13 Sustainable Use of African Palm Shell Waste Applied to Paraben Adsorption from Aqueous Solutions

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Abstract

The utilization of agricultural waste residues has been explored as an alternative to costly conventional activated carbon production methods. This study addresses the potential use of agricultural waste from the processing of palm oil (African palm shell) to produce activated carbons modified with metal salts at 973 K and 1173 K, as adsorbents for methylparaben (MePB) and propylparaben (PrPB), a type of emerging contaminants present in personal care products (PCPs). The carbons obtained were able to retain parabens, but the highest adsorption was found for PrPB in carbon with the highest contribution of micropores to the total pore volume and with the highest content of acid surface groups, which were favored by the effect of the higher activation temperature.

Keywords

Adsorption · Methylparaben · Propylparaben · Agroindustrial waste · African palm shell · Activated carbon · Personal care products

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13.1 Introduction: Water and Pollution

It is widely known that water is a limited natural resource, necessary for the development and sustainability of life, which constitutes an essential part of every ecosystem. However, the constant increase in demand for this resource due to its excessive use in various activities of our daily lives, results in the release of tons of biologically active substances through the water. Wastewater, whatever its origin, has not been considered beyond being a contaminated or altered supply with no other purpose than to dispose of. However, as mentioned in the 2017 edition of the United Nations World Water Development Report: “Wastewater: The Untapped resource” shows that this conception is beginning to change, not only because of the associated pollution problems, but because the scarcity of this resource has increased in many regions. Thus, the importance of the collection, treatment, and reuse of wastewater begins to be recognized, that is, in the management that is given to these, which generates essential social, environmental, and economic benefits for sustainable development (Ryder 2017).

The behaviors and adverse impacts of various chemical compounds such as heavy metals, colorants, pesticides, or polycyclic aromatic hydrocarbons, among others, have been known for a long time (*World Health Organization: Guidelines for Drinking-water Quality. Recomendations* 2008), which are mostly regulated. However, the development of more sensitive analytical methods has made it possible to warn of the presence of new or less known pollutants, whose accumulation of scientific evidence derived from new research is beginning to acquire greater relevance and concern about their impacts on public health or the environment (Recommendations Report: Contaminants of Emerging Concern Workgroup 2019). These pollutants are called emerging contaminant (EC) whose study appears among the priority research lines of the main organizations dedicated to the protection of public and environmental health, such as the World Health Organization (WHO), the Environmental Protection Agency (EPA) (OW/ORD Emerging Contaminants Workgroup 2008), or the European Commission (European Environment Agency 2012; Martin and Kortenkamp 2009). The risk associated with the presence of these pollutants in the environment is not due so much to their acute toxicity but to the development of resistance to pathogens and endocrine alterations due to continuous exposure, mainly of aquatic organisms to these pollutants. Many of these are classified as carcinogens, endocrine disruptors, or with other toxic effects for humans and the ecosystem (OW/ORD Emerging Contaminants Workgroup 2008; Pal et al. 2014; Schriks et al. 2010; WHO 2006).

The list of emerging contaminants includes a wide variety of compounds with different structures and uses, as well as their metabolites and transformation products that are part of pharmaceutical and personal care products (PCPs), among others (USEPA 2016). Global production of pharmaceutics and PCPs is estimated to increase 3% each year (Kwarciak-Kozłowska 2019). Reason why a continuous introduction of these pollutants into the environment is generated, since not everything is used or absorbed by the body, thus becoming part of the wastewater.

Table 13.1 Emerging contaminants most representative (Dey et al. 2019; Freyria et al. 2018)

Subgroup	Emerging contaminants
PCPs	
Parabens	Methyl-, ethyl-, propyl-, and butylparaben
Antiseptics/disinfectants	Triclosan, chlorophene, chloramines
Sunscreen agents	Benzophenones, benzylidene, homosalate
Fragrances	Nitro, polycyclic and macrocyclic fragrances, musk xylol
Insect repellents	*N*, *N*-diethyltoluamide
Pharmaceutics	
Antibiotics	Amoxicillin, ciprofloxacin, erythromycin, penicillin
Steroids and hormones	Estrogen, estrone, estriol, testosterone, 17β-estradiol
Nonsteroidal anti-inflammatory drugs (NSAIDs)	Aspirin, ibuprofen, naproxen, ketoprofen, paracetamol, diclofenac, morphine
Psychiatric	Benzodiazepines, barbiturates
Illicit drugs	Cocaine, codeine, heroin, methadone, amphetamines

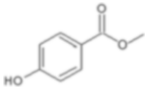
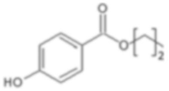
Table 13.1 shows a list of some of the emerging contaminants found in PCPs and pharmaceutics.

The risk associated with the presence of these contaminants in the environment is due to development of resistance to pathogens and endocrine disfunction. Several studies have shown that the effects of endocrine disruptors chemicals (EDCs) on living organisms are multiple, the most alarming are related to the reproductive system, where the anomalous development of the reproductive organs has been evidenced in some fish, that leads to the acquisition of male and female genetic and phenotypic characteristics (Niemuth and Klaper 2015). In humans, it produces hormonal alterations, influences reproductive function, in addition to generating antimicrobial resistance (Sanderson et al. 2016). These compounds are found in low concentrations on the order of μg L^{-1}, ng L^{-1} even pg L^{-1} (Kalia 2019), where adverse estrogenic effects have been assigned at concentrations as low as 1 ng L^{-1} (Kuster et al. 2008). Among the compounds listed above, PCPs have acquired great notoriety due to their widespread use. And within these, parabens have specifically received attention since their use is widely distributed.

13.2 Parabens: What Are They?

Parabens (PBs) are esters of 4-hydroxybenzoic acid with alkyl or aril substituents ranging from methyl to butyl, benzyl, or phenyl. These PBs are widely used as preservatives in a wide variety of cosmetic products and pharmaceutics (Haman et al. 2015) although they are also often used in food and industrial products (Brand et al. 2017). Methylparaben (MePB) is widely used as a preservative in drugs, often combined with propylparaben (PrPB) to obtain a synergistic antimicrobial effect. Although PrPB is not approved in food if it is allowed in the manufacture of plastic materials and articles intended to come into contact with food (European

Table 13.2 Physical–chemical properties of parabens (Andersen and Larsen 2013; Błędzka et al. 2014; Yalkowsky et al. 2010)

Parameter	MePB	PrPB
N° CAS	99-76-3	94-13-3
Molecular formula	$C_8H_8O_3$	$C_{10}H_{12}O_3$
Molecular weight (g mol^{-1})	152.15	180.21
Water solubility (mg L^{-1}) at 25 °C	2.50×10^3	5.00×10^2
Log K_{ow}	1.66	2.71
pK_a	8.17	8.35
Area (nm^2)[a]	0.406	0.754
Structure		

[a]Value determined using HyperChem software (version 8.0.7 for Windows)

Commission Regulation No. 10/2011) and can, through migration, also enter the food (Brand et al. 2017). In fact, PBs are present in 80% of PCPs (Błędzka et al. 2014), with MePB and PrPB being the main preservatives used in this type of products (Nowak et al. 2018), which is related to their greater presence in wastewater compared to other PBs. The maximum authorized concentration in ready-made preparations for the individual esters and their salts is 0.4% (w/w) for MePB and 0.14% for PrPB, while for paraben mixtures it is 0.8%, as established by the European Union (Brand et al. 2017; Hessel et al. 2019). Thus, the estimated exposure in children and adults is about 3 mg/kg/day and 0.2 mg/kg/day for these parabens, related to PCPs since the contribution of food is less than 1% (Brand et al. 2017).

PBs show chemical stability in a wide pH range (3.0–6.5) (Angelov et al. 2008) and broad spectrum of antimicrobial activity, which is proportional to the chain length of the ester group (Brand et al. 2017; Mackay et al. 2006). As the length of the alkyl chain increases, the hydrolysis resistance of aqueous paraben solutions increases (Masten 2005). However, the value of the octanol–water partition coefficient (log K_{ow}) increases, which results in a decrease in water solubility (Table 13.2), so that sodium salts of parabens are also frequently used in formulations. The values of the acid dissociation constant (pK_a) are around 8.3 and therefore, in aquatic environments they are in their free acid form (Andersen and Larsen 2013; Błędzka et al. 2014).

13.2.1 Environmental Impact of Parabens

Parabens are compounds that can mimic the effects of the main natural estrogen; therefore, they are listed in the EU list of possible endocrine disruptors (EDCs) within category 1, where substances for which endocrine disrupting activity has been documented a living organism is found in at least one study and is given the highest priority for further studies (Andersen and Larsen 2013). EDCs are known as a class of chemicals that have xenobiotic and exogenous origins while interfering by mimicking or inhibiting the normal activity of the hormonal system, causing alterations in the health of the reproductive system and metabolism in general (European Environment Agency 2012).

Among the alterations that have been related to the effects of EDCs, especially due to exposure to them during pregnancy, childhood, and puberty, are breast and prostate cancer, reproductive disorders such as infertility, metabolism disorders such as diabetes and obesity, autoimmune diseases, asthma, cardiovascular problems such as hypertension, mental disorders such as Alzheimer's and Parkinson's, and behaviors such as memory, motility, attention, among others. Some studies have shown the possible estrogenic effects of parabens, especially in fish (Diamanti-Kandarakis et al. 2009; European Environment Agency 2012). Some studies have shown the possible estrogenic effects of parabens, especially in fish (Andersen and Larsen 2013; Brausch and Rand 2015; Haman et al. 2015) and crustaceans (Lee et al. 2018) at high exposure levels. Other studies in young male rats have shown adverse effects on sperm production and testosterone levels after oral exposure to PrPB (Andersen and Larsen 2013). MePB is generally considered to have a much lower potential to cause endocrine disrupting effects compared to PrPB, in addition to several studies that have shown PrPB to have estrogenic and/or antiandrogenic effects in vivo and in vitro (Andersen and Larsen 2013; Andersen 2008).

EDC effects towards animals are well reported, although direct effects for humans are still debated and require further study. However, few studies suggest that the effect of exposure to EDCs on human health includes a decrease in male sperm count, an increase in testicular, prostate, ovarian, and breast cancer (Brand et al. 2017), as well as reproductive dysfunctions (Bolong et al. 2009). PBs can be degraded in the human body into various metabolites, being p-hydroxybenzoic acid the most common to all parabens, a product of its hydrolysis (Pugazhendhi et al. 2005), so it cannot be used directly to discriminate the metabolites of each paraben, added because they are not always completely metabolized, so a small fraction of the free parent substance can also be found. These parabens and their metabolites are mainly excreted in the urine, and as the length of the alkyl chain increases, the urinary excretion rate of *p*-hydroxybenzoic acid decreases (Brand et al. 2017; Hessel et al. 2019).

13.2.2 Remotion Treatments of PCPs from Water

Wastewater treatment technologies are classified according to their stage of operation and application in a large-scale system. In general terms they are classified as conventional and advanced treatment methods (Kaur et al. 2019). Conventional treatments including coagulation/flocculation and sedimentation are ineffective in removing PCPs (<30%) (Yang et al. 2017), so they can still be detected in the effluents after the conventional treatment process, although their concentrations are low (Wang and Wang 2016). Thus, PCPs residues have been found in the tissues of plants when bio-solids or manure-amended soils were used or when sewage was used for irrigation (Rajapaksha et al. 2014).

Due to the inefficiency of conventional treatment methods for the significant removal of PCPs, advanced methods have been developed employing oxidation, membrane filtration, phytoremediation, and adsorption processes. Oxidation treatments include ozonation, UV irradiation, photocatalysis with Titania, among others, which involve the generation of highly reactive radicals (especially • OH radicals). Membrane filtration techniques include nanofiltration (NF), ultrafiltration (UF), and reverse osmosis (RO), considering that the removal efficiency of NF/UF is affected by the physicochemical properties of PCPs, such as hydrophobicity, charge, and molecular weight. Phytoremediation for its part is a cost-efficient plant-based approach that takes advantage of the natural ability of certain plants to bioaccumulate, degrade, immobilize, degrade contaminants from the environment, and metabolize various molecules in their tissues. It is potentially the least harmful method because it uses living organisms and preserves the environment in a more natural state. However, it is limited to the surface and depth that the roots occupy, and plant survival is affected by the toxicity of the contaminated environment and the general state of the soil (Farraji et al. 2016; Hauptvogl et al. 2020). Within a sustainable bioeconomy, studies are also focusing on the development of adsorbents from phytoremediation residues for the adsorption of pollutants (Abu Hasan et al. 2020).

Finally, adsorption treatments mainly involve carbonaceous materials such as activated carbon, graphene, and carbon nanotubes; however, performance is also affected by the physicochemical properties of PCPs, as well as their solubility in water (Kaur et al. 2019). Within the methods of removal of PCPs in wastewater (Table 13.3) it is evident that each process has advantages, disadvantages, and limitations, so new methods are continually being improved or proposed.

Currently there are a series of processes that are used in the elimination of parabens. Oxidation methods such as ultraviolet photodegradation (Álvarez et al. 2020), persulfate oxidation and ozonization (Hernández-Leal et al. 2011; Kwarciak-Kozłowska 2019; Tay et al. 2010a) with a high percentage of elimination but the possible formation of toxic degradation by-products. The study by Tay et al. (2010b) discovered that the hydroxylation of parabens is the main reaction that occurred during ozonation with the detection of a number of compounds including hydroquinone and 4-Hydroxybenzoic acid. In another study by Canosa et al. (2006) it was reported the formation of chlorinated parabens during the chlorination process, as well as that the levels of chlorine generally contained in tap water are sufficient to produce significant amounts of its chlorinated by-products in a few minutes that can become more resistant to additional oxidation than the original parabens.

Because of this there is a growing need for more efficient, cost-effective, and safe methods for treating wastewater. Therefore, the adsorption method can offer a much safer way to remove parabens from water and wastewater, as it is a method free of harmful substances and it is more environmentally friendly. In general, a wide variety of adsorbent materials have been applied for the removal of parabens such as organic textile fibers (Ran et al. 2020), composites (Mashile et al. 2020), polymers

Table 13.3 Conventional and advanced methods to removal of PCPs in wastewater

Method	Advantages	Disadvantages	Ref.
Conventional treatments			
Coagulation/ flocculation/ sedimentation	• Simple (low technology) • Easy installation and operation • Low cost • Removal of lipophilic compounds	• Low elimination capacity (<20%) • Incomplete degradation resulting in toxic degradation products • High sludge production • Disposition problems	Bolong et al. (2009), Chang et al. (2009) and Kaur et al. (2019)
Tratamiento biológico	• Less amount of biomass per unit of substrate degraded • Economic	• The removal depends on the biodegradability of the compound • Variable elimination rate	Bolong et al. (2009) and Chang et al. (2009)
Advance treatments			
Oxidación avanzada (UV, O_3, TiO_2)	• High efficiency (>90%) • Complete mineralization of micropollutants	• Generation of subproducts with unknown effects • 50–80% removal with UV • Removal efficiency is generally proportional to dose • High cost due to longer contact time and higher dosage required • High energy requirement • UV lamp replacement frequency	Kaur et al. (2019), Kwarciak-Kozłowska (2019) and Morone et al. (2019)
Membrane filtration (RO, NF)	• High removal (almost complete with RO) • Removes wide range of contaminants (NF) • Small space requirement	• High energy consumption (RO) • Removal depends on the properties of membrane • Generation of huge volume of concentrates	Kaur et al. (2019), Kwarciak-Kozłowska (2019) and Morone et al. (2019)
Phytoremediation	• Suitable for various types of contaminants • Financial costs low (energy from solar radiation)	• Not applicable to all plants or contaminants • Process is slower than normal physicochemical methods • Applicable to moderately contaminated land • Contaminants cannot be completely removed	Farraji et al. (2016) and Hauptvogl et al. (2020)
Adsorption (AC)	• High efficiency for most (>90%) • No transformation by-products generated • Little environmental impact • Regeneration of adsorbent	• Cost of the adsorbent material • Dependence with pH • Adsorbent saturation • Less removal of polar compounds • Disposal of spent adsorbent • Nonselective adsorbent	Chang et al. (2009), Katsigiannis et al. (2015), Morone et al. (2019) and Rossner et al. (2009)

(Chin et al. 2010), fly ash (De Oliveira et al. 2020), magnetic nanoparticles (Chen et al. 2017), bioadsorbents (Mallek et al. 2018), among others. However, the adsorption of parabens using activated carbons has been little studied, compared to other emerging pollutants such as pharmaceutical compounds.

Mailler et al. (2014) studied the adsorption of a number of emerging pollutants including methyl butyl and benzyl paraben using powdered commercial activated carbon (PAC). They determined adsorption capacities greater than 70%, particularly for PrPB. They identified the adsorbent dose as the most influential operating parameter, which correlates with the performance of the process. Delgado et al. (2016) used a commercial granular activated carbon (GAC) which exhibited a high adsorption capacity for MePB (300 mg g^{-1}). The results presented by de los Ángeles Bernal-Romero et al. (2019) show that between 80% and 90% of MePB and PrPB can be removed from real water and noted that removal of both parabens was improved at higher doses of PAC. They concluded that the higher solubility in water and the lower log K_{ow} values could explain the lower adsorption capacity evidenced for MePB.

13.3 Activated Carbon: Properties and Production

13.3.1 Properties of Activated Carbon

Activated carbon (AC) is considered an amorphous solid consisting mainly of carbon atoms which join the other carbon atoms forming angles of 120° giving rise to flat sheets of hexagonal rings displaced from each other, forming a criss-cross structure of basal planes joined by forces. of Van der Waals. In fact, the folding of the hexagonal sheets takes place producing a rigid structure, with very little mobility, which avoids the ordering by creating interstices that give rise to the different types of porosity (Marsh and Rodríguez-Reinoso 2006). According to the IUPAC it is possible to make a classification of the pores according to their size as: micropores ($\leq$2 nm), mesopores (between 2 and 50 nm), and macropores ($>$50 nm) (Thommes et al. 2015). Micropores contribute more to the high surface areas of activated carbon and provide high adsorption capacities for small molecules such as gases and most solvents. These in turn can be classified into two subcategories, for example, narrow micropores ($<$0.7 nm) and super micropores (0.7–2 nm) or primary micropores ($<$0.8 nm) and secondary micropores (0.8–2 nm) (Daud and Houshamnd 2010).

Graphene layers can present a large number of imperfections, impurities, non-aromatic rings, as well as edges that constitute highly energetic sites, associated with higher densities of unpaired electrons and therefore show a strong tendency to chemisorb other heteroatoms, such as oxygen, hydrogen, nitrogen, sulfur, etc., giving rise to stable surface compounds (Rouquerol et al. 2014b).

The presence of these surface groups determines the apparent chemical character of the activated carbon surface (Rodriguez-Reinoso and Molina-Sabio 1998), as well as its hydrophobic or hydrophilic character (Aburub and Wurster 2006). The exact nature of these surface groups is not fully established; however, it is known that there

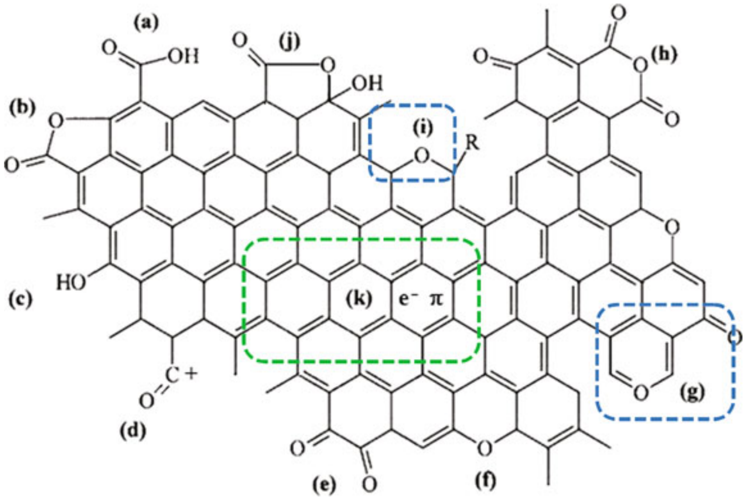


Fig. 13.1 Schematic representation of the oxygenated functional groups present on the surface of activated carbon: (**a**) carboxyl, (**b**) lactone, (**c**) hydroxyl, (**d**) carbonyl, (**e**) quinone, (**f**) ether, (**g**) pyrone, (**h**) carboxylic anhydride, (**i**) chromene, (**j**) lactol, and (**k**) π electron density in the basal planes of activated carbon. (Taken and modified from Bandosz et al. (Bandosz and Ania 2006))

are various types of surface groups. The acid character is associated with surface groups such as carboxylic acid, lactone, phenol, anhydride, and carbonyl in the form of quinone and hydroquinone, so much so that the pyrone and chromene type groups are related to the basic character. Conversely, the nonpolar surface of activated carbon has basic properties associated with regions rich in π electrons located in the basal graphene layers (Boehm 2002; Daud and Houshamnd 2010). Some studies have suggested that the basic property derived from the basal planes is weak compared to that derived from basic functional groups and that the increase in acid groups on the surface usually leads to a decrease in the basic groups (Daud and Houshamnd 2010).

In Fig. 13.1, the most common oxygenated surface groups present on the surface of activated carbon are shown, capable of forming specific interactions between the solute and the adsorbent. Highlighted in blue are the functional groups to which the basic character is attributed and in green are the apolar regions of the basal surface of activated carbon that intervene in nonspecific interactions with the apolar regions of the solute.

13.3.2 Agroindustrial Waste

Lignocellulosic residues from agriculture have been widely used for the preparation of activated carbons (Attia et al. 2008; da Silva Lacerda et al. 2015; Guo et al. 2003; Iwasaki et al. 2002; Torrellas et al. 2015; Tseng et al. 2006; Venkatramanan et al. 2021). Among these, African palm residues have demonstrated their potential as activated carbon precursors for the adsorption of various compounds (Arami-Niya et al. 2012; Guo and Lua 2002; Pamidimukkala and Soni 2018; Rashidi and Yusup 2017; Tan et al. 2008). African palm shell is a by-product of the processing of African palm oil (*Elaeis guineensis*), constituting the endocarp that covers the palm fruit. This industry has an important presence in the world economy, especially in Southeast Asian countries such as Malaysia and Indonesia, where it is estimated that in 2008, they had a palm oil production of 17.7 and 19.3 million tons, respectively, generating approximately 1.1 tonnes per hectare of this by-product (Abdullah and Sulaiman 2013). Currently, Colombia is the fourth largest producer of palm oil worldwide and the first in America, with a production of 1.6 million tons in 2017, which generates around 0.73 tons per hectare of palm kernels (Ruiz and Romero 2011) and constitutes a large amount of waste that is necessary to dispose of. In the literature, the preparation of activated carbon from palm shell has been reported (Daud and Ali 2004; Jung et al. 2014; Nizamuddin et al. 2015; Ruiz et al. 2015), given its high carbon content (50%) consisting of cellulose (17%), lignin (53%), and hemicellulose (30%), as well as high density, high volatile matter, and low ash content (Daud and Ali 2004; González-García 2018). Physicochemical characteristics that allow the production of activated carbon with high density and large pore volume.

The preparation of activated carbons can be carried out in two stages. The first stage of the production process is carbonization, where the precursor material is subjected to a heat treatment in an inert atmosphere (usually nitrogen) at temperatures below 1073 K. This treatment seeks to eliminate the volatile matter content of the precursor, decrease its density, and increase the carbon content, generating the initial porosity of the carbonized. In this stage there is a degradation of the lignocellulosic material due to the carbonization and aromatization of the carbon skeleton, giving rise to the initial porous structure. However, during the carbonization process, some of the pores in the resulting carbon are partially filled or blocked with tars, thus requiring an activation step to improve the textural characteristics. The second stage of the process is activation, whose objective is to transform the carbonized into a highly adsorbent material due to the increase and widening of its internal porosity.

13.3.3 Activation with Metallic Salts

Chemical activation using various agents is used to modify the characteristics of activated carbons because they act as dehydrating agents to inhibit tar formation during pyrolytic decomposition (Marsh and Rodríguez-Reinoso 2006; Molina-Sabio and Rodríguez-Reinoso 2004). Previous studies have shown the benefits of adding metal salts to catalyze the coal gasification reaction ($C - CO_2$ y $C - H_2O$), leading to materials with a broader pore size distribution (Gryglewicz and Lorenc-Grabowska 2004; Juárez-Galán et al. 2009; Molina-Sabio et al. 1994), which favor the adsorption process.

Liu et al. (2009) evaluated the catalytic effect on the degradation of cellulose and hemicellulose in corn stubble of several metallic salts among which are $MgCl_2$ and $CaCl_2$, showing a slight positive effect dissolving the hemicellulose fraction. During the carbonization of the impregnated precursor, the conversion of $CaCl_2$ is shown in the following equations (Mondal et al. 2007):

$$CaCl_{2(s)} + CO_{2(g)} + H_2O_{(l)} \leftrightharpoons CaCO_{3(s)} + 2HCl_{(g)} \tag{13.1}$$

$$CaCO_{3(s)} + C_{(s)} \leftrightharpoons CaO_{(s)} + 2CO_{(g)} \tag{13.2}$$

$$CaO_{(s)} + CO_{(g)} \rightarrow Ca_{(g)} + CO_{2(g)} \tag{13.3}$$

As the impregnated precursor is heated within the reactor in the absence of oxygen $CaCO_3$ is first produced, which is then converted to CaO by the carbon attached to the activated carbon. This CaO can form a layer on the surface of activated carbon. Rufford et al. (2010) performed the thermogravimetric analysis (TGA) of ground coffee treated with $MgCl_2$, the decomposition profile showed that the loss of water molecules ($MgCl_2.6H_2O$) that occurs in multiple steps dominates the TGA curve at temperatures below 200 °C. Between 210 °C and 510 °C there are several weight loss steps including $MgCl_2.6H_2O$ dehydration to $MgCl_2$, anhydrous (~ 300 °C) and gasification of the carbon precursor. At temperatures above 500 °C, $MgCl_2$ decomposes directly to MgO leaving MgO particles within the carbon matrix.

During the carbonization of the precursor impregnated with $MgCl_2$ the conversion occurs as shown in the following equations (Huang et al. 2011; Kirsh et al. 1987; Rongti et al. 2002):

$$MgCl_2 \cdot nH_2O_{(s)} \overset{203^\circ C}{\rightarrow} MgCl_2 \cdot (x-y)H_2O_{(s)} + yH_2O_{(l)} \tag{13.4}$$

$$MgCl_2 \cdot H_2O_{(s)} \overset{235^\circ C}{\rightarrow} Mg(OH)Cl + HCl_{(g)} \tag{13.5}$$

$$Mg(OH)Cl \overset{415^\circ C}{\rightarrow} MgO_{(s)} + HCl_{(g)} \tag{13.6}$$

$$MgO_{(s)} + C_{(s)} \rightarrow Mg_{(g)} + CO_{(g)} \tag{13.7}$$

$$MgO_{(s)} + CO_{(g)} \rightarrow Mg_{(g)} + CO_{2(g)} \tag{13.8}$$

The following indirect reaction can also occur with both salts:

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \tag{13.9}$$

Activation with dehydrating metals salts such as $CaCl_2$ and $MgCl_2$ have been less studied compared to $ZnCl_2$. However, some works have been done in which these

Table 13.4 Activated carbons from various biomass precursors using different activation conditions

Biomass precursor	Activating (concentration)/relation (AA:P)	Activation temperature (time)	Surface texture properties	Ref.
Rice husk	$CaCl_2$ (0–2.5% w/w)/1 L: 100 g	873 K (4 h)	109–173[a]	Mondal et al. (2007)
Olive stone	$CaCl_2$ (7% w)/NR	1097 K (4 h) 1023 K (12 h) 1073 K (6 h)	656[a]; 0.91[b]; 0.27[c]; 0.64[d] 669[a]; 1.22[b]; 0.28[c]; 0.94[d] 670[a]; 1.39[b]; 0.27[c]; 1.12[d]	Juárez-Galán et al. (2009)
Waste coffee grounds	$MgCl_2$ (NR)/1:1 mass ratio	1173 K (1 h)	123[a] 0.21[b] 0.01[c] 0.2[d]	Rufford et al. (2010)
Carnauba palm leaves/macauba seeds endocarp/pine nut shell	$CaCl_2$ (1 M)/0.1 L: 8 g	773 K (1 h)	265–431[a] 0.12–0.25[b] 0.082–0.12[c]	da Silva Lacerda et al. (2015)
Palm shell	$MgCl_2$ $CaCl_2$ (3, 5 y 7% w/v)/2 mL:1 g	773–1073 K (6 h)	20–501[a]; 0.02–0.29[b] 19–453[a]; 0.03–0.25[b]	Acevedo et al. (2017)

P precursor, *AA* activating agent, *NR* no reported
[a] BET surface ($m^2\ g^{-1}$)
[b] Pore volume ($cm^3\ g^{-1}$)
[c] Micropore volume ($cm^3\ g^{-1}$)
[d] Mesopore volume ($cm^3\ g^{-1}$)

agents are used in the production of activated carbon showing micro- and mesoporosity development.

Table 13.4 summarizes some of the main results found in the literature on the use of calcium and magnesium salts as activating agents in obtaining activated carbons using lignocellulosic precursors and their effect on their textural properties. The results show an increase in the area with the increase in the concentration of salt, which favors the formation of porosity. Other results show that the decrease in salt concentration and the increase in temperature favor the development of porosity in solids, as well as with these activating agents it is possible to obtain micro-mesoporous carbons. Therefore, the properties of adsorbents depend not only on the nature of the activating agent and its concentration, but also on the activation temperature.

These two parameters are then evaluated on a series of activated carbons obtained from African palm shell (*Elaeis guineensis*) as precursor lignocellulosic material, chemically modified by impregnation with metallic salts solution of $MgCl_2$ (ACM1,

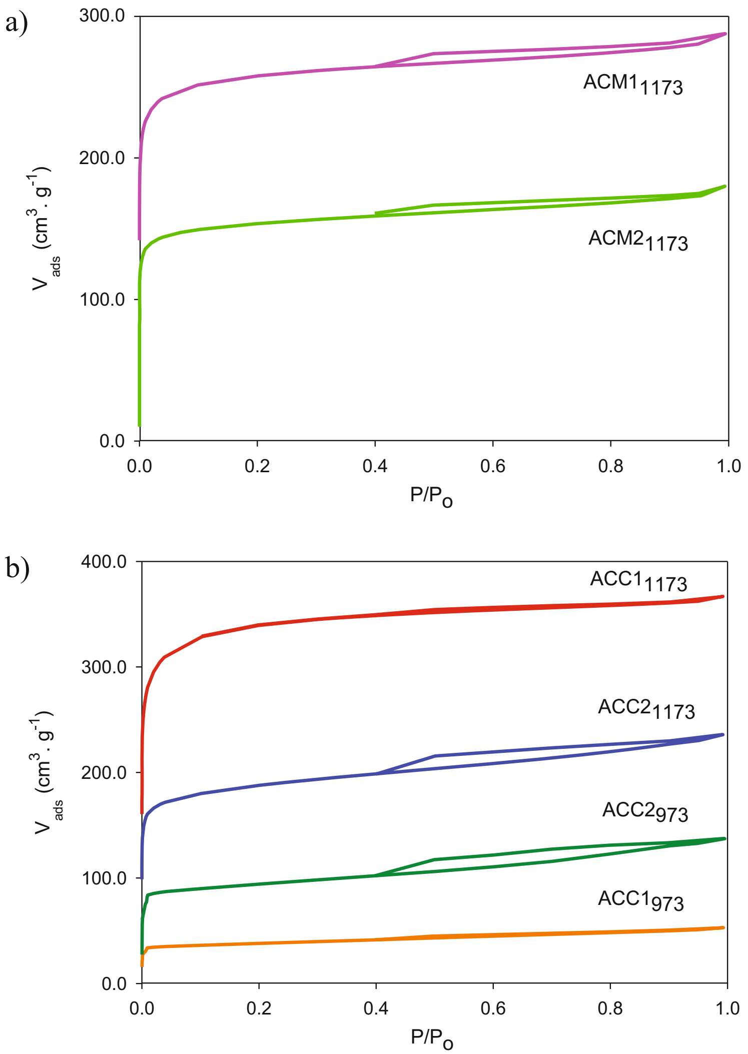


Fig. 13.2 Nitrogen adsorption isotherms of (**a**) ACM1 and ACM2; (**b**) ACC1, ACC2 at 77 K

ACM2) and $CaCl_2$ (ACC1, ACC2) at different concentrations (1% and 2% w/v) and carbonized in a carbon dioxide atmosphere at 973 K and 1173 K for 2 h.

Nitrogen adsorption isotherms for activated carbons are shown in Fig. 13.2. In Fig. 13.2a, the ACM1$_{1173}$ and ACM2$_{1173}$ carbons essentially exhibit type I adsorption isotherms, according to the IUPAC classification (Thommes et al. 2015), characteristic of microporous solids, due to the fact that the hysteresis loop formed in desorption is small, which is related to a low amount of mesopores, in this figure the isotherms of the ACM1$_{973}$ and ACM2$_{973}$, carbons were omitted, this because these samples presented a very low nitrogen adsorption and the isotherms were not clearly identified with any of the types according to the IUPAC classification, which suggests that the collapse or destruction of the porous structure occurred during the production process under the conditions used (Moreno-Marenco et al. 2019). Conversely, the samples $ACC2_{973}$ and $ACC2_{1173}$ (Fig. 13.2b) show a behavior composed of the type I and II isotherms, showing a more pronounced adsorption at low relative pressures ($P/P_o < 0.1$) corresponding to the filling of the micropores, while at higher pressures ($P/P_o > 0.2$) there is an increase in the slope corresponding to capillary condensation, accompanied by an H4 type hysteresis loop associated with solids whose pore size distribution is mainly in the range of micropores (Rouquerol et al. 2014a), although it is also characteristic of micro-mesoporous carbons (Thommes et al. 2015).

It should be noted that the coals obtained at 1173 K exhibit greater nitrogen adsorption, which suggests that a greater porosity develops at this temperature than at 973 K. These results are attributed to the strong dependence of the gasification reaction ($C\text{-}CO_2$) with temperature, as shown by Guo et al. (Guo and Lua 2002) in the characterization of an activated carbon prepared from palm kernel by activation with CO_2. Regarding the effect of the concentration of the activator, two behaviors are observed. On the one hand, in the series at 973 K, the increase in calcium concentration generates an increase in the nitrogen adsorption capacity, while in the 1173 K series, the increase in concentration, independent of salt, produces a decrease in the nitrogen adsorption capacity of solids and their textural characteristics.

The textural characteristics obtained from the adsorption isotherms of N_2 at 77 K (Table 13.5) from the BET and Dubinin-Radushkevich models show solids with BET surface areas (S_{BET}) between 2 and 392 $m^2\ g^{-1}$, volumes of micropores (V_o) between 0.001 and 0.14 $cm^3\ g^{-1}$, and mesopore volumes (V_{meso}) between 0.005 and 0.073 $cm^3\ g^{-1}$ for the samples activated at 973 K. Surface areas between 608 and 1370 $m^2\ g^{-1}$, and micropore volumes between 0.24 and 0.54 $cm^3\ g^{-1}$and mesopore volumes (V_{meso}) between 0.028 and 0.065 $cm^3\ g^{-1}$ for the samples activated at 1173 K.

Decrease in the concentration of salts of impregnation reduces the capacity of nitrogen adsorption and therefore the textural parameters of activated carbons at 973 K. Considering that the catalytic action of the activating agent increases with

Table 13.5 Textural parameters of activated carbons from N_2 isotherms at 77 K

	BET	DR		
Activated carbon	S_{BET} ($m^2\ g^{-1}$)	$V_{T\ 0.99}$ ($cm^3\ g^{-1}$)	V_o ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)
$ACM1_{973}$	2	0.006	0.001	0.005
$ACM2_{973}$	4	0.010	0.001	0.009
$ACC1_{973}$	156	0.082	0.056	0.026
$ACC2_{973}$	392	0.21	0.14	0.073
$ACM1_{1173}$	1087	0.44	0.41	0.030
$ACM2_{1173}$	608	0.28	0.24	0.038
$ACC1_{1173}$	1370	0.57	0.54	0.028
$ACC2_{1173}$	791	0.36	0.30	0.065

concentration, so there is a greater removal of carbon atoms from the precursor matrix, which favors the development of porosity in the material (Juárez-Galán et al. 2009; Silvestre-Albero et al. 2012; Vargas Delgadillo 2013). While at 1173 K there is an opposite effect with respect to the concentration of activating agent evidencing the decrease in the area and volume of micropore with the increase in the concentration of activating agent, although the volumes of mesoporous increase for $ACC2_{1173}$ and remain almost constant for $ACM2_{1173}$ (Fig. 13.3) suggesting that the increase in calcium concentration causes a greater removal of carbon atoms from the matrix which generates a wider porosity at the expense of microporosity and therefore the decrease of the surface area.

Also, it can be observed that the increase in the activation temperature brings an increase in the microporosity and therefore in the surface area, because gasification process is favored (Lua and Yang 2004); therefore, an increase in temperature is required to develop a highly porous structure. Regarding the nature of the impregnating salt (Fig. 13.3), it is evident that calcium activation develops mainly microporous carbons with a contribution of mesoporosity almost independently of the activation temperature, while activation with magnesium develops mainly mesoporous materials at 973 K.

In relation to the chemical characteristics of the activated carbons (Table 13.6) obtained at 973 K, a weakly basic character is presented, close to neutrality for all samples except the sample activated by magnesium $ACM1_{973}$, which has an acid

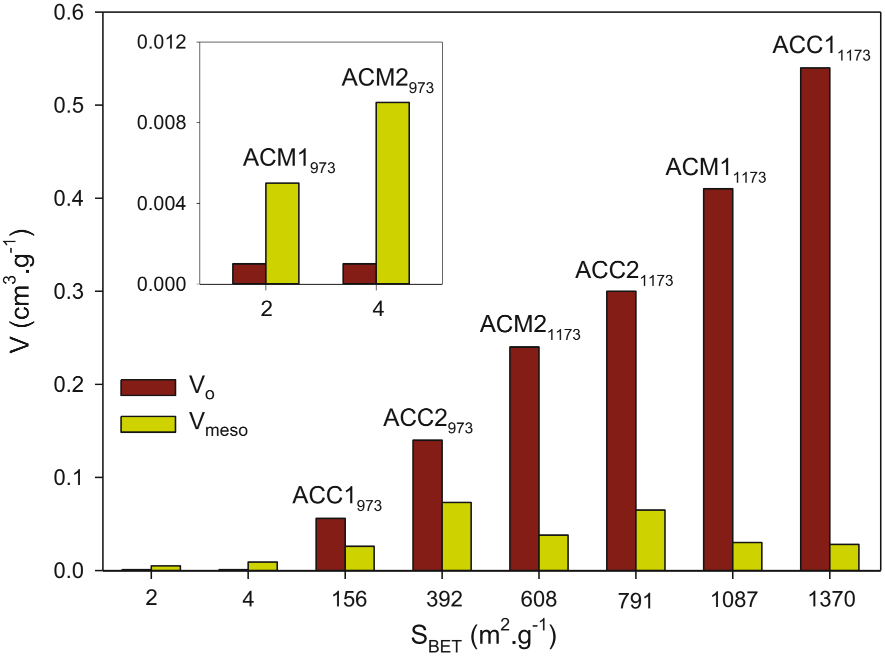


Fig. 13.3 Relation between superficial area and pore volume

Table 13.6 Chemical characterization of activated carbons

Activated carbon	Basic groups (mmol g^{-1})	Acid groups (mmol g^{-1})	Oxygen groups (mmol g^{-1})	pH_{PZC}
$ACM1_{973}$	0.014	0.46	0.48	5.6
$ACM2_{973}$	0.045	0.050	0.095	7.3
$ACC1_{973}$	0.12	0.18	0.30	7.4
$ACC2_{973}$	0.13	0.20	0.32	7.2
$ACM1_{1173}$	0.46	0.28	0.74	8.8
$ACM2_{1173}$	0.59	0.20	0.79	9.5
$ACC1_{1173}$	0.61	0.40	1.0	9.1
$ACC2_{1173}$	0.62	0.24	0.86	9.2

character, related to the presence of carboxylic acids, anhydrides, lactones, phenols, and carbonyl compounds (Boehm 2002). While at 1173 K the carbons have a greater basic character, which is related to the presence of oxygenated groups with structures such as pyrone and chromene (Boehm 2008), as well as enriched regions of delocalized π electrons in the graphene layers that act as bases of Lewis (Moreno-Castilla 2004), these being the major contributors to the basicity of activated carbon (Thommes et al. 2012). It should also take in mind that heat treatment eliminates surface functional groups that are susceptible to decomposition with temperature, such as carboxylic acids from 373 to 673 K, lactones and anhydrides from 463 to 900 K, phenols from 873 to 973 K, and at higher temperatures carbonyls, phenols, ethers, and some quinones (Figueiredo et al. 1999), which increase the enriched regions of electrons in the graphene layers that act as Lewis bases (Moreno-Castilla 2004). However, there is also an increase in the content of acid groups, which can be attributed to the reaction of free radicals formed in the reduction of oxygenated groups and carbon dioxide during thermal treatment (da Silva et al. 2017).

13.4 Parabens Adsorption on Activated Carbon from African Palm Shell

The harmful nature of emerging pollutants such as parabens, as well as the different elimination processes was presented previously, with adsorption on activated carbon being one of the most important. Adsorption is defined as a physicochemical process by which adsorbate molecules in the gas or liquid phase are concentrated on an adsorbent surface, generally solid. It arises as a result of decompensated molecular forces present on each solid surface, which are satisfied by the attraction and retention of those molecules. Depending on the affinity between the adsorbate-adsorbent and the strength of the interactions established between them, the process is classified as physisorption and chemisorption. When the interactions are weak, the adsorbate binds to the surface mainly by Van der Waals and London forces, this type of adsorption is nonspecific and occurs in any adsorbate-adsorbent system. Conversely, when the interactions are strong, the exchange of electrons is generated between the adsorbate molecules and the adsorbent surface, that is, it is carried out between the functional groups of the adsorbent and the pollutant (Moreno-Castilla 2004).

Adsorption isotherms are an experimental tool to diagnose the nature of adsorption processes and evaluate the adsorption capacity of activated carbons with a particular molecule. Below are the adsorption isotherms of the AC-PB systems studied (Figs. 13.4 and 13.5), which were measured by varying the initial concentration of each of the parabens in a range between 20 and 200 mg L^{-1} at 291 K. The adsorption isotherms obtained for the AC-MePB systems are shown in Fig. 13.4 and for the AC-PrPB systems they are shown in Fig. 13.5. In the curves obtained with the 1173 series carbons (Figs. 13.4b and 13.5b) it is observed that the adsorption of PBs increased abruptly, while with the carbons of the 973 series (Figs. 13.4a and 13.5a) the increases were moderate. This behavior is associated with the diffusion of PBs molecules to the micropores through the larger pores (meso- and macropores) and once the micro- and mesopores have been occupied, the possibility of the PB molecule to find an active site in which it can be retained (Sotelo et al. 2012). By increasing the concentration at equilibrium, progressive AC saturation occurs, which is evidenced as a plateau that is less pronounced in the 973 series.

The experimental data obtained from the adsorption isotherms were adjusted to the mathematical models of Langmuir and Freundlich. The Langmuir model assumes that the surface of the adsorbent is energetically homogeneous and that adsorption is a chemical process in which the coverage of the adsorbent surface occurs by formation of a monolayer, while the Freundlich model is appropriate to describe the adsorption of heterogeneous systems, with the possibility of intermolecular interactions between adsorbate molecules, regardless of the saturation of the adsorption surface and, therefore, indicates the appearance of physisorption (Shahbeig et al. 2013).

The resulting parameters of the models are summarized in Table 13.7. When comparing the fit to the models with all the systems (AC-PB) it is observed that they present a better fit to the Langmuir model, therefore considering the principles of this model suggests the formation of homogeneous energetic interactions with the basal planes of activated carbons, obtaining adsorption capacities (Q_{mL}) of 199.6 mg g^{-1} and 247.1 mg g^{-1} for MePB and PrPB, respectively, in both cases with carbon $\mathrm{ACC1}_{1173}$. Conversely, the Langmuir adsorption coefficient (K_{L}) is related to the apparent adsorption energy, showing a lower favorability for the adsorption of MePB, probably due to the weak interaction between these molecules and the surface of the activated carbon. The Freundlich model was chosen to estimate the adsorption intensity (n_{F}) of the adsorbate on the adsorbent surface and the favorability of the process. The values obtained ($n_{\mathrm{F}} > 2$) indicate that both, MePB and PrPB are adsorbed on the activated carbons, but it is particularly favorable for $\mathrm{ACC1}_{1173}$ and $\mathrm{ACM1}_{1173}$ with PrPB, which is related to the increase in affinity for the possible mechanisms heterogeneous which leads to a strong interaction between these carbons and PrPB. Similar results have been reported in the methylparaben and propylparaben adsorption (de los Ángeles Bernal-Romero et al. 2019; Mashile et al. 2020).

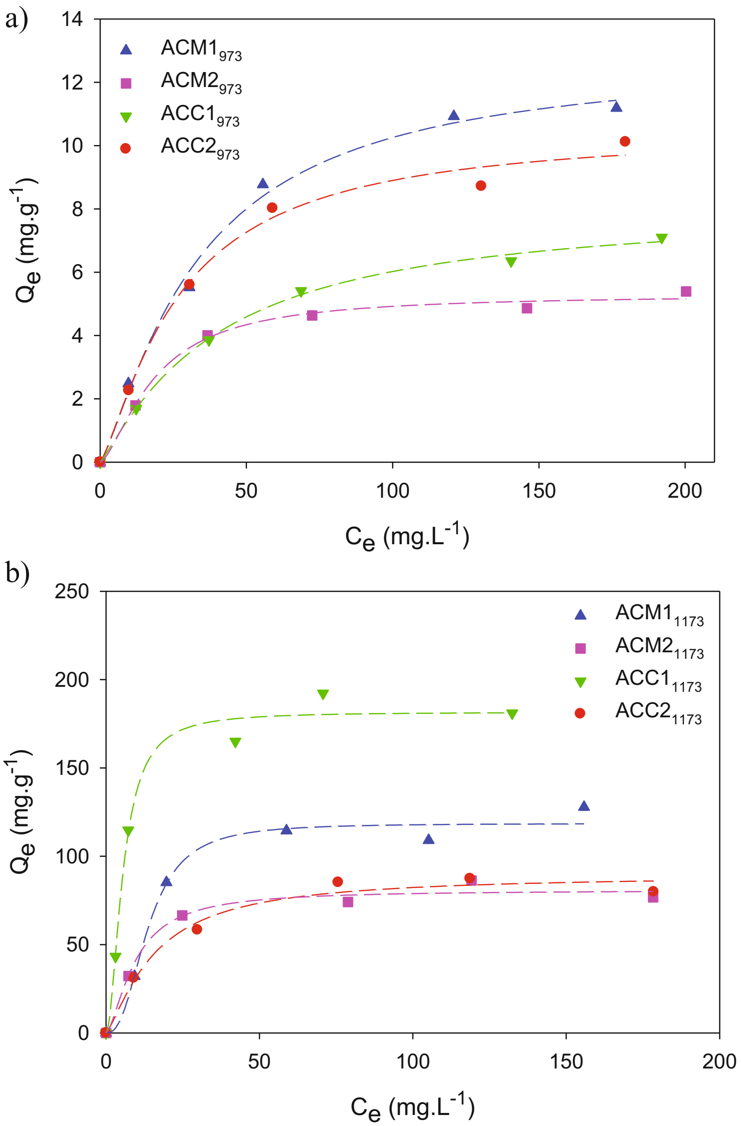


Fig. 13.4 Methylparaben adsorption isotherms of activated carbons obtained at (**a**) 973 K and (**b**) 1173 K

The adsorption process of organic contaminants is related to the porous structure of activated carbon because typically micropores are considered active sites of adsorption. In Fig. 13.6 the relationship between the adsorption capacity and the micropore volume of the activated carbons is shown, where the increase in the amount of paraben adsorbed is observed as the micropore volume increases. This

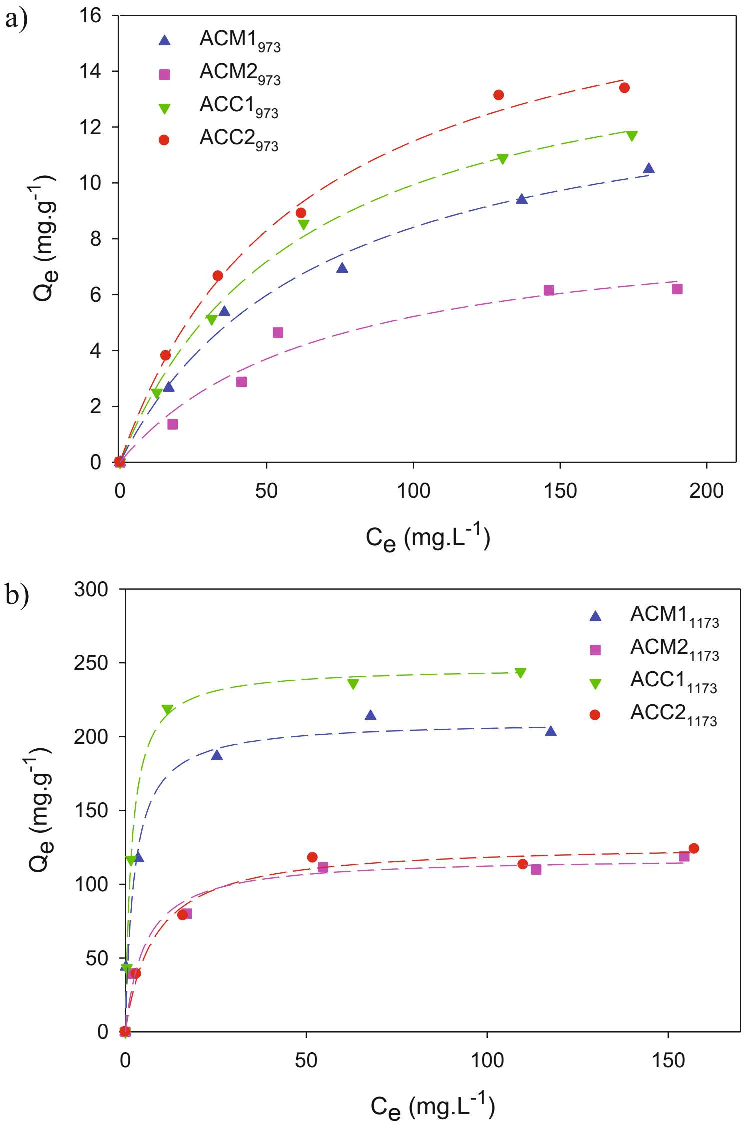


Fig. 13.5 Propylparaben adsorption isotherms of activated carbons obtained at (**a**) 973 K and (**b**) 1173 K

indicates that the microporous structure of activated carbons favors adsorption, due to the improved adsorption potential produced by the effect of the proximity of the adjacent pore walls (Hadi Madani et al. 2016) that enables dispersive π–π interactions with parabens. Likewise, it is important to mention that the adsorption capacity will depend on the accessibility of paraben to the internal surface of the

Table 13.7 Isotherm constants models for adsorption of MePB onto activated carbons

Activated carbon	Langmuir $q_e = \frac{Q_{mL} K_L C_e}{1+K_L C_e}$ Q_{mL} (mg g^{-1})	K_L (L mg^{-1})	r^2	Freundlich $q_e = K_F C_e^{1/n\mathrm{F}}$ K_F (mg g^{-1}) (L mg^{-1})$^{n-1}$	n_F	r^2
MePB						
$ACM1_{973}$	14.4	0.023	0.99	1.37	2.4	0.96
$ACM2_{973}$	5.91	0.045	0.99	1.23	3.5	0.95
$ACC1_{973}$	8.7	0.021	1.00	0.81	2.4	0.98
$ACC2_{973}$	11.7	0.030	0.99	1.42	2.6	0.96
$ACM1_{1173}$	140.7	0.050	0.90	27.3	3.2	0.91
$ACM2_{1173}$	107.4	0.070	0.99	27.9	4.6	0.93
$ACC1_{1173}$	199.6	0.14	0.98	57.3	3.9	0.92
$ACC2_{1173}$	96.2	0.060	0.96	22.3	3.7	0.93
PrPB						
$ACM1_{973}$	14.2	0.015	0.99	0.82	2.0	0.99
$ACM2_{973}$	8.8	0.014	0.97	0.52	2.1	0.94
$ACC1_{973}$	16.1	0.016	1.00	0.98	2.0	0.98
$ACC2_{973}$	18.7	0.016	1.00	1.20	2.1	0.99
$ACM1_{1173}$	202.6	0.463	0.97	113.6	7.3	0.91
$ACM2_{1173}$	118.5	0.181	0.98	41.0	4.6	0.97
$ACC1_{1173}$	247.1	0.572	1.00	120.4	6.1	0.93
$ACC2_{1173}$	127.6	0.124	0.99	39.0	4.2	0.96

adsorbent and considering that MePB and PrPB have molecular dimensions of 0.406 and 0.754 nm^2 it is clear that both molecules can enter the micropores.

Surface chemistry strongly influences hydrophobicity, electronic density of graphene layers, and adsorbate-adsorbent interaction type. Such interactions can be specific and nonspecific, the former is predominant in systems where the adsorbate and the adsorbent have functional groups capable of interacting with each other, while the nonspecific ones are related to hydrophobic interactions between the graphene layers of activated carbon. and the parts adsorbate apolar (Moreno-Castilla 2004). So, the overall adsorption process of both MePB as PrPB is given by the contribution of the microporosity developed in the carbons during the activation. So the overall adsorption process of both MePB as PrPB is given by the contribution of the microporosity developed in the carbons during the activation treatments, as well as by the establishment of specific interactions. Depending on the characteristics of each system, both can contribute as observed for $ACC1_{1173}$ (Fig. 13.6a, b) or one of them prevails as in the case of $ACM1_{973}$ (Fig. 13.6a), where MePB adsorption is related to the higher content of oxygenated groups rather than microporosity which in this solid is very poorly developed, but there is a greater adsorption compared to the other carbons of the 973 series.

The oxygenated groups present on the surface of activated carbons can be acidic or basic in nature. As mentioned above the acid character is associated with the

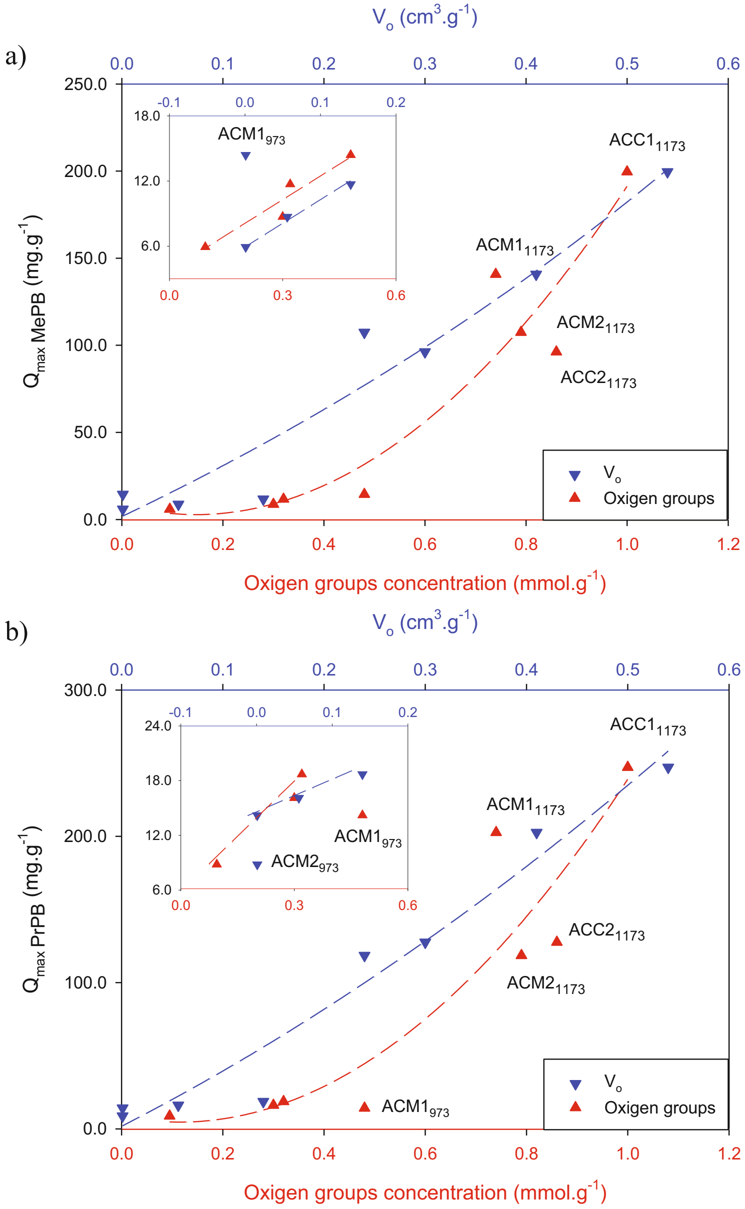


Fig. 13.6 Relation between oxygen groups concentration and micropore volume with adsorption capacity of (**a**) MePB and (**b**) PrPB

presence of carboxylic acids, lactones, phenols, and anhydrides, while the basic character is associated with the pyrone, chromene, ether, quinone, and carbonyl groups. Given that African palm shell is constituted by lignin, cellulose, and hemicellulose, being polymers abundant in phenolic groups it is expected that the activated carbons obtained have a high content in this group at least in the activated carbons at 973 K, where they have not been seen affected by its thermal stability. Conversely, the thermal treatment at high temperature favored the increase in the total basicity of the activated carbons due to the formation of π electrons during the rearrangement of the graphene layers.

In Fig. 13.7 the relationship between acid and basic groups concentration with adsorption capacity of PBs is presented. From these results it is evident that the surface chemistry plays a relevant role in the adsorption process and in the interactions established between parabens and activated carbons, as evidenced by $ACC1_{1173}$ and $ACM1_{1173}$. However, it is noteworthy that with $ACM1_{973}$ it does not manifest itself with high adsorption when compared to $ACC1_{1173}$ which has a lower concentration of acid groups, because the process with $ACM1_{973}$ is also conditioned by textural characteristics associated with the decrease in surface area that prevents a better organization of the molecules that bind to the surface groups. Within the scientific literature related to the adsorption of polluting compounds, it is suggested that there are two types of interactions between adsorbate and activated carbon: electrostatic and dispersive. Dispersive interactions are described by three mechanisms: hydrogen bond formation, π–π dispersion interaction, both proposed by Coughlin and Ezra (1968), and donor–acceptor complex formation, proposed by Mattson et al. (1969). It is considered that of these three mechanisms, the last two take place in the micropores. It is often assumed that there is competition between the adsorption of solutes at the smallest micropores and at active sites located at the largest micropores. In the smallest micropores, dispersive interactions are predominant, mainly due to the attraction between the π orbitals in the basal planes of the carbon and the electron density in the aromatic rings of the organic pollutant (π–π interactions). However, in the larger micropores, surface functional groups can be found that participate in the formation of specific electrostatic interactions when the molecule and the functional groups on the surface of activated carbon are dissociated (Moreno-Castilla 2004; Podkościelny and Nieszporek 2011; Terzyk 2004).

Next, the properties of PBs will be considered as another determining aspect in the adsorption process. Figure 13.8 illustrates the variation in the adsorption capacity as a function of the type of PB. As previously evidenced, PrPB has a higher adsorption than MePB that correlates well with the increase in molecular weight. Traube's rule establishes the relationship between adsorption in aqueous solution and the increase in a homologous series that at the same time follows the same trend with the increase in the partition coefficient (Log K_{ow}), being a parameter related to the hydrophobicity of the PBs. This is because parabens can form hydrogen bonds with water molecules in solution, but as the size of the paraben molecule increases, its hydrophobicity increases, which generates the repellency of water, but favors interactions of dispersive type between the π electrons of the aromatic ring of paraben and those of the aromatic structure of activated carbon (Hamdaoui and Naffrechoux 2007). These results are in agreement with other studies of paraben adsorption on various adsorbents (Chen et al. 2017; Chin 2013; Chin et al. 2010). Conversely, the Lundelius rule establishes an inverse dependence between the

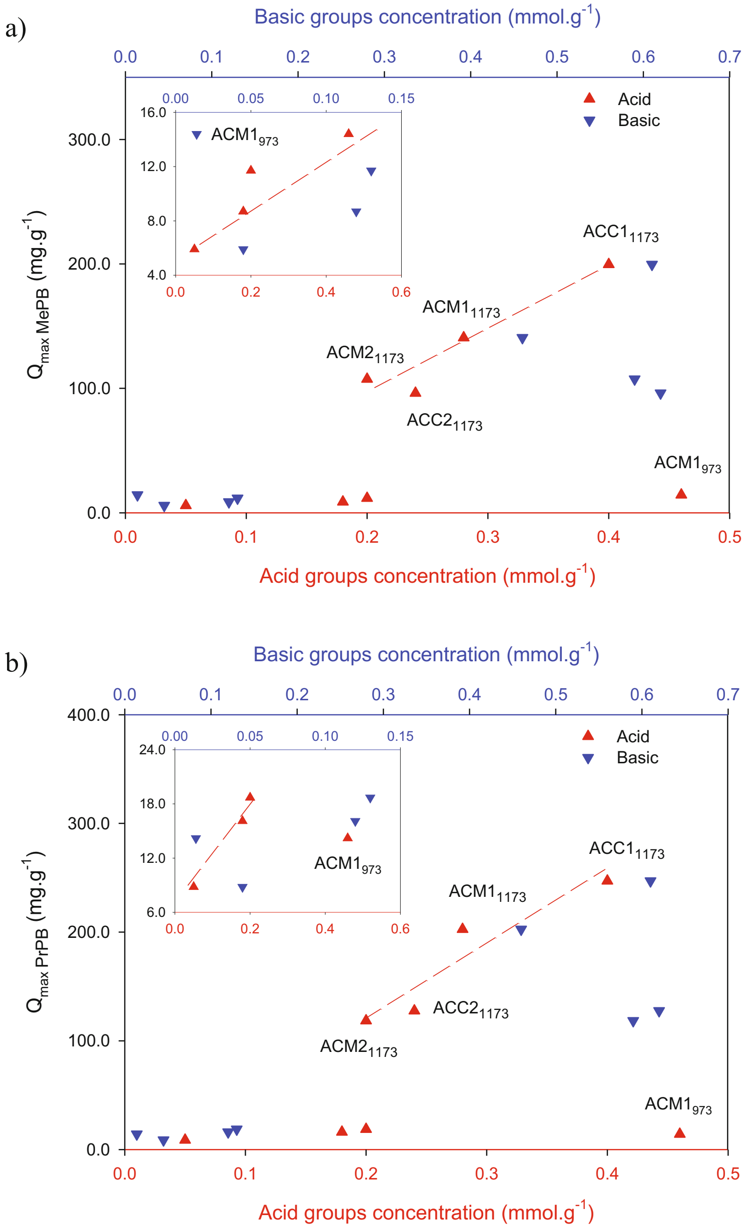


Fig. 13.7 Relation between acid and basic groups concentration with adsorption capacity of (**a**) MePB and (**b**) PrPB

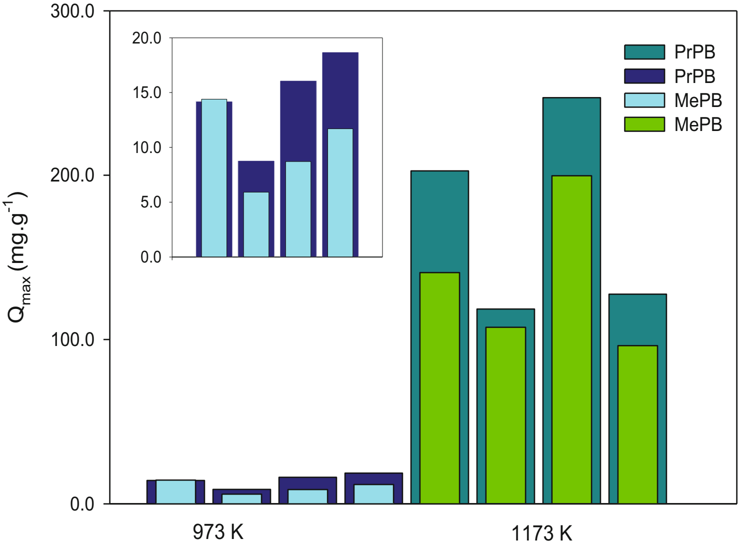


Fig. 13.8 Comparison between MePB and PrPB adsorption capacity of activated carbons obtained at different temperatures

degree of adsorption of an adsorbate and its solubility in the solvent. This can be explained if it is considered that the physical bond between paraben and water must be broken to achieve adsorption on activated carbon and the greater the solubility of a compound in water, the stronger the bond formed between them. Solubility decreases with increasing aliphatic chain length in parabens, being lower for PrPB with 3 carbon atoms (500 mg L^{-1}) and higher for MePB with one carbon atom (2500 mg L^{-1}), so the AC–PrPB interaction will be stronger than the water–PrPB interaction in all activated carbons, which indicates that adsorption will also be induced by the low affinity of PrPB for the solvent and explains the lower capacity of adsorption for MePB.

13.5 Conclusions

In this research, the main results were presented that show the potential use of the African palm kernel to obtain activated carbons chemically modified with calcium and magnesium salts for the adsorption of emerging pollutants in water such as parabens, which could also contribute to the reduction in the disposal of this by-product generated in the obtaining of palm oil.

The differences in the textural characteristics found among the activated carbons show that the concentration of activating agent and the activation temperature are determining factor in the preparation of the activated carbons, because the modifications on the surface in the samples were greater with the increase in temperature and decrease in the concentration of impregnating agent, particularly in the series activated at 1173 K. This means that for a low salt concentration, a high temperature favors the gasification process, which is more catalyzed by the presence of calcium. While at high salt concentration, the gasification process is favored when the temperature decrease represents a factor that contributes to the formation of a porous structure. Similarly, it was evidenced that the greatest effect on adsorption is related to the concentration of the impregnating salt during preparation, rather than to the nature of the metal salt. So, the selection of the synthesis conditions will continue to be the most important factor to tailoring the final microstructure, textural properties, adsorption capacity, and surface chemistry of the produced carbons.

Although it is noteworthy that this greater interaction and therefore greater adsorption is given by the contribution of surface chemistry and microporosity developed in the carbons due to the effect of metal salts and thermal treatments, the greater adsorption of PrPB respect to MePB is correlated with the increase of hydrophobicity (log K_{ow}), molecular weight, and decrease in water solubility of PrPB, where dispersive-type interactions are favored between the π electrons of the aromatic ring of paraben and those of the aromatic structure of activated carbon.

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