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NANOTECHNOLOGY WITH APPLICATION IN AIR PURIFICATION: ADSORPTION OF HAZARDOUS GASES ONTO METALORGANIC FRAMEWORKS[1]

NANOTECNOLOGIA COM APLICAÇÃO NA PURIFICAÇÃO DO AR: ADSORÇÃO DE GASES PERIGOSOS EM ESTRUTURAS METALORGÂNICAS

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ABSTRACT

Among the environmental problems generated from anthropogenic activities, the atmospheric pollution is of the most concern due to the great risks to society and environment. This pollution is directly related to the particulate matter and the hazardous industrial gases and vapors emitted to air. Thus, some technologies like adsorption are characterized as efficient and relatively low-cost technology to ameliorate this problem, in which metal-organic frameworks (MOFs) nanoadsorbents are used. Thus, this review aims to report the main advances in hazardous gases adsorption research area using MOFs and to understanding the adsorption mechanisms. From this study, 51 scientific papers were found involving the application of MOFs, confirming their potential in the air purification. Although MOFs are more advantageous than conventional nanoadsorbents (organic/inorganic one), mainly due to the high specific surface area, thermal/chemical stabilities, their occurrence in Brazil is quite low once few works are reported in Brazilian literature.

Keywords: Sustainability, Nanoadsorbents, Atmospheric Pollution.

RESUMO

Dentre os problemas ambientais gerados pelas atividades antrópicas, a poluição atmosférica é um dos mais preocupantes devido aos grandes riscos à sociedade e ao meio ambiente. Essa poluição está diretamente relacionada a materiais particulados, gases e vapores industriais perigosos emitidos para o ar. Assim, algumas tecnologias como a adsorção caracterizam-se como tecnologias eficientes e relativamente baratas para amenizar este problema, nas quais são utilizados nanoadsorventes de estruturas metal-orgânicas (MOFs). Assim, esta revisão visa relatar os principais avanços na área de adsorção de gases perigosos utilizando MOFs e compreender os mecanismos de adsorção. Com este estudo, foram encontrados 51 trabalhos científicos envolvendo a aplicação de MOFs, confirmando seu potencial na purificação do ar. Embora os MOFs sejam mais favoráveis que os nanoadsorventes convencionais (orgânicos/inorgânicos), principalmente devido à sua alta área superficial específica e estabilidade térmica/química, sua ocorrência no Brasil é baixa, visto que poucos trabalhos são relatados na literatura brasileira.

Palavras-chave: *Sustentabilidade, Nanoadsorventes, Poluição Atmosférica.*

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INTRODUCTION

Along the years, the pollution of the air, water and soil have increased considerably as the industrial sector expands (MACEY *et al*., 2014). Among them, the air pollution is characterized as the environmental problem with great concern due to the risk posed to public health, such as eye, skin and respiratory issues (BAMBERGER; OSWALD, 2012). In addition, it causes ecosystem imbalance and contributes to water pollution and soil contamination through the generation of acid rain (LEE *et al*., 2019). Thus, many respiratory problems are due to exposure to toxic vapors and gases generated mainly by the industrial sector (ADGATE; GOLDSTEIN; MCKENZIE, 2014).

Industries such as metal-mechanics, electroplating factory, oil processing and refining and thermoelectric emit large amounts of persistent organic vapors and highly acidic inorganic gases (GERSEN *et al*., 2014). In this view, hydrogen sulfide (H_2S), carbon monoxide (CO), sulfur oxides (SO_X) and nitrogen oxides (NO_X) are the main gaseous residues of inorganic or strongly acidic origin whereas the organic vapors emitted are mostly volatile organic compounds, also known as BTEX - Benzene, Toluene, Ethylbenzene and Xylene (CUMERAS; CORREIG, 2018; BUNCH *et al*., 2014).

The air quality standards are determined by the National Environmental Council through Resolution No. 382/2006, which establishes the maximum permitted values of gaseous pollutants emitted by fixed sources (FRIEHS *et al*., 2016). In this view, gaseous pollutants need to be removed from atmospheric air and for this, technologies such as chemical oxidation, membrane separation and incineration have been used (SHEN; ZHANG, 2019). However, the high cost of implementation and operation, the low efficiency and the generation of secondary pollutants make the use of these technologies unfeasible (ZHANG *et al*., 2017).

Therefore, the adsorption technology emerges as an economic and sustainable alternative in air remediation, due to the smaller amount of material used in the gas purification treatment, the easy separation and little or no generation of hazardous by-products (CHEN; NANAYAKKARA; GRASSIAN, 2012). In this context, metal-organic hybrid nanoadsorbents (MOFs) are an efficient alternative in the removal of gaseous pollutants from the atmosphere, being used in several adsorption processes due to their multifunctional properties (chemical reactivity, high surface area, thermal stability, and mesoporosity) (ZHANG *et al*., 2018).

The MOFs based on zirconium, zinc, aluminum and iron, functionalized or not with amine and amide groups, are the most commonly found in the adsorption of gases. In this context, the present investigation has the general objective of approaching the main advances in air remediation using MOFs to remove hazardous gaseous pollutants, as well as confirming their potential in relation to conventional (in)organic nanoadsorbents.

AIR POLLUTION DUE TO FIXED INDUSTRIAL SOURCES

Air pollution is characterized as an adverse environmental impact and has increased considerably over the years as the industrial sector expands (KAMAL; RAZZAK; HOSSAIN, 2016). Atmospheric pollution is mainly due to human activities, which consist of fixed sources of high polluting potential (KUMAR *et al*., 2019). The main pollutants generated are acidic gases (CO, CO_2, NO_X, SO_X and H_2S), hydrocarbons and volatile organic compounds (VOCs) (BAREA; MONTORO; NAVARRO, 2014). Most of these pollutants are commonly emitted from the burning of fossil fuels and are responsible for the occurrence of environmental problems such as climate change resulting from the greenhouse effect, the generation of acid rain and photochemical dust (ZHAO *et al*., 2013; PARALOVO *et al*., 2019).

The toxic character of pollutants is one of the main factors that emphasize the need for efficient air remediation technologies (PETIT; BANDOSZ, 2015; VELLINGIRI *et al*., 2016; VIKRANT *et al*., 2020; YAN *et al*., 2020). For further clarification, the exposure limits of some of the pollutants emitted by fixed sources were searched in the Brazilian literature and the results are presented in table 1, which informs the toxicity limits or IDHL (Immediately Dangerous to Life or Health Toxicity Levels). (BAREA *et al*., 2014).

Table 1 - Toxicity limits for gaseous pollutants emitted from fixed sources.

Pollutant	Chemical Formula	Exposition limit (mg L^{-1})
Carbon monoxide	CO	1200
Nitric oxide	NO	100
Nitrous oxide	N_2O	20
Carbon dioxide	CO_2	-
Sulfur dioxide	SO_2	100
Hydrogen sulfide	H_2S	100
Hydrogen cyanide	HCN	50
Ammonia	NH_3	300
Cyclohexane	c-C_6H_{12}	1300
Benzene	C_6H_6	500
Dimethyl sulfide	$(CH_3)_2S$	7
Formaldehyde	CH_2O	0.1*
Fluorine gas	F_2	15
Chlorine gas	Cl_2	10
Bromine gas	Br_2	3

*ppb (exposition time of 30 min)

Source: Adapted from NIOSH (2005).

According to Table 1, it can be inferred that the pollutants of the halogen class (fluorine, chlorine and bromine) and of organic origin (benzene, formaldehyde and dimethyl sulfide) are characterized as the most dangerous, since they can react easily with atmospheric gases (O_2) in the presence of UV radiation from the sun, generating reactive oxygen species (OH; DE; YIM, 2018). In addition, it is worth mentioning that of these, organic pollutants are more reactive than those of inorganic origin (WEN *et al*., 2019) and are highly prevalent in wastewater (METCALF; EDDY, 2014). capturing or degrading these pollutants has been the focus of investigation by several authors, due to their mutagenic and carcinogenic character (KIM *et al*., 2017; GELLES *et al*., 2020).

ADSORPTION

Nanotechnology consists of the control and manipulation of matter at the nanometer scale (corresponding to 10^{-9} m) and the exploration of phenomena at this scale for the development of new technologies (International Organization Standardization-ISO, 2015). Nanomaterials are classified as materials that have at least one of their dimensions in the range from 1 to 100 nm and have different physical, chemical and biological properties than bulk material, even if they have the same composition (THERON; WALKER; CLOETE, 2008). Given this scenario, adsorption is based on the application of solid nanomaterials with a high surface area and different functionalities capable of concentrating pollutants on their surface.

Adsorption process can occur through physical or chemical mechanisms. Thus, physical adsorption involves weak interactions of the Van der Waals type, of reversible character, while chemical adsorption is governed by chemical bonds between reactive functional groups present both on the surface of the adsorbent and the adsorbate, being generally irreversible (LEE *et al*., 2018). In general, the adsorption energy is in the order of 20 to 40 kJ mol^{-1} for physical adsorption and 80 kJ mol^{-1} for chemical adsorption (WORCH, 2012).

The factors that strongly influence the adsorption process in are mainly the partial pressure(s) of the component(s) to be adsorbed, the contact time between the adsorbate and the adsorbent, the mass of adsorbent, as well as its specific surface area, pore size and distribution, porosity and number of functional groups found on its surface (BUNCH *et al*., 2014). In this context, a nanoadsorbent is any nanostructured material containing a significant number of pores or reactive surface groups capable of retaining pollutants on its surface (THERON *et al*., 2008).

ADSORPTION EQUILIBRIUM

The main influencing factors in the gas-phase adsorption process are the surface area of the adsorbent material, the relative humidity of the environment where the adsorption process takes place, in addition to the chemical and thermal stabilities of the nanoadsorbent (GELLES *et al*., 2020). Thus, the main parameters evaluated in studies involving adsorption of gaseous pollutants in nanoadsorbents are their adsorptive capacity, in addition to their hydrophobic character and chemical and thermal stabilities (MAITLO *et al*., 2019).

The adsorptive capacity consists of the amount of pollutant that is deposited on the solid surface per unit mass of nanoadsorbent. Additionally, it is important to investigate which conditions favor the desorption of pollutants and the mechanism of interaction between adsorbate and nanoadsorbent (WEN *et al.*, 2019).

To better understand the behavior of the adsorbate-adsorbent interaction, experimental data determined in scientific works are often fitted into equilibrium models (WORCH, 2012). These are intended to represent the experimental data of adsorption equilibrium, as well as to analyze the behavior or adsorption profile as the adsorbate concentration in the fluid phase increases. For this, the models of Langmuir (LANMGUIR, 1918), Freundlich (FREUNDLICH, 1907), Dubinin-Radushkevic (D-R) (DUBININ; RADUSHKEVIC, 1947), Tenkim (TEMKIN; PYZHEV, 1940) and Redlich-Peterson (VILELA *et al.*, 2019) have been used, the first two being the most widespread in the literature (DO NASCIMENTO *et al.*, 2014).

The Langmuir model (or Langmuir isotherm) considers an ideal adsorption, where the active sites of the adsorbent material are equivalent in energy (TIEN, 2019). Furthermore, the model assumes that each active site is able to accommodate only one adsorbate molecule, forming a monolayer once equilibrium is reached (WORCH, 2012). Langmuir isotherm and the separation factor (R_L) are described by Eqs. (1) and (2).

$$q_e = \frac{q_{max} \cdot P}{1 + K_L \mathrm{P}} \quad (1)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

Where q_{max} (mmol g^{-1}) is the amount of adsorbate adsorbed onto the adsorbent at equilibrium; q_e (mmol g^{-1}) is s the maximum amount of adsorbate adsorbed to form monolayer; KL is the Langmuir constant (kPa^{-1}) and P is the partial pressure of the adsorbate (kPa). C_0 is the initial concentration of the adsorbate and can be determined from Eq. (3).

$$q_e = \frac{\pi}{RT} = \frac{y_{io} P}{RT} \quad (3)$$

Where T is the absolute temperature (K), R is the ideal gas universal constant (8.314 J mol^{-1} K^{-1}); y_{i0} and P are the molar fraction of the component *i* (solute/adsorbate); $\boldsymbol{\pi}$ is the total pressure of the system (kPa).

From conventions, the adsorption is considered favorable for R_L values less than 1 and an unfavorable adsorption for values greater than 1 (WORCH, 2012). Regarding Freundlich isotherm, the adsorption capacity of the adsorbent increases with an increase of the adsorbate pressure exponentially as described by Eq. (4)

$$q_e = K_F P^{1/n} \quad (4)$$

Where K_F (g^{-1} mmol) (kPa)$^{-1/n}$ is the Freundlich constant and the exponent *1/n* represents the adsorption intensity (adsorbent-adsorbent interaction) being favorable when values of *n* lie between 1 and 10 (WORCH, 2012).

ADSORPTION KINETICS

The kinetic models most applied to experimental data consist of pseudo-first order and pseudo-second order models, which are described by Eqs. (5) and (6) (LAGERGREN, 1898; HO; MCKAY, 1999).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

Where q_t (mmol g^{-1}) is the theoretical amount adsorbed per unit mass of adsorbent at time t (min); qe (mg g^{-1}) is the theoretical amount adsorbed per unit mass of adsorbent estimated from kinetic models; k_1 (min^{-1}) and k_2 (g mmol^{-1} min^{-1}) are pseudo-first and pseudo-second order are rate constants.

The pseudo-first order model represents a linear relationship between the adsorbate and the adsorbent. In this model, it is assumed that the deposition of the adsorbate on the surface of the adsorbent is the limiting step (LUEKING *et al*., 2016). Also, the model suggests an inversely proportional relationship between the initial concentration of adsorbate in the fluid phase and the kinetic adsorption constant. Thus, the higher the value of the initial adsorbate concentration, the longer the time required for the adsorption equilibrium to be reached.

The pseudo-second order model suggests that the amount of adsorbate deposited on the surface of the adsorbent is dependent on a concentration gradient between the fluid phase and the surface of the adsorbent material. Thus, it can be inferred that the rate at which solute adsorption occurs depends directly on the number of active sites available on the surface of the adsorbent. In addition, the model is characterized by the strong bond between the adsorbate and the solid surface of the adsorbent, which refers to chemical adsorption (Song *et al*., 2016). Them, applying the boundary conditions (t=0, q(0)=0 and t=∞, q(∞)=qe) for Eqs. (5) and (6) and integrating them, Eqs. (7) and (8) are obtained.

$$q_t = q_e(1 - e^{-k_1 t}) \tag{7}$$

$$q_t = \frac{k_2(q_e)^2 t}{1 + k_2 q_e t} \tag{8}$$

In general, fitting the experimental data to the pseudo-first-order model suggests a physical mechanism of adsorption, while the fitting to the pseudo-second-order model infers a chemical mechanism of adsorption (chemisorption) (CHANG *et al*., 2020).

MOFs

Hybrid nanoadsorbents are crystalline materials of organic and inorganic chemical composition with pore diameters in the range of 2 to 50 nm (mesoporous structure) or less than 2 nm (microporous structure) (TIEN, 2019). These nanostructured materials are also called metal-organic frameworks (MOFs) and are characterized by their high surface area, high chemical reactivity and great chemical and structural diversity (FENG *et al*., 2018; GELLES *et al*., 2020). Also, these porous nanomaterials have considerable thermal and chemical stability, relative hydrophobicity, some of them being electron-deficient and therefore can be applied as potential nanoadsorbents (Yan *et al*., 2020), in addition to other applications (XIE *et al*., 2020).

The use of MOFs is more advantageous compared to conventional (in)organic nanoadsorbents (VIKRANT *et al*., 2019; G. ZHANG *et al*., 2019) such as silica ($nSiO_2$) and alumina (nAl_2O_3) nanoparticles, nanozeolites and activated carbon, since they involve predominantly physical mechanisms in the adsorption of toxic gases and vapors (KUMAR *et al*., 2016; DOU *et al*., 2011). In addition, the search for controlling pore size and morphology, at the nanometer scale, has contributed to obtaining MOFs with improved properties (WEN *et al*., 2019). In order to provide an overview of the topic, some MOFs with their respective application and synthesis method are listed in Table 2.

As future perspectives, it is necessary to investigate the toxicity tests of MOFs when in contact with living organisms and research involving scale-up. In addition, it is essential to invest in research aimed at the synthesis, characterization and application of MOFs in Brazil, since from this research few works on the subject were found in the literature.

Table 2 - Toxicity limits for gaseous pollutants emitted from fixed sources.

MOF	**Research**	**Commentary**	**Reference**
ZIF-8	Incorporation of MOF in ABS filter produced by additive manufacturing	Gaseous adsorption	PELLEJERO *et al*., 2020
X-DOBDC XMOF-74 (X=Mg, Zn, Co, Ni)	Theoretical-Experimental study of the potential of MOF in gas-phase	Adsorption of CO, NO, NO_2, NH_3, e H_2S	ZHOU *et al*., 2018
Zu-13 (TIFSIX-14-Cu-I)	Theoretical-experimental study of the separation of trace pollutants in gaseous mixtures	Application in the adsorption of propyne in MOF Zu-13 from propyne-propylene gas mixture (C_3H_4/C_3H_6)	YANG *et al*., 2018
IRMOF-1, Cu-BTC, MIL-74 (V), Zn-MOF-74, Mg-MOF-74, MOF-177, ZIF-8, ZI-10	Theoretical-comparative study between MOFs and zeolites in CO_2 adsorption	Application in CO_2 adsorption via adsorption on 13X commercial zeolites and on MOFs Mg-MOF-74, CuBTC	MOHIDEEN *et al*., 2017
CeBTC MIL-125(Ti)	Comparative study between MOFs and MOFs based on metal oxides	Application in CO_2 adsorption via adsorption onto MOFs and metal oxides	MOHIDEEN *et al*., 2018
HKUST-1	Functionalization of HKUST-1 with graphene oxide (GO)	Application in the adsorption of H_2S in hybrid nanoadsorbent HKUST-1/GO	BHORIA *et al*., 2020
Mg@ZIF-8 Zn@ZIF-8	Study of CO_2 adsorption/desorption in zeolitic MOF	Applied in the adsorption of CO_2 in MIF-8-(NH_2) and MIF-8/GO	CHANG *et al*., 2020
ZIF-8	Functionalization of MOF with amine group and comparative study between the adsorption of gases in functionalized and non-functionalized ZIF-8	Applied in the adsorption of CO_2 in MIF-8-(NH_2) and MIF-8/GO	POKHREL *et al*., 2018
Kag-MOF	Adsorption of inorganic gases and volatile organic compounds	Low affinity for BTX and high affinity for H_2O, H_2Se CO_2	MOHIDEEN *et al*., 2017
Mg-MOF-74 Cu-BTC	Computational study on the effect of impurities on mono- and multi-component adsorption. Low impurity MOFs	Adsorption CO_2, O_2, N_2, H_2O, SO_2 e NO	BAHAMON *et al*., 2018
CeBTC MIL-125	Adsorption of CO_2 e SO_2 onto MOFs	High affinity and adsorptive capacity for pollutants, despite considerable chemical stability	MOUNFIELD *et al*., 2016

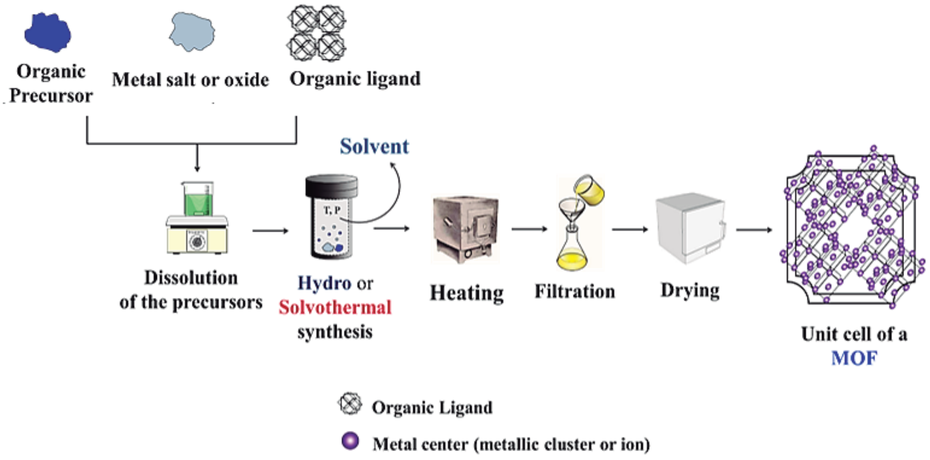
* ppb (exposition time of 30 min)

Source: Author.

SYNTHESIS AND CHARACTERIZATION OF MOFS

As shown in table 2, the synthesis of MOFs can be mainly through solvothermal and hydrothermal methods, the latter being the most used (ZHOU *et al*., 2018; PELLEJERO *et al*., 2020; MOHIDEEN *et al*., 2017; MOUNFIELD *et al*., 2016). The difference between the methods consists only in the nature of the solvent used: water is used as a solvent in hydrothermal synthesis and organic solvent in solvothermal synthesis, both at temperature and pressure above ambient conditions (LIMA *et al*., 2019). It is also important to analyze that the aforementioned methods are performed in a closed system (STOCK; BISWAS, 2011), as illustrated in Figure 1.

Figure 1 - Schematic representation of the MOF synthesis process.



Source: Author.

The advantage of using these methods lies in the possibility of obtaining a material of high purity and versatility (YANG *et al*., 2018), as in the case of metal-organic hybrid nanoadsorbents, characterized by great structural and chemical diversity (MOHIDEEN *et al*., 2017).

FUNCTIONALIZATION OF MOFS

Although it is possible to obtain nanostructured materials (MOFs) of high purity, chemical diversity, high surface area and pore density (JAMES, 2003; CALERO *et al*., 2011; SUN *et al*., 2014), one of the challenges encountered in current scenario is the low chemical stability of these materials. It is known from several studies that MOFs undergo degradation under acidic conditions (WEN *et al*., 2019). In addition, they have reduced adsorptive capacity for gaseous contaminants when applied in environments with considerable moisture content (BURTCH; JASUJA; WALTON, 2014). This is because water vapor has a high affinity for the active sites of MOFs and, consequently, competes strongly with pollutants of interest (SUPRONOWICZ; MAVRANDONAKIS; HEINE, 2013; ZHANG *et al*., 2019).

Given this scenario, functionalization with amines (KANG; KANG; HONG, 2019), amides (LIU *et al*., 2019) and graphene oxide - GO, (BHORIA *et al*., 2020) emerges. as an alternative to these operational problems, since its insertion into the hybrid metal-organic structure gives it hydrophilic groups that can interact with water vapor (FARHA *et al*., 2012; LOLLAR *et al*., 2018). In this way, a greater number of active sites of porous material is available for adsorption of toxic gaseous pollutants (HWANG *et al*., 2008).

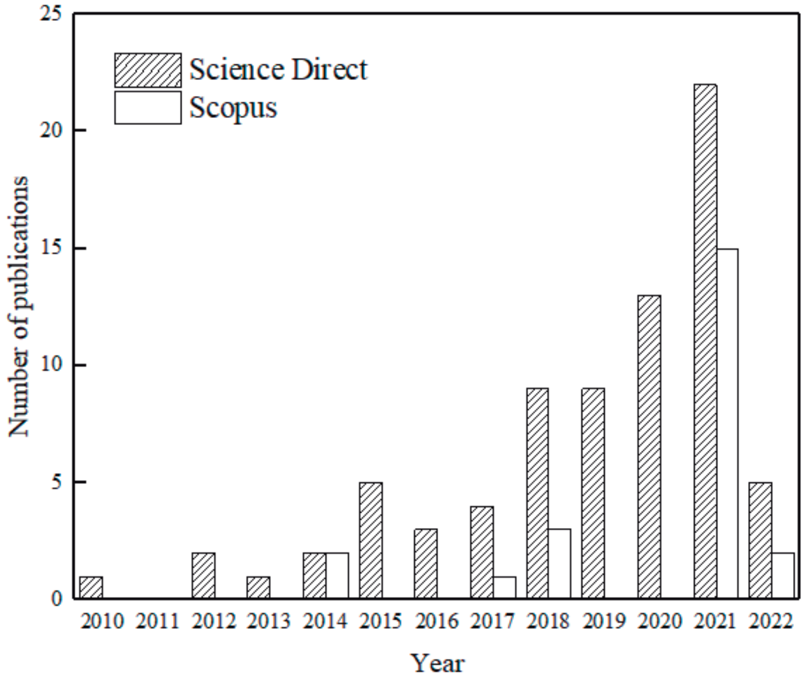
Regarding the theme presented here, it is worth mentioning the main characterization used to evaluate or describe the MOFs' properties as nanoadsorbent. In this sense, once adsorption is a surface phenomenon, N2 physisorption (nitrogen porosimetry), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and thermogravimetry analysis (TGA/DTG) are useful before the experimental procedures of gas adsorption onto MOFs (TIEN, 2019). Therefore, N2 physisorption is based on the obtention of adsorption and desorption data of molecular nitrogen on the MOFs sample. Thus, through the use of Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH), the textural properties of the MOFs (i.e., surface area, pore volume, pore diameter) are evaluated.

XRD and FTIR are useful for the investigation of the structure (phases and crystallinity) of the nanoadsorbetns and the functional groups present in their composition. Therefore, the organic matter of the MOFs has been commonly determined from FTIR, whereas the inorganic counterpart was from XRD. Furthermore, Scanning Electron Microscopy with Energy-dispersive X-ray spectroscopy (SEM-EDS) is one of the characterization techniques very useful to describe MOFs, where the main feature is the identification of the nanoadsorbent morphology and elemental composition. Moreover, X-ray photoelectron spectroscopy (XPS) characterization assay has been used to identify the surface chemistry, elemental composition and electronic state of the MOFs (ANADEBE et al., 2022).

MATERIAL AND METHODS

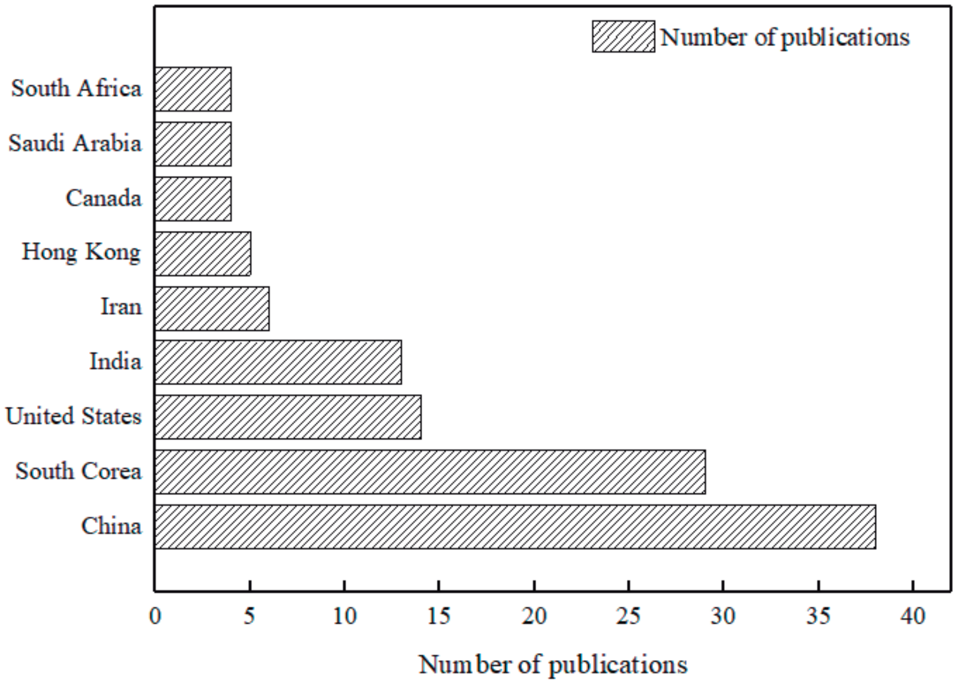
The present study was based on a literature review on the topic metal-organic hybrid nanoadsorbents (metal-organic frameworks - MOFs) applied in the purification of hazardous gases. For this, a scientific article was searched on the Scopus and Science Direct platforms, where 55 articles were found, 21 of which were excluded because they were repeated in one of the bases, because they dealt with adsorption in liquid phase or involved applications other than the purification of the material. atmospheric air. The descriptors used were "MOF" AND "adsorption" AND "gas removal", according to Boolean Logic. Figure 2 illustrates the results found during the years 2010 to 2020, while Figure 3 provides, in the same period, information about the number of publications worldwide.

Figure 2 - Published scientific papers from January 2010 to December 2022, using the keywords "MOF" AND "adsorption" AND "gas removal".



Source: Author.

Figure 3. Published scientific papers per country from January 2010 to December 2022.



Source: Author.

As observed in the figures, it is possible to affirm that the number of publications involving MOFs has increased considerably over the years, being more common in developed countries.

RESULTS AND DISCUSSION

ADSORPTION ISOTHERMS

Due to most papers investigated in this review were predominantly theoretical, few make direct use of mathematical models of adsorption equilibrium, such as Freundlich and Langmuir. Thus, some characterization techniques such as thermogravimetric analysis - TGA and Fourier Transform infrared spectroscopy - FTIR have been applied to determine the adsorption of gaseous pollutants quantitatively and qualitatively in MOFs. CO_2 and H_2S adsorption analyzers are frequently reported in the literature (POKHREL *et al.*, 2018; WU *et al.*, 2018; (CHANG *et al.*, 2020).

On the other hand, from the present search, a linear isotherm was found as an adjustment model to the experimental data of adsorption (CH_4, N_2 and BTX), obtaining 1.8 mmol g^{-1} for CH_4 at a pressure of 0.5-1 bar, at 298 K. At the same time, the Langmuir model was found to fit the experimental data of adsorption of CH_4, CO_2 (25 °C, 20 bar, 2h) and H_2S (25 °C, 10 bar, 2h), with maximum adsorption capacities of 4.4, 10.8 and 18.8 mmol g^{-1} in ZIF-8 type MOFs.

Although most of the studies found have a theoretical nature, the experimental works report an adsorptive capacity of gaseous pollutants (CO_2, H_2S, SO_2 and NH_3,) in the order of 0.5-2.5 mmol g-1 under typical adsorption in gas-phase: 298 K, 1-4 bar and adsorbate saturated environments. Given this scenario, the MOFs ZIF-8, Cu-BTC and Mg-MOF-74 are the ones with the highest adsorption capacity for the gases mentioned in the present investigation. In parallel, for the adsorption of CO_2, H_2S and a mixture of C_3H_4 and C_3H_6, performance of 80 and 90% of ZIF-8 and Cu-BTC or copper-based MOFs are reported after 4 and 6 adsorption cycles - T= 298 K, 1-20 bar, 30-50 mg nanoadsorbent (YANG *et al.*, 2018; CHANG *et al.*, 2020).

KINETIC OF ADSORPTION

Although several studies found from this review analyze the time required to reach adsorption equilibrium, only one research mentions the adjustment of experimental data to pseudo-first and pseudo-second order kinetic models. In their research, Chang *et al.* (2020) reports the adsorption of CO_2 on nanoadsorbent ZIF-8 associated with MgO. It is confirmed, through his research, that the best fit of the data is obtained when applied to the pseudo-second order model. Therefore, it can be inferred that adsorption in the mentioned system occurs predominantly by chemical mechanisms (SONG *et al.*, 2016).

Furthermore, it is reported by the same author that when using the same nanostructure (ZIF-8), but associated with ZnO, the physical adsorption mechanism predominates. This is due to the fact that magnesium is characterized as a stronger Lewis acid than zinc, interacting more intensely with CO_2 molecules (LUEKING *et al.*, 2016).

Nevertheless, it is worth mentioning that several authors have evaluated the kinetics of adsorption using the rupture time test, in a continuous regime (POKHREL *et al*., 2018; BHORIA *et al*., 2020; PELLEJERO *et al*., 2020). From the selected works, it can be seen that when MOFs are functionalized or associated with oxides, not only is the break-up time doubled, but also its adsorptive capacity results in an increase of approximately 30 to 40% (POKHREL *et al*., 2018; PELLEJERO *et al*., MOHIDEEN *et al*., 2017; CALERO *et al*., 2011). In this context, the potential of both isolated MOFs and MOFs functionalized or associated with other compounds (graphite, graphene oxide, polyethyleneimine) is confirmed in the remediation of hazardous gases with a strongly acidic character, on an industrial scale.

DESORPTION

The desorption step proves to be crucial to evaluate the application of a nanoadsorbent at an industrial level (SUN *et al*., 2014; BAHAMON *et al*., 2018). Therefore, in all the studies investigated in this review, the conditions of the process of desorption of gaseous pollutants from MOFs were evaluated. As noted, the desorption processes employed are based on gas entrainment or N_2 purge (PELLEJERO *et al*., 2020), as well as thermal methods (CHANG *et al*., 2020).

It should be noted that MOFs alone, as they present a predominantly physical mechanism of adsorption of gaseous pollutants, are characterized as viable from an industrial point of view, since they require low temperatures or reduced inert gas entrainment flows (ZHOU *et al*., 2018) to be regenerated. However, when associated with oxides or functionalized, they result in more favorable conditions of the desorption process, since the temperature used is significantly reduced - in the order of 100 to 200 °C (JAMEH *et al*., 2019; PETIT; BANDOSZ, 2015).

CONCLUSIONS

From the works found in the literature, it is possible to confirm the metal-organic hybrid nanoadsorbents (MOFs) as potential atmospheric air purifiers. These nanostructured materials are characterized by their significant thermal stability and high affinity with inorganic vapors (CO, CO_2, NO_X, H_2S, SO_2), volatile and semi-volatile chemical compounds (aromatic compounds, aliphatic hydrocarbons, volatile fatty acids and formaldehyde) of high toxicity, whether of organic or inorganic origin. For this reason, MOFs have been used in various processes of gas storage and separation, wastewater purification to remove highly toxic contaminants, as well as applications in industrial gas sensors. It is important to mention that there is a lack of a detailed discussion of the thermodynamic and kinetic mechanisms and models of gas-phase adsorption, as well as the exploration of equilibrium models.

As future perspectives, it is necessary to investigate the toxicity tests of MOFs when in contact with living organisms and research involving scale-up. In addition, it is essential to invest in research aimed at the synthesis, characterization and application of MOFs in Brazil, since from this research few works on the subject were found in the literature.

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