensitivity and selectivity of analytical methods, it has been possible to detect micropollutants even at low concentrations (μg L^{-1} e ng L^{-1}) (SILVA, 2019), since they remain in practically unchanged concentrations in the environment, due to their constant insertion, even with high rates of transformation/removal (MESTRE *et al.*, 2007).

Given its low potential for biodegradability, ibuprofen ecotoxicity has been investigated at different trophic levels. Regarding acute and chronic toxic effects, in daphnia and fish, for example, ibuprofen is considered a substance of environmental risk (BOUISSOU-SCHURTZ *et al.*, 2014), in addition, affecting fish reproduction decreasing spawning time and, simultaneously, increasing number of eggs produced per day (FLIPPIN; HUGGETT; FORAN, 2007).

Kayani *et al.* (2009) observed that ibuprofen conjugation with diacylglycerol (Ibuprofen-DAG) was responsible for genotoxic damage, such as cell division inhibition and chromosomes nondisjunction in several pairs. Additionally, it has been identified as a compound of endocrine disruption in humans, leading to reproductive disorders in men (KRISTENSEN *et al.*, 2018), as well as presenting adverse effects on human liver and kidney cells, on gut microbiota species and on bacteria such as *A. fischeri*, even at short-term exposure (ELLEPOLA *et al.*, 2020).

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In this context, methods for removing these emerging contaminants have increasingly gained interest, emphasizing the use of biochar, which has a high efficiency removing micropollutants (MESTRE *et al.*, 2009). These adsorbents produced from biomass, are highly porous materials with a high surface area and high adsorption capacity, synthesized from carbonization (pyrolysis) or precursor oxidation. This high porosity can be improved by a two-step process (carbonization and activation), physical or chemical (ALVEAR-DAZA *et al.*, 2022). As some industrial adsorption processes require adequate adsorbent porosity, it is still possible to combine activation processes to obtain more efficient adsorbent materials (MARSH; REINOSO 2006).

Thus, the present work aimed to verify, through a survey, the technology progress for low-cost adsorbents production, derived from biomass for ibuprofen adsorption, to analyze the state of the art and the evolution of scientific production on this subject, as well as the main types of research carried out and their possible applications, in addition to the methods of publishing the results.

2. METHODOLOGY

2.1. Search strategy and eligibility criteria

To verify Brazilian and international state of the art of biochar production, the present study adopted the *Mapping Study* methodology. The technique consists of scientific database systematic survey, aiming to qualify and quantify the data collected. Thus, it was possible to perform a bibliometric analysis from scientific publications on biochar production used for ibuprofen removal by adsorption in liquid medium (FU; WANG; HO, 2013; DEUS; BATTISTELLE; SILVA, 2015).

The systematized searches were performed on scientific databases *Scopus* [*Elsevier Publishing*] and *Web of Science* [*Main Collection* (*Clarivate Analytics*)], from October 27, 2021, to November 1, 2022. In the fields *Article title*, *Abstract* and *Keywords*, was adopted the combinations of keywords: Adsorption, Ibuprofen and Biochar, as well as their respective translations in Portuguese; using the boolean expression *AND* in both bases, without any temporal restriction. From the articles obtained, the selection was made by applying the following inclusion criteria: (i) articles in English or Portuguese; (ii) articles dealing with biochar production; and (iii) articles that adopted adsorption as method of ibuprofen removal.

2.2. Review process

Article duplicates were deleted using *RStudio® software*. Then, analyzing their titles and abstracts content, the exclusion criteria were applied to delimit the main subject in articles in which: (i) articles in which the adsorbent used was not produced; (ii) articles in which biomass was not used to produce biochar; and (iii) articles that have not used ibuprofen as at least one of the adsorbates.

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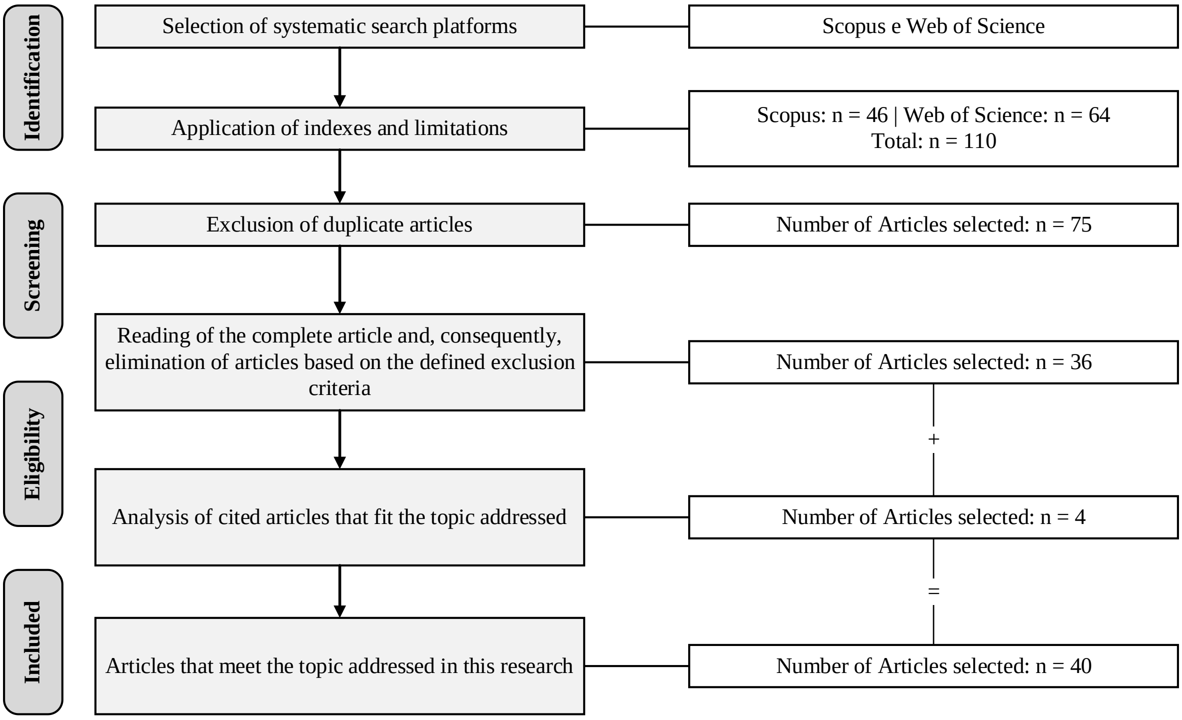
Subsequently, by reading the articles in full, we sought to answer some established questions on the subject: (i) What are the type of precursor materials most used for biochar preparation of biochar? (ii) What type and activation methodology were commonly used for biochar production process?; (iii) What were the experimental conditions used in adsorption tests and which models describe process?.

According to methodology proposed by Aria and Cuccurullo (2017), metadata analysis was performed in *RStudio® software* with *Bibliometrix* package, a bioinformatics tool for quantitative research in scientometrics and bibliometrics. Additionally, metadata analysis included the most cited articles that met aforementioned criteria, in addition to evaluating whether they answered the established research questions. Figure 1 summarizes the steps for the elaboration of the present study.

Figure 1. Flowchart of the bibliographic research.



Source: Prepared by the authors.

Finally, the number of articles and the impact factor of resulting data from research, were verified by *Journal Citation Report, Institute for Scientific Information 2020* (JCR) and the *SCImago Journal & Country Rank 2021* (SJR), to verify each publication relevance (CARVALHO; LONGARAY, 2021).

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3. RESULTS AND DISCUSSION

3.1. Bibliometric analysis

Using the keywords in databases returned 110 articles, which after excluding duplicates were reduced to seventy-five. Subsequently, inclusion and exclusion criteria were applied resulting in 36 articles, where 4 more articles were added, which resulted from metadata analysis.

Twenty-four journals were listed among the publications surveyed, of which only 9 had more than one published article. The journals with the highest number of publications, with four publications each, were: *Chemical Engineering Journal*, *Journal of Environmental Chemical Engineering and Process Safety and Environmental Protection*.

The impact factor of each journal by *SCImago Journal & Country Rank* 2021 (SJR) and the *Journal Citation Report* 2020 (JCR) can be seen in Table 1.

Table 1. Bibliographic portfolio regarding the origin of the publications.

Journals	Number of publications	References	JCR	SJR
Chemical Engineering Journal	4	Dubey *et al*. (2010); Baccar *et al*. (2012); Essandoh *et al*. (2015); Jung *et al*. (2015).	13,273	2,42
Journal of Environmental Chemical Engineering	4	Chakraborty *et al*. (2018b); Lima *et al*. (2020); Choudhary; Philip (2022); Shin *et al*. (2022).	5,909	1,04
Process Safety and Environmental Protection	4	Chakraborty *et al*. (2018a); Chakraborty *et al*. (2019); Turk Sekulic *et al*. (2019); Show *et al*. (2021a).	6,158	1,26
Biomass Conversion and Biorefinery	3	Show; Karmakar; Halder (2022); Alvear-Daza *et al*. (2022); Show *et al*. (2022).	4,987	0,55
Bioresource Technology	2	Mestre *et al*. (2009); Naima *et al*. (2022).	9,642	2,35
Environmental Science and Pollution Research	2	Oh; Seo (2016); Du *et al*. (2021).	4,223	0,83
Journal of Hazardous Materials	2	Jung *et al*. (2013); Shin *et al*. (2020).	10,588	1,99
Journal of Water Process Engineering	2	Chakraborty *et al*. (2020); Yang *et al*. (2022).	5,485	1,03
Science of the Total Environment	2	Ocampo-Perez *et al*. (2019); Delgado-Moreno *et al*. (2021).	7,963	1,81
Adsorption Science & Technology	1	Ai *et al*. (2020)	4,232	0,63
Carbon	1	Mestre *et al*. (2007)	9,594	1,99
Chemosphere	1	Pap *et al*. (2021)	7,086	1,51
Colloids and Surfaces A-Physicochemical and Engineering Aspects	1	Moreno-Perez *et al*. (2021)	4,539	0,76
Ecological Engineering	1	Mondal; Aikat; Halder (2016)	4,035	1,02
Environmental Engineering Science	1	Nguyen *et al*. (2021)	1,907	0,46

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Environmental Pollution	1	Shin *et al*. (2021)	8,071	1,95
Industrial & Engineering Chemistry Research	1	Yu *et al*. (2020)	3,764	0,82
International Journal of Energy Research	1	Ganesan *et al*. (2021)	5,164	0,81
International Journal of Pharmacology	1	Salem; Yakoot (2016)	0,751	Does not have
Journal of Environmental Management	1	Mondal *et al*. (2016);	6,789	1,48
Journal of Membrane Science	1	Kim *et al*. (2019)	8,742	1,77
Materials Research Express	1	Yudha *et al*. (2019)	1,62	0,4
RSC Advances	1	Chakraborty; Halder (2020)	3,361	0,67
Water (Switzerland)	1	Mojiri; Kazeroon; Gholami (2019)	3,103	0,72

JCR: Journal Citations Report (2020); SJR: SCImago Journal & Country Rank (2021).
Source: Prepared by the authors.

Regarding JCR, the mean value is 5.874 with a standard deviation of 3.060. For the SJR data, a mean value of 1.178 was obtained with a standard deviation of 0.662. In both classifications, *Chemical Engineering Journal* has the best classification among the impact factors studied (13.273 [JCR] and 2.42 [SJR]), in addition to being one of the most sought-after options, as mentioned above. Note that only one of the journals does not have classification by SRJ (*International Journal of Pharmacology*).

For countries with highest number of publications, there is India in first place (11 publications); China and the U.S. in second (5 publications each); Korea in fourth (4 publications); followed by Brazil, Portugal and the United Kingdom (2 publications each), with English as predominant language for all publications, preferably the official language in the authors origin country. It is worth noting that the language chosen for publication can directly affect the research impact, due to a wider circulation and larger potential audiences, which can constitute an incentive to publish in English, as if this language had a certain "neutrality" (DAHLER-LARSEN, 2018).

For authors who published the most among the articles analyzed, it is verified that *Halder, G*. showed highest number of publications (10 publications). With five publications, *Chakraborty, P*. and *Show, S*. appear in second place among the most relevant authors, since all the articles of *Chakraborty, P*. were published with *Halder, G*. Moving on, *Yoon, Y*., *Kim S*., *Lee Y*. and *Shin J*. appear in third place, with three publications each.

Of these, there is a trend in the choice of keywords, which may have influenced the cut made by the present research. For example, as for the texts with *Halder, G*. participation, the presence of the terms "Ibuprofen" occurs in 9 of 10 publications and "Kinetics" occurs in 8 of 10, among the keywords "plus", as verified in metadata analysis, since the publication in *RSC Advances* journal does not have keywords.

The temporal distribution of publications ranged from 2007 to 2022, with an increase in the number of publications from 2015, with gaps in the number of publications in some years (2008, 2011, 2014 and 2017). The year with the highest number of publications on the thematic cut was 2021 (8 publications/year), followed by 2022 (7 publications/year) and 2019 and 2020 (6 publications/year, each). It is noteworthy that COVID-19 pandemic may justify the decrease in number of publications since social distancing was adopted in several countries as disease control measure, paralyzing or postponing several studies (KÖPSEL; KIIPPER; PECK, 2021).

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3.2. Biochar production

Due to its relatively simple design and operation, cost-effectiveness and energy efficiency, coal synthesis generated from biomass (biochar) for contaminants adsorption, is one of the applications for residue management from many human activities processes (KYZAS *et al.*, 2013).

The solids from pyrolysis process are highly recognized for their effective agricultural and environmental applications, as well for contributing to greenhouse gas emissions reduction, by carbon sequestration (MUBARAK *et al.*, 2014; XIE *et al.*, 2015).

Table 2 presents some materials used as precursors of raised biochar, their respective temperatures and carbonization times.

Table 2. Precursor materials used and preparation conditions of the adsorbents found.

<table>
<tr><th>Precursor material</th><th>Burning Temperature (°C)</th><th>Burning time</th><th>Authors</th></tr>
<tr><td>Green tea waste</td><td>200</td><td>12 h</td><td>Yudha et al. (2019)</td></tr>
<tr><td>Rice straw</td><td>220</td><td>8 h</td><td>Yu et al. (2020)</td></tr>
<tr><td rowspan="3">Torrefied loblolly pine chips</td><td rowspan="4">300</td><td rowspan="3">15 min</td><td>Jung et al. (2013)</td></tr>
<tr><td>Jung et al. (2015)</td></tr>
<tr><td>Kim et al. (2019)</td></tr>
<tr><td>White Wormwood (P. hysterophorus)</td><td>1 h</td><td>Mondal; Aikat; Halder (2016)</td></tr>
<tr><td>Sugarcane bagasse</td><td rowspan="2">400</td><td rowspan="2">1 h</td><td>Chakraborty et al. (2018b)</td></tr>
<tr><td>Water hyacinth leaves (Eichhornia crassipes)</td><td>Lima et al. (2020)</td></tr>
<tr><td>Olive waste cake</td><td rowspan="3">450</td><td>30 min</td><td>Baccar et al. (2012)</td></tr>
<tr><td>Coconut shell</td><td>2 h</td><td>Chakraborty et al. (2019)</td></tr>
<tr><td>Artemisia vulgaris</td><td>1 h</td><td>Dubey et al. (2010)</td></tr>
<tr><td>Mungo bean peel</td><td rowspan="3">550</td><td rowspan="3">1 h</td><td>Mondal et al. (2016)</td></tr>
<tr><td>Almond shells (Terminalia katappa)</td><td>Show et al. (2021)</td></tr>
<tr><td>Residues of Tamarindus indica seeds</td><td>Show et al. (2022)</td></tr>
<tr><td>Alternanthera philoxeroides</td><td rowspan="3">600</td><td>1 h</td><td>Du et al. (2021)</td></tr>
<tr><td>Bovine bones</td><td rowspan="2">2 h</td><td>Moreno-Perez et al. (2021)</td></tr>
<tr><td>Plane tree leaf waste</td><td>Yang et al. (2022)</td></tr>
<tr><td>Wood apple (Aegle quinces) fruit shell</td><td>650</td><td>1 h</td><td>Chakraborty et al. (2018a)</td></tr>
<tr><td>Pepper stem</td><td rowspan="6">700</td><td>-</td><td>Naima et al. (2022)</td></tr>
<tr><td>Date Seeds</td><td rowspan="4">1 h</td><td>Chakraborty et al. (2020)</td></tr>
<tr><td>Date Seeds</td><td>Chakraborty; Halder (2020)</td></tr>
<tr><td>Cork powder waste</td><td>Mestre et al. (2007)</td></tr>
<tr><td>Cork powder waste</td><td>Mestre et al. (2009)</td></tr>
<tr><td>Coffee grounds</td><td>1,5 h</td><td>Shin et al. (2022)</td></tr>
<tr><td>Agricultural waste (Chitosan)</td><td rowspan="3">800</td><td rowspan="3">2 h</td><td>Mojiri; Kazeroon; Gholami (2019)</td></tr>
<tr><td>Coffee grounds</td><td>Shin et al. (2020)</td></tr>
<tr><td>Coffee grounds</td><td>Shin et al. (2021)</td></tr>
<tr><td>Peanut shell biomass</td><td>900</td><td>2 h</td><td>Nguyen et al. (2021)</td></tr>
<tr><td>Pine wood chips</td><td>110-120 | 425</td><td>20 - 30 s</td><td>Essandoh et al. (2015)</td></tr>
<tr><td>Cherry beans</td><td>180 | 500</td><td>45 min | 1 h</td><td>Pap et al. (2021)</td></tr>
<tr><td>European plum tree (Prunus domestica L.)</td><td>180 | 500</td><td>45 min | 1 h</td><td>Sekulic et al. (2019)</td></tr>
<tr><td>Orange peel powder</td><td>200 | 200 > 600 | 600</td><td>12 | 6 | 2 h</td><td>Ai et al. (2020)</td></tr>
<tr><td>Cambará stem (Lantana camara)</td><td>200 | 700</td><td>1 | 2 h</td><td>Ganesan et al. (2021)</td></tr>
<tr><td>Residue from palm oil extraction</td><td>250; 450; 750</td><td>30 min</td><td>Choudhary; Philip (2022)</td></tr>
</table>

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Pruning of olive trees (P); Pitted and reprocessed wet olive mill waste (OMW); Olive stones (S)	300(S + P); 500 (S + P); 190 (OMW); 240 (OMW)	1 h (S+P); 6 h (OMW)	Delgado-Moreno *et al*. (2021)
Sunflower seed shell	300-600	1 h	Alvear-Daza *et al*. (2022)
Wastewater biosolids (BS); Fallen leaves (oak) (FL); Used coffee grounds (CF); Corn stalks (CS); Rice straw (RS).	400 (BS); 550 (FL; CF; CS); 400; 550; 700; 900 (RS)	4 h	Oh; Seo (2016)
Rice straw	400 - 600	1 h	Salem; Yakoot (2016)
Chili Seeds	450; 550; 600	2 h	Ocampo-Perez *et al*. (2019)
Tamarind Seeds	-	-	Show; Karmakar; Halder (2022)

(|): Indicates process in stages; >: Indicates gradual heating; -: Indicates ramp of temperature variation.
Source: Prepared by the authors.

As noted, 72.50% (29 publications) of the studies used only one temperature for pyrolysis of adsorbents produced, where the verified firing processes were hydrothermal carbonization (YUDHA *et al*., 2019; YU *et al*., 2020); torrefaction (JUNG *et al*., 2013; JUNG *et al*., 2015; KIM *et al*., 2019; MONDAL; AIKAT; HALDER, 2016); instantaneous carbonization (BACCAR *et al*., 2012); rapid pyrolysis with preheating (ESSANDOH *et al*., 2015) and the remainder slow pyrolysis (21 publications), with temperatures ranging from 200 °C to 900 °C. Four publications used staged pyrolysis to produce adsorbents (SEKULIC *et al*., 2019; AI *et al*., 2020; GANESAN *et al*., 2021; Pap *et al*., 2021)

Some of these studies sought to analyze the best burning temperatures for the precursor material (OH; SEO, 2016; SALEM; YAKOOT, 2016; OCAMPO-PEREZ *et al*., 2019; DELGADO-MORENO *et al*., 2021; ALVEAR-DAZA *et al*., 2022; CHOUDHARY; PHILIP, 2022) Nevertheless, only one article did not specify the temperature or burning time in the methodology (SHOW; KARMAKAR; HALDER, 2022).

Except for two publications that used wastewater biosolids (BS), as one of their precursor materials (OH; SEO, 2016) and bovine bones (MORENO-PEREZ *et al*., 2021) in adsorbents production; the precursor materials listed in the publications are mostly from agricultural origin. Agricultural waste receives greater attention due to its wide and abundant availability, regardless the origin region (VADIVELAN; KUMAR, 2005). On the other hand, very heterogeneous materials, such as BS from water treatment plants, can interfere with the adsorption process due to the presence of different functional groups on adsorbent surface, or even contaminants in its composition (KACAN, 2016).

Nevertheless, some of precursor materials listed were used in more than one work including: rice straw, coffee grounds, pine waste, residues from olive processing, cork powder residues, roasted pine chips and date seeds. Of these, variations can be verified precursor material treatment, in carbonization process, in temperatures used and in burning times, indicating high versatility and adaptability of these materials for new products manufacture.

3.3. Activation process

In principle, any carbonaceous material can be converted into activated carbon, resulting in byproducts with unique characteristics and directly influenced by precursor material, activating agent, carbonization process and activation conditions. Although, pyrolysis process contributes independently to the adsorbent porosity, its potential may be limited since these pores are filled, totally or partially, by tar or decomposition products, or might be partially closed by disordered carbon, evidencing the need for activation, aiming to clear the pores formed (BANSAL; GOYAL, 2005).

Acids and alkaline hydroxides, for example, are two of the most widely used chemical activators for pores unclogging. In lignocellulosic precursors, the first induces depolymerization, followed by dehydration and precursor material condensation, while the second causes fragmentation of cellulose, lignin and hemicellulose; promoting high porosity during impregnation step (MOLINA-SABIO; RODRÍGUEZ-REINOSO, 2004). In terms of physical activators, CO_2 atmospheres or superheated water vapor are used, rather than an O_2 atmosphere due to the high exothermic enthalpy, which makes difficult to control the reaction temperature. However, these methods require external heat injection, which allows more and accurate control of the experimental conditions (ANIA; RAYMUNDO-PIÑERO, 2019).

Regarding the analyzed physical biochar activation, 8 publications showed adsorbents activated by superheated water vapor, the only physical activating agent detected in the research, and activation always occurred after pyrolysis of the material. In two of these adsorbents, previous chemical activation occurred, followed by physical activation (MESTRE *et al.*, 2007; MESTRE *et al.*, 2009).

Of those that used chemical active agents, some compounds stood out as phosphoric acid (H_3PO_4), used as at least one of the activators in 25% of the publications, while another 25% used sodium hydroxide (NaOH) to activate at least one of the adsorbents, followed or not by hydrochloric acid (HCl) wash. Other chemical agents were used less frequently, including sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium carbonate (K_2CO_3), potassium ferrate (K_2FeO_4), and acetone.

Additionally, literature demonstrate that some modifications were applied on adsorbent surfaces aiming to magnetize the material (DUBEY et al., 2010; CHAKRABORTY; HALDER, 2020; DELGADO-MORENO et al., 2021), as well as immobilizations of the adsorbent material in alginate facilitating solids separation from bulk solution (DELGADO-MORENO et al., 2021; SHOW et al., 2022).

3.4. Ibuprofen adsorption

The following factors that affect the adsorption process can be highlighted: the adsorbent properties, the adopted adsorbent dosage, the contact time between adsorbate and adsorbent, and solution pH. As for the characteristics related to the adsorbate include molecular hydrophobicity, size, and structure, functional groups and complex structure (LUO *et al.*, 2014).

Thus, it was verified that solution pH was prevalent factor for ibuprofen adsorption processes, as it alters absorbent surface charge, and the of compound species (molecular and anionic) distribution in the solution, at the same time. Ibuprofen adsorption capacity tends to increase in acidic circumstances (pH 2.0 - 6.0), eventually stabilizing. However, as pH increases to more alkaline configurations, adsorption capacity tends to decrease (MESTRE *et al.*, 2007; BACCAR *et al.*, 2012; AI *et al.*, 2020).

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It is known that biochar surface is neutral at pH = pHzcp, negatively charged at pH greater than pHzcp, and positively charged at pH below pHzcp, while adsorbate is characterized by charges determined by pKa values. Since ibuprofen is an acidic drug, its molecule has neutral charge at pH below the pKa value, and negative charge when pH is above the pKa value, due to drug molecules dissociation into carboxylate anions. Thus, the adsorption of this drug, on activated carbon, can be partially controlled by interactions other than π electrons, considering electrostatic interactions, hydrogen bonds and hydrophobic-hydrophobic mechanisms, explaining the experimental data of the process (BACCAR *et al.*, 2012).

Two publications were identified (OCAMPO-PEREZ *et al.*, 2019; MORENO-PEREZ *et al.*, 2021) applying a relatively new methodology to measure the kinetics of processes, formed by a Three-dimensional Model of Pore Volume and Surface Diffusion (3D-PVSDM), defining the mass transport by an ordinary differential equation, describing the decay curve, and a partial differential equation obtaining mass balance and describing mass transport within the particle.

Using determination coefficient (R^2) to test experimental data model adequacy, 29 of the analyzed publications reported better representation by the pseudo-second order kinetic model, in at least one of the adsorbents produced. This empirical kinetic model commonly describes adsorption rates involved in chemisorption processes but must be evaluated with caution due to the possibility of incorrect applications, with linearization mathematical transformations, whose implementation has been criticized (SIMONIN, 2016).

Regarding adsorption equilibrium, 18 publications reported a better fit to the Freundlich model in at least one of the adsorbents, while 17 reported a better representation by Langmuir model. Although the adsorbents present better adjustments by R^2 value for a given model, it does not mean that they are "misrepresented" by others, only certain generated models better represent a sample of the experimental data, since the values obtained in each study are relatively close for the different studied models.

21 publications developed some thermodynamic analysis, on environments with temperatures between 20 °C to 25 °C, the values obtained for ΔG° (Gibbs free energy) are negative, in some cases can become positive increasing temperature. Of these, only seven publications simultaneously returned negative process values for enthalpy and entropy, while another seven returned positive values, for the same parameters. The first result indicates the exothermic nature of the adsorption process, driven by enthalpy, with low degree of freedom and slower bonds, as well as spontaneity and favorability at lower temperatures. The second indicates its endothermic nature, with affinity between ibuprofen and biochar, and high degree of freedom.

A possible explanation for convergent data, is that drug molecules are well dissolved in aqueous solution. Thus, to be adsorbed, they need to lose part of their hydration sheath, requiring energy (endothermic phenomenon). This endothermicity is practically equal to the molecules exothermicity binding to the surface. Consequently, overall adsorption process is almost athermal (BACCAR *et al.*, 2012).

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4. CONCLUSIONS

Through the conducted bibliometric survey, the objectives proposed of the research were successfully achieved. It has been observed that the utilization of adsorbents for pollutant removal has emerged as an increasingly captivating alternative, as evidenced by the surge in publications on the subject in the past six years. Notably, the consistent involvement of certain authors in the identified publications, indicates a tendency to employ specific keywords, which may have influenced the results obtained in this systematic survey.

The analysis reveals a substantial utilization of agricultural residues as precursors in adsorbent preparation. Despite the distinctive aspects of each study, the methods employed in the preparation of these adsorbents exhibited discernible trends in terms of precursor material selection, burning duration, and pyrolysis temperature preference. In cases where activation methods were employed, chemical activation with the use of particular agents predominated, indicating a preference for chemical activators over physical ones.

Regarding the adsorption processes, it is noteworthy that pH plays a crucial role in ibuprofen adsorption, with more favorable outcomes observed in acidic pH ranges. The adsorption mechanisms suggest a chemical nature of the adsorbate-adsorbent bonds, with minimal influence from temperature variations on the adsorption process.

5. REFERENCES

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