Review on Activated Carbons by Chemical Activation with FeCl$_3$

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Abstract: This study reviews the most relevant results on the synthesis, characterization, and applications of activated carbons obtained by novel chemical activation with FeCl$_3$. The text includes a description of the activation mechanism, which compromises three different stages: (1) intense de-polymerization of the carbon precursor (up to 300 °C), (2) devolatilization and formation of the inner porosity (between 300 and 700 °C), and (3) dehydrogenation of the fixed carbon structure (>700 °C). Among the different synthesis conditions, the activation temperature, and, to a lesser extent, the impregnation ratio (i.e., mass ratio of FeCl$_3$ to carbon precursor), are the most relevant parameters controlling the final properties of the resulting activated carbons. The characteristics of the carbons in terms of porosity, surface chemistry, and magnetic properties are analyzed in detail. These carbons showed a well-developed porous texture mainly in the micropore size range, an acidic surface with an abundance of oxygen surface groups, and a superparamagnetic character due to the presence of well-distributed iron species. These properties convert these carbons into promising candidates for different applications. They are widely analyzed as adsorbents in aqueous phase applications due to their porosity, surface acidity, and ease of separation. The presence of stable and well-distributed iron species on the carbons’ surface makes them promising catalysts for different applications. Finally, the presence of iron compounds has been shown to improve the graphitization degree and conductivity of the carbons; these are consequently being analyzed in energy storage applications.

Keywords: activated carbons; chemical activation; iron chloride; adsorption

1. Activated Carbons

Activated carbons are amorphous carbon materials, mainly characterized by a well-developed porous texture [1]. They are widely used in many different applications including (1) adsorption, both in gas and liquid phases [2–4], (2) catalysis, mostly as supports of the active phases [5–9] but also as bulk catalysts [10–13], and (3) in electrochemical or energy storage applications for use as supercapacitors [14–18]. There is currently a reborn interest in research of the synthesis, characterization, and applications of activated carbons, as shown by recent reviews and the high number of publications on this topic that can be found in the technical literature [19–24]. Activated carbons can be synthesized from any carbonaceous precursor, such as coal [25–27], discarded tires [28–30], lignin [31–33], or biomass waste [34–37], among others, preferably with low inorganic content. Nowadays, most of the research is focused in the synthesis of activated carbons from biomass waste due to some unquestionable advantages: (1) this process results in the revalorization of waste, (2) the synthesized activated carbons have a lower cost since they are produced from low economic value precursors, (3) they are obtained...
from renewable resources, and (4) after their lifetime, the combustion of these activated carbons does not increase CO₂ accumulation in the atmosphere because this CO₂ has been previously captured during plant growth [38,39].

There are two different procedures for synthesizing activated carbons, namely physical activation and chemical activation (Figure 1) [1,22]. The former consists of two different thermal steps. The first one is a pyrolysis or carbonization of the carbonaceous precursor at high temperatures, usually in the range of 700–900 °C, under inert an atmosphere to avoid combustion on the carbonaceous matter. In this step, heteroatoms are removed and volatiles are released, resulting in chars with high carbon content (the increase of the carbonization temperature increases carbon content) but with still low porosity development. The second step of the physical activation process is gasification. This consists of a selective removal of the most reactive carbon atoms by controlled gasification reactions that generate the characteristic porosity of the activated carbons. The gasification temperature depends on the gasification agent used, usually water vapor, CO₂, or O₂ (air). Temperatures in the range of around 700–900 °C are used with water vapor or CO₂ gasification. In contrast, when using pure O₂ or air, the gasification temperatures should be much lower (around 300–450 °C) due to the much higher reactivity of O₂ than CO₂ and water vapor. Moreover, the use of O₂ hinders the control of the gasification and thus porosity development, due to the high reactivity and exothermicity of the reaction with O₂.

![Figure 1. Synthesis of activated carbons (adapted from [22]).](image)

The second procedure for synthesizing activated carbons is chemical activation. This process has only one thermal step, although it indeed consists of three different synthesis stages (Figure 1). The first is the impregnation of the precursor with the activating agent. Different activating agents have been traditionally studied in the literature, such as ZnCl₂, H₃PO₄, NaOH, or KOH, among others. FeCl₃ activation, the subject of this review, has received increasing attention in recent years. The impregnation procedure can be accomplished by different techniques. For example, some authors use an aqueous solution of the activating agent put in contact with the carbonaceous precursor. However, other studies perform a direct and simpler physical mixing of the precursor and the activating agent. Probably one of the most influential synthesis parameters with respect to the texture characteristics of the final activated carbon is the impregnation ratio or mass ratio between the activating agent and the carbonaceous precursor. Impregnation ratios between 0.5 and 5 are most commonly found in the literature. After impregnation, the second step of the chemical activation procedure is thermal treatment in an inert atmosphere at different temperatures depending on the chosen activating agent. The usual temperatures employed depend on the activating agent and are summarized in Figure 1.
During this step, reactions of de-polymerization, dehydration, and condensation take place, resulting in higher carbon yields than in physical activation due to the restriction in the formation of tars and volatiles. Finally, the last stage involves washing to remove the remaining activating agents and reaction byproducts that occlude the newly formed porosity, and drying. In the case of NaOH or KOH activation of “soft” carbon precursors (i.e., biomass waste), an initial carbonization step is usually needed, because otherwise, these strong bases can dissolve the organic matter of the precursor, making the subsequent activation impossible.

In this review, the activation mechanism, synthesis conditions, characterization, and applications of activated carbons obtained by chemical activation with FeCl$_3$ will be summarized and analyzed. The use of FeCl$_3$ has some advantages with respect to other more traditional chemical activation agents. For example, it has a lower cost and is more environmentally friendly. Other traditional activating agents, such as KOH, NaOH, or H$_3$PO$_4$, are very strong bases and acids. The handling of these materials requires stricter security measures and materials more resistant to corrosion, increasing the cost of the synthesis process. In the case of ZnCl$_2$, Zn ions and derived oxides are toxic \cite{40,41}, and therefore should be submitted to stricter discharge regulations. All these facts mean that FeCl$_3$ activation can be considered as low cost and environmentally benign in comparison to those traditional activating agents. Another interesting characteristic of this activation procedure is that it can produce magnetic activated carbons \cite{42,43}.

2. Activation Mechanism

Xu et al. \cite{44,45} recently analyzed the mechanism of pore formation in the activation of waste cotton with iron chloride. They concluded that the activation process consists of several subsequent stages, as schematized in Figure 2. The presence of iron chloride reduces the temperature of the cellulose hydrolysis and causes an intense de-polymerization reaction with the release of a high amount of low molecular weight hydrocarbons. At pyrolysis temperatures between 200 and 300 °C, iron chlorides break the glycoside bonds of cellulose, and H$_2$O molecules are simultaneously released from the hydrated salt, resulting in the formation of glucose monosaccharides. In this temperature range, hydrated iron chloride salt decomposes into amorphous FeOOH through the following reactions \cite{46}:

\[
\text{FeCl}_3 + 2\text{H}_2\text{O} \rightarrow \text{FeOCl} \cdot \text{H}_2\text{O} + 2\text{HCl} \quad (1)
\]

\[
\text{FeOCl} \cdot \text{H}_2\text{O} \rightarrow \text{FeOOH} + \text{HCl} \quad (2)
\]

The second stage occurs at pyrolysis temperatures between 330 and 700 °C. As the activation temperature increases, glucose molecules suffer successive ring opening, dehydration, and cyclization into 5-hydroxymethylfurfural, which after decarbonylation is transformed into furfural \cite{47}. With the increase of the temperature, FeOOH is firstly decomposed into Fe$_2$O$_3$, which is subsequently reduced by the carbon surface to form Fe$_3$O$_4$ according to the following chemical reactions \cite{48}:

\[
2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (3)
\]

\[
3\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO} \quad (4)
\]

These iron oxides catalyze the generation of the microporosity on the carbon matrix \cite{49}. Besides, different hydrocarbons produced during pyrolysis are deposited on the Fe$_2$O$_3$ and Fe$_3$O$_4$ surfaces and form mesopores after the removal of the iron species in the acid washing step. A further increase of the activation temperature (>700 °C) resulted in an increase of the fixed carbon proportion of the solid while releasing volatile matter, water vapor, and carbon dioxide, as a consequence of the polymerization and polycondensation that occurred between furfural and 5-hydroxymethylfurfural \cite{50,51}. At these high temperatures iron species are reduced to zerovalent iron by the surface of the carbon surface (Equations (5)–(7)) \cite{52}:

\[
2\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Fe} + 3\text{CO}_2 \quad (5)
\]
Finally, crosslinking and structure reorganization with transformation of the iron species resulted in the formation of a highly porous activated carbon with highly stable Fe anchored on its surface. Figure 2 schematizes the main reaction occurring during decomposition (I–IV) and char-forming (V–VI) of waste cotton woven with FeCl$_3$. At low temperatures (>100 °C) iron chloride breaks the hydrogen bonds, reducing the polymerization degree of cellulose. Simultaneously, glycoside bonds were also broken by FeCl$_3$, generating monosaccharides and disaccharides [53]. Subsequently, as pyrolysis proceeds, (1) cellulose monomers suffer ring opening and chlorine anions (Cl$^-$) substitute hydrogen atoms, forming chlorine-banded esters (Figure 2, II), and (2) FeCl$_3$ catalyze decarbonylation and decarboxylation reactions, cracking organic acids and esters into short-chain chlorinated hydrocarbons and releasing CO$_2$ and CO (Figure 2, III) [53]. Conjugated olefins, which can be considered as a carbon precursor, are produced by dehydrochlorination reaction (Figure 2, IV).

Char formation can proceed through two alternative mechanisms. In the first, the Cl$^-$ of a carbon chain is easily incorporated to FeCl$_3$ due to its Lewis acid character, and produces FeCl$_4^-$ Later, carbenium ions are crosslinked with olefins or conjugated unsaturated structures to constitute long organic molecules and more complex carbon structures (Figure 2, V). FeCl$_3$, as Lewis acid, catalyzes the hydrogenation and cyclization of the long organic molecules, which constitute the onset of the char formation [54]. The second mechanism, FeCl$_3$ catalyzes the dechlorination of conjugated olefins by parallel isomerization, aromatization, and cyclization reactions, with the formation of an enriched carbon matrix through inhibition of the tar production (Figure 2, VI) [55].

$$Fe_3O_4 + 2C \rightarrow 3Fe + 2CO_2$$

$$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$$
3. Conditions of Chemical Activation with FeCl₃

As aforementioned, the synthesis procedure of activated carbons by FeCl₃ chemical activation shows three successive steps, namely, (1) impregnation, (2) thermal activation or pyrolysis, and (3) washing. Table 1 summarizes the most relevant activation conditions used for the synthesis of FeCl₃-activated carbons in terms of the technical conditions. Impregnation is the mixture of the carbonaceous precursor with FeCl₃, and it is usually performed by two different methods, in aqueous solution or by physical mixing between the carbon precursor and the iron chloride activating agent. In aqueous solution, the carbonaceous precursor is suspended under stirring in an aqueous solution of FeCl₃, controlling the mass impregnation ratio (R). This parameter is defined as the mass ratio of activating agent to carbon precursor. Usual impregnation mass ratio values are in the range of 0.5:1 up to 5:1. This procedure requires an additional drying step prior to pyrolysis to remove the water. The physical mixing impregnation procedure is simpler since it avoids the drying step, with a consequent cost reduction. This method consists of a mere mixing in the solid state of both the carbonaceous precursor and the iron chloride, in a specific impregnation ratio. In this case, it is advisable to perform a grinding of both materials to assure a better contact among them. The comparison of the characteristics of the activated carbons synthesized using these methods does not draw any clear conclusion. The selection of the mass impregnation ratio is very relevant, as it has shown a very significant effect on the characteristics of the resulting activated carbons, especially in the development of porous texture.

Table 1. Summary of FeCl₃ activation conditions.

| Carbon Precursor      | Type of Contact | R * | Tₜₐₓ * (°C) | tₜₐₓ * (h) | Ref.   |
|-----------------------|-----------------|-----|-------------|------------|--------|
| Waste cotton          | In solution     | 1.62| 400–700     | 1.0        | [44]   |
| Waste cotton          | In solution     | 0.5–2.5| 300–800     | 1.0–2.0    | [45]   |
| Lignin                | In solution     | 1.0 | 500–850     | 2.0–6.0    | [56]   |
| Sewage sludge         | In solution     | –   | 750         | 0.5        | [57]   |
| Biomass waste         | In solution     | –   | 800         | 6.0        | [58]   |
| Waste cotton          | In solution     | 1.0 | 400         | 1.0        | [59]   |
| Eucalyptus sawdust    | In solution     | 2.0 | 700         | 1.25       | [60]   |
| Lotus stem            | In solution     | 4.0 | 700         | 1.5        | [61]   |
| Sawdust               | In solution     | 0.5–2.0| 500–800     | 1.0        | [62]   |
| Coconut shell         | In solution     | 1.0–3.0| 700         | 1.5        | [48]   |
| Date pits             | In solution     | 1.5 | 700         | 1.0        | [63,64]|
| * Arundo donax        | In solution     | 1.65| 700         | 1.0        | [65]   |
| Coffee grounds        | In solution     | 1.0 | 900         | 1.0        | [66]   |
| Coffee husks          | In solution     | 1.0 | 280         | 3.0        | [67]   |
| Grape seeds           | Solid mixing    | 2.0–4.0| 500         | 2.0        | [68]   |
| Chestnut waste        | Solid mixing    | 0.5 | 220–800     | 1.0        | [69]   |
| Sewage sludge         | Solid mixing    | 0.5–3.0| 750         | 2.0        | [70]   |
| Alfalfa leaves        | Solid mixing    | 3.0 | 900         | 2.0        | [71]   |
| Tara gum              | Solid mixing    | 0.5–3.0| 400–1000    | 2.0        | [72]   |
| Lignin                | Solid mixing    | 3.0 | 800         | 2.0        | [73]   |
| Oily sludge           | Solid mixing    | 1.0–3.0| 500–700     | 1.0        | [74]   |

* R: Impregnation ratio; Tₜₐₓ: Activation temperature; tₜₐₓ: Activation time.

The thermal activation step or pyrolysis is the heating of the impregnated mixture under an inert atmosphere (usually N₂) to avoid the oxidation of the carbonaceous matter, from room temperature up to the selected activation temperature (Tₜₐₓ). The samples are maintained at the activation temperature during the activation time (tₜₐₓ) and are subsequently cooled down to room temperature under an inert atmosphere. The most relevant parameter of this synthesis stage is without doubt the activation temperature, which controls the extent of the activation mechanism detailed in the previous section. To obtain activated carbons with significant porous development the activation temperature should be equal or higher than 500 °C.
The final washing step is aimed at extracting the remaining activating agent and reaction byproducts to free the newly developed porous texture of the activated carbon. The activated sample is suspended in aqueous acid solutions at temperatures up to 80 °C. Subsequently, the solid activated carbon is filtered and rinsed with plentiful water generally until there is no presence of Cl\textsuperscript{−} ions or neutral pH in the filtered water. Finally, the activated carbon is dried and ready for use.

**Mixtures of Activating Agents**

Some studies employed mixtures of iron chloride with other activating agents, even including an activating step in the presence of a gasification agent. In this sense, Guo et al. [75] combined different mixtures of metal activators (FeCl\textsubscript{3}/MgCl\textsubscript{2}, FeCl\textsubscript{3}/ZnCl\textsubscript{2}, and ZnCl\textsubscript{2}/MgCl\textsubscript{2}) under CO\textsubscript{2} to synthesize peanut shell-derived activated carbons used as supercapacitors. This work concludes that FeCl\textsubscript{3} and ZnCl\textsubscript{2} are responsible for microporosity development, while MgCl\textsubscript{2} promotes mesopore formation. Tian et al. [59] also prepared activated carbon by activation of waste cotton with an FeCl\textsubscript{3} promoted the thermal cracking of the hydrochar, resulting in higher porous development. In contrast, peanut shell-derived activated carbons used as supercapacitors. This work concludes that FeCl\textsubscript{3} and ZnCl\textsubscript{2} are responsible for microporosity development, while MgCl\textsubscript{2} promotes mesopore formation. Tian et al. [59] also prepared activated carbon by activation of waste cotton with an FeCl\textsubscript{3}/ZnCl\textsubscript{2} mixture. According to this study, the pore development process is due to the creation of molten ZnCl\textsubscript{2} and Fe species, which act as templates to create porosity, and the dehydration effect of ZnCl\textsubscript{2} and FeCl\textsubscript{3} on the carbonaceous cotton waste precursor. Thue et al. [76] prepared activated carbons from wood chips and some inorganic components (lime, ZnCl\textsubscript{2}, and FeCl\textsubscript{3}) by microwave heating in very short pyrolysis times (around 11 min). Iron oxide was detected in the synthesized carbons by X-ray diffraction analysis. In another study [77], magnetic activated carbon was obtained by consecutive KOH and FeCl\textsubscript{3} chemical activations. This carbon showed excellent dispersion, easy separation of the aqueous media, and high dye adsorption capacities. Quian et al. [78] analyzed the catalytic effect of different iron salts in the simultaneous magnetization and CO\textsubscript{2} activation of a hydrochar. It was concluded that iron salts had a clear influence on the reaction between the carbon matrix and CO\textsubscript{2} gas, although in the case of iron oxide, the reaction was inhibited by the presence of CO\textsubscript{2}. It was also confirmed that FeCl\textsubscript{3} salt promoted the thermal cracking of the hydrochar, resulting in higher porous development. In contrast, other iron salts (Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}, FeC\textsubscript{6}O\textsubscript{6}, Fe(NO\textsubscript{3})\textsubscript{3}, and FeC\textsubscript{6}H\textsubscript{5}O\textsubscript{7}) do not enhance the porosity due to their inhibition effect on the thermal cracking of hydrochar. Sun et al. [79] used FeCl\textsubscript{3}, MnCl\textsubscript{2}, and AlCl\textsubscript{3} as complementary activating agents in the chemical activation of *Arundo donax* Linn (a perennial grass) with H\textsubscript{3}PO\textsubscript{4} under microwave heating. The use of MnCl\textsubscript{2} yielded the activated carbon with the highest porous surface area and pore volume, although the activated carbon prepared using FeCl\textsubscript{3} showed the highest Cr(VI) adsorption capacities. Arroyo-Gómez et al. [80] synthesized activated carbons from peach stones by chemical activation with only ZnCl\textsubscript{2} and a mixture of ZnCl\textsubscript{2} and FeCl\textsubscript{3} (1:1). The study affirmed that the activated carbon obtained with the ZnCl\textsubscript{2}–FeCl\textsubscript{3} mixture showed the highest sensitivity in caffeine detection, probably due to the lower roughness and the presence of mesopores resulting in a better mobility of the caffeine molecules. Activation with ZnCl\textsubscript{2} generally yields activated carbons with a very heterogeneous porous size and the simultaneous presence of both micro- and mesopores. In contrast, as explained in this review (Table 2), FeCl\textsubscript{3} activation yields mainly microporous carbons. Therefore, it is expected that the combination of both activating agents (FeCl\textsubscript{3} and ZnCl\textsubscript{2}) produces carbons with intermediate properties. The use of CO\textsubscript{2} gasification in the presence of a melt of FeCl\textsubscript{3} for coal activation has also been analyzed [81]. It was observed that melt infiltration of coal with FeCl\textsubscript{3} resulted in the formation of Fe nanocrystals confined in the inner structure of the coal (Figure 3), which, during the subsequent physical activation with CO\textsubscript{2}, catalyzed the CO\textsubscript{2} gasification of the coal and acted as templates for the formation of the mesoporosity. In the absence of FeCl\textsubscript{3}, the reactivity is much lower, resulting in a lower porosity development. Traditional liquid impregnation with FeCl\textsubscript{3} also improves the reaction of CO\textsubscript{2} and coal, increasing the porosity. However, the presence of iron aggregates, mainly on the external surface of the coal particles, produces a gasification of the external surface with lower porosity development than that of melt infiltration (Figure 3).
Table 2. Characteristic parameters of the porous texture and conditions used to maximize the surface area of activated carbons obtained from different carbon precursors, using FeCl$_3$ as activating agent.

| Carbon Precursor       | R  | $T_{\text{act}}$ (°C) | $S_{\text{BET}}$ (m$^2$·g$^{-1}$) | $S_{\text{EXT}}$ (m$^2$·g$^{-1}$) | $V_{\text{mic}}$ (cm$^3$·g$^{-1}$) | $V_{\text{Total}}$ (cm$^3$·g$^{-1}$) | $S_{\text{mic}}/S_{\text{BET}}$ (%) | Ref. |
|------------------------|----|------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------|
| Waste cotton           | 1.5| 700                    | 942                               | 124                               | 0.33                              | 0.64                              | 87.3                              | [45] |
| Lignin                 | 1.0| 800                    | 818                               | 31                                | 0.35                              | 0.37                              | 96.2                              | [56] |
| Biomass waste          | n.p.| 800                    | 600                               | n.p.                              | n.p.                              | n.p.                              | n.p.                              | [58] |
| Waste cotton           | 1.0| 400                    | 504                               | 151                               | 0.17                              | n.p.                              | 72.0                              | [59] |
| Eucalyptus sawdust     | 2.0| 700                    | 645                               | n.p.                              | 0.28                              | 0.44                              | n.p.                              | [60] |
| Lotus stem             | 4.0| 700                    | 374                               | n.p.                              | n.p.                              | 0.20                              | n.p.                              | [61] |
| Date pits              | 1.5| 700                    | 780                               | n.p.                              | 0.47                              | 0.57                              | n.p.                              | [63,64] |
| Arundo donax           | 1.65| 700                    | 927                               | 106                               | 0.36                              | 0.51                              | 88.6                              | [65] |
| Coffee grounds         | 1.0| 900                    | 846                               | n.p.                              | 0.21                              | n.p.                              | n.p.                              | [66] |
| Coffee husks           | 1.0| 280                    | 965                               | n.p.                              | 0.53                              | 0.65                              | n.p.                              | [67] |
| Grape seeds            | 3.0| 500                    | 417                               | 54                                | 0.17                              | 0.19                              | 86.8                              | [68] |
| Chestnut waste         | 0.5| 800                    | 568                               | n.p.                              | 0.29                              | n.p.                              | n.p.                              | [69] |
| Sewage sludge          | 3.0| 750                    | 836                               | 148                               | 0.33                              | 0.62                              | 82.3                              | [70] |
| Alfalfa leaves         | 3.0| 900                    | 773                               | n.p.                              | n.p.                              | n.p.                              | n.p.                              | [71] |
| Tara gum               | 2.0| 800                    | 1680                              | 143                               | 0.75                              | 0.99                              | 91.0                              | [72] |
| Lignin                 | 3.0| 800                    | 951                               | 34                                | 0.44                              | 0.53                              | 96.4                              | [73] |
| Oily sludge            | 2.0| 700                    | 683                               | 254                               | 0.20                              | 0.68                              | 62.7                              | [74] |

n.p.: not provided.

Figure 3. A schematic illustration of the porosity development mechanism by various strategies (reprinted from [81] with the permission of Elsevier, 2018).

4. Characterization of the Activated Carbons

4.1. Porous Texture

The main feature of activated carbons is most probably their well-developed porous texture. Due to this, many of the studies in the literature analyzed the porosity of the carbons obtained by FeCl$_3$ chemical activation in detail. Table 2 summarizes the characteristic parameters of the porous texture
and the activation conditions used to maximize the total surface area, using FeCl$_3$ as the activating agent (without the participation of other activation or gasification reagents), where $S_{\text{BET}}$ is the total surface area, $S_{\text{EXT}}$ the external area, $V_{\text{mic}}$ the micropore volume and $V_{\text{tort}}$ the total pore volume BET surface areas between 500 and almost 1700 m$^2$g$^{-1}$ have been reported in the literature, with total pore volumes of almost 1 cm$^3$g$^{-1}$. The activated carbons prepared through chemical activation with FeCl$_3$ are essentially microporous, as indicated by the higher percentage values of the $S_{\text{mic}}/S_{\text{BET}}$ parameter. The activation temperatures needed to obtain activated carbons with the most developed porosity, apart from the low values reported by Tian et al. [59] and Oliveira et al. [67], are usually in the range of 700 to 900 °C. Impregnation ratios from 1.0 up to 4.0 were used.

Among the different synthesis parameters, those with more relevance in the final porous texture of the resulting activated carbons are undoubtedly the activation temperature and the impregnation ratio, besides the type of carbon precursor employed. Several works have analyzed the effect of some of these variables in porous texture development. Xu et al. [45] prepared activated carbons from waste cotton woven at different impregnation ratios, activation temperatures, and activation times. It was concluded that activation time has less of an influence on porosity than impregnation ratio and activation temperature. Initially, the increase of the activation time promoted a disordered arrangement. However, a further increase of the activation time resulted in the formation of intermediates that blocked some of the pores and collapsed part of the pore walls. These observations are in agreement with those previously reported by Zazo et al. [56], who obtained activated carbons with surface areas of 791, 818, and 749 m$^2$g$^{-1}$ when lignin was activated with FeCl$_3$ at 800 °C for 2, 4, and 6 h, respectively. The effect of the impregnation ratio and the activation temperature was also studied for the FeCl$_3$ activation of Tara gum and can be observed in Figure 4A,B [72]. The N$_2$ adsorption–desorption isotherms are characteristic of predominantly microporous materials, although with a contribution of mesoporosity. An initial increase of the impregnation ratio produced an increase of the porosity, as indicated by the higher amount of N$_2$ adsorbed. However, when the impregnation ratio increased from 2 to 3, a reduction of the amount of N$_2$ adsorbed is clearly observed (Figure 4A). This reduction can be ascribed to different mechanisms [45]. An excessive amount of FeCl$_3$ can more intensely catalyze the activation reaction, especially at high activation temperatures, resulting in pore merging and therefore in a reduction of the porosity of the resulting activated carbon [82]. Besides, higher amounts of FeCl$_3$ can result in larger particles of iron oxides, which can act as a template for the formation of mesopores and/or precipitate in the carbon matrix, altering porous development [83,84]. Similarly, Diaz et al. [68] obtained the maximum surface area at an impregnation ratio equal to 2.0 (in a 1.0–3.0 range) when activating grape seed hydrochars.

The increase of the activation temperature produced activated carbons with more developed porosity. In this sense, Rodríguez-Sánchez et al. [69] observed an increase of the total surface area with activation temperatures in the range of 220 to 800 °C when activating chestnut industrial wastes. However, the use of very high activation temperatures resulted in a lower porosity, as indicated by the lower amount of N$_2$ adsorbed (mainly in the micropore range, $P/P_0 < 0.4$) when increasing the activation temperature from 800 up to 1000 °C (Figure 4B). This change of trend at the highest activation temperature has different explanations. Bou dou et al. [85] affirmed that FeCl$_3$ is decomposed into iron oxides (Fe$_2$O$_3$ and Fe$_3$O$_4$), which act as catalysts to gasify the nearest carbon atoms into CH$_4$ or CO. The porosity reduction is also explained by the shrinkage of the porous texture and the rearrangement of the carbon matrix as a consequence of sintering effects [86]. Finally, Bedia et al. [72] ascribed the decrease in porosity to the increase in the ash content of the carbon with increasing activation temperature. The use of the highest activation temperature resulted in a stronger interaction of the iron with the carbon matrix. This iron is not efficiently extracted during the washing step (indicated by a significant increase in the ash content), blocking part of the porosity.
Figure 4. $N_2$ adsorption–desorption isotherms at $-196 \, ^\circ C$ of the activated carbons prepared from Tara gum at (A) different impregnation ratios and 800 $^\circ C$ and at (B) impregnation ratio of 2 and different activation temperatures (reprinted from [72] with the permission of Elsevier, 2018).

Figure 5 represents the values of the BET surface area of activated carbons synthesized by FeCl$_3$ of different carbonaceous precursors reported in the literature versus their activation temperatures. As can be seen, there seems to be a clear correlation between porosity development (quantified by the BET surface area) and activation temperature, regardless of other synthesis variables such as impregnation ratio, activation time, or type of carbonaceous precursors. It is also true that some of the values do not fit this general trend. For instance, Oliveira et al. [67] obtained an activated carbon with high porosity from coffee husks at a very low activation temperature of 280 $^\circ C$. Besides, Bedia et al. [72] synthesized activated carbons with very high values of surface area when using Tara gum as a carbonaceous precursor. In contrast, Mojoudi et al. [74] analyzed the activation of oil sludge. The resulting carbons showed slightly lower surface area values than those observed in the general trend. These divergences are probably due to the effect of the characteristics of the different carbon precursors analyzed in the different studies.

Figure 5. BET surface area of the activated carbons synthesized by FeCl$_3$ of different carbonaceous precursors versus the activation temperature.
As can be seen, activation with FeCl$_3$ yields activated carbon with very well-developed porosity and high surface areas up to 1700 $\text{m}^2\cdot\text{g}^{-1}$. These surface area values are comparable and even higher than those of activated carbons obtained by chemical activation with more traditional activation agents, such as ZnCl$_2$ or H$_3$PO$_4$. However, the porosity development achieved with FeCl$_3$ is still far from that obtained when activating with strong bases such as KOH and NaOH.

4.2. Surface Chemistry

FTIR analyses of FeCl$_3$-derived activated carbons obtained at different activation temperatures showed a disappearance of the absorption peaks with increasing activation temperatures (Figure 6). The bands at around 3420 cm$^{-1}$ are ascribed to the stretching vibrations of O–H in carbonyl and phenol groups [87]. Conversely, Cazetta et al. [48] affirmed that the FTIR spectra of magnetic activated carbon obtained from biomass waste by FeCl$_3$ activation did not show bands at these wavelength values, suggesting the absence of hydroxyl groups on these carbons. The authors explained this behavior by the conversion of the surface oxygen groups into iron oxides (magnetite, maghemite, and/or hematite). The other band that remains at an activation temperature of 700 °C is located at 1550 cm$^{-1}$ and is related to the C=O stretching vibration in aromatic rings [44,48]. The intensity of this band decreased with increasing activation temperature due to the structure reorganization of the carbon matrix. Finally, the bands located between 1000 and 1300 cm$^{-1}$ are related to the stretching vibration in C–O–C ether bonds. The rest of the bands observed in the sample synthesized at 400 °C disappeared when the activation temperature increased. Those at 2520 and 1690 cm$^{-1}$, related to the stretching vibration of O–H and conjugated stretching vibration of C=O, respectively, disappeared as a consequence of the carbonyl decomposition [88]. Stretching vibrations of aliphatic C–H at 2900 and 1390 cm$^{-1}$ are indicative of an incomplete carbonization of the carbon precursor. Consequently, these bands also disappeared with increasing activation temperature. Finally, low-intensity bands at 735 and 876 cm$^{-1}$ are ascribed to the out-of-plane bending vibrations of aromatic C–H. Other studies reported bands at 557 and 465 cm$^{-1}$ associated to the Fe-O vibrations bonds in Fe$_3$O$_4$ [62].

![Figure 6](image-url)

**Figure 6.** FTIR spectra for activated carbon samples obtained at different pyrolysis temperatures (reprinted from [44] with the permission of Elsevier, 2019).

FTIR analyses suggest the presence of a significant number of acidic surface groups on the activated carbons synthesized by FeCl$_3$ activation, which was confirmed by measurements of the point of zero charge (pH$_{PZC}$). In this sense, Tian et al. [59] reported a pH$_{PZC}$ value of 2.41 for an activated carbon obtained from cotton and washed with a 3.2-M solution of HCl. Similar values were obtained also for the activation of cotton waste to prepare an activated carbon washed with a 1-M
HCl aqueous solution [44]. Slightly higher values were obtained by Cazetta et al. [48], who reported pH_{PZC} values of 4.51, 4.12, and 4.10 for magnetic activated carbons synthesized by FeCl_{3} activation of coconut shell at impregnation ratios of 1, 2, and 3, respectively. In this latter study, the carbons were submitted to a final washing step with a 1-M HCl aqueous solution. Fu et al. [65] prepared an activated carbon from biomass after washing with a 0.1-M solution of HCl and with a pH_{PZC} of 5.70. The activation of chestnut waste with FeCl_{3} at different activation temperatures yielded carbons with surface pH values between 2.3 and 5.2 after washing with distilled water [69]. Our research group synthesized an activated carbon from lignin by FeCl_{3} activation using microwave irradiation and a washing step with a 0.1-M aqueous solution of HCl with a pH_{PZC} of 5.0 (results not published). As can be seen, regardless of the conditions of the acid washing step, the activated carbons obtained show predominantly acidic surfaces. This characteristic is particularly relevant when these activated carbons are used as adsorbents.

The analysis of the different XRD results reported in the literature shows some discrepancies between the different studies. Figure 7 represents a standard XRD pattern of an activated carbon (after washing step) obtained through FeCl_{3} chemical activation. The broad peaks at around 25 and 43° are the typical characteristic peaks of the (002) and (100) planes of carbon, respectively [89]. The iron-related structures evolve as the carbonization temperature increases. Initially, hydrated iron chloride salts decompose into α-Fe_{2}O_{3} (hematite) at temperatures of around 400 °C [67,90]. When the carbonization temperature reaches 500 °C, new peaks appear at around 24.3, 33.3, 41.0, 49.6, and 57.7°, corresponding to basal planes (012), (104), (113), (024), and (122) of Fe_{3}O_{4} hematite, respectively. This hematite is formed through the carbothermal reduction of Fe_{2}O_{3} in the presence of the pyrolysis gases and the carbon surface [91]. Some authors affirm that at activation temperatures equal or higher than 700 °C, all the Fe species are reduced to Fe_{3}O_{4}, which confers the magnetic behavior of these carbons [44,60,65,92,93]. In contrast, other studies indicate that at activation temperatures higher than 800 °C, part of the Fe_{3}O_{4} can be transformed into Fe_{2}C or Fe_{3}C species due to the interaction with the carbon matrix [62,94].

![Figure 7. Standard XRD pattern of an activated carbon obtained through FeCl_{3} chemical activation at 700 °C (reprinted from [89], RSC, 2018).](image)

XPS analyses have also been extensively employed to characterize the surface chemistry of activated carbons obtained by chemical activation with FeCl_{3}. Most of the studies that have used this technique analyzed the Fe2p XPS spectra of the activated carbons in detail. These spectra present a doublet with a separation of 13.6 eV corresponding to Fe2p_{1/2} and Fe2p_{3/2} signals [95]. Most of the studies agree on the presence of a main band associated to Fe2p_{1/2} at approximately 712.0 eV (with a secondary one related to Fe2p_{3/2} at around 725.0 eV) and a satellite peak at 718.8 eV, as can be seen in Figure 8 [56,65,70,72]. These peaks are characteristics of Fe^{3+} species, like those in Fe_{2}O_{3} and
partially in Fe$_3$O$_4$ as previously observed in XRD patterns. The presence of Fe$^0$ that is observed at binding energies of around 708.0 eV is discarded [48,96]. Other authors also include a main Fe$^{2+}$ peak at around 710.2 eV (with its corresponding secondary contribution), ascribed to the presence of Fe$^{2+}$ [44,62] as present in Fe$_3$O$_4$.

**Figure 8.** Fe$^{2+}$ XPS spectrum of an activated carbon obtained from lignin by FeCl$_3$ activation (reprinted from [56] with the permission of Elsevier, 2012).

Some studies have analyzed the iron species by Mössbauer spectroscopy more deeply. Figure 9 represents the room-temperature Mössbauer spectra of activated carbons obtained by chemical activation with FeCl$_3$ of chestnut industrial waste at different activation temperatures [69]. At the lowest activation temperature, 220 °C, very low absorption is observed because of the low iron concentration. The spectrum shows a single paramagnetic doublet with Mössbauer parameters ($\delta = 0.37$ mms$^{-1}$; $\Delta = 0.85$ mms$^{-1}$), characteristic of Fe$^{3+}$ in a distorted oxygen octahedral coordination. The authors ascribed this behavior to the presence of small-particle Fe$^{3+}$-containing oxides [97]. At higher activation temperatures (400–600 °C), the spectra show two sextets and a paramagnetic Fe$^{3+}$ doublet. The sextets ($\delta_A = 0.30$ mms$^{-1}$; $2\epsilon_A = 0.02$ mms$^{-1}$; $H_A = 48.6$ T; $\delta_B = 0.66$ mms$^{-1}$; $2\epsilon_B = -0.01$ mms$^{-1}$; $H_B = 45.2$ T) are related to the presence of Fe$^{3+}$ tetrahedral (A) and Fe$^{2.5+}$ octahedral (B) sites of magnetite (Fe$_3$O$_4$) [97]. The doublet is similar to that of the carbon activated at the lowest temperature, and therefore it is also characteristic of superparamagnetic Fe$^{3+}$ oxides. The increase of the activation temperature resulted in more complex Mössbauer spectra. At 700 °C, magnetite and paramagnetic components are also observed, with a new contribution ($\delta = 0.31$ mms$^{-1}$; $2\epsilon_A = 0.02$ mms$^{-1}$; $H_A = 49.8$ T) characteristic of maghemite ($\gamma$-Fe$_2$O$_3$). Finally, at 800 °C, non-stoichiometric magnetite, maghemite, a small paramagnetic Fe$^{3+}$ contribution, nanophase iron oxide, metallic iron ($\delta = 0.00$ mms$^{-1}$; $2\epsilon_A = 0.00$ mms$^{-1}$; $H_A = 33.0$ T), and iron carbide cementite (Fe$_3$C) ($\delta = 0.17$ mms$^{-1}$; $2\epsilon_A = 0.00$ mms$^{-1}$; $H_A = 20.8$ T) were all observed [98].
4.3. Magnetic Properties

One of the main features of these materials is their magnetism. Magnetic carbons are more suitable for specific applications (e.g., liquid-phase applications) because they are more easily separated from the reaction media using magnets, avoiding the necessity for lengthy centrifugation and/or filtration steps [99–103]. The magnetic properties of FeCl₃-derived activated carbons have been analyzed using their magnetic hysteresis curves (Figure 10). Those studies showed magnetic hysteresis curves with very low coercivity and almost negligible magnetic hysteresis cycles, characteristic of superparamagnetic materials. Yang et al. [62] reported a maximum specific saturation magnetization close to 60 emu·g⁻¹ for activated carbons synthesized from sawdust. This study showed an increase of this value with the impregnation ratio (0.5–2.0 range), and a maximum at an activation temperature of 600 °C (in the 500–800 °C interval). Cazetta et al. [48] also observed an increase of the specific saturation magnetization from 17.01 up to 28.74 emu·g⁻¹ with increasing impregnation ratio from 1 up to 3, respectively. This study shows coercivities in the range of 77–140 Oe and remnant-to-saturation magnetism ratios between 0.11 and 0.21, confirming the superparamagnetic character of the prepared carbons. Chen et al. [60] reported a saturation magnetization value of 30.37 emu·g⁻¹ with a coercivity force equal to 108.51 Oe and a remnant magnetization of 2.46 emu·g⁻¹ (remnant-to-saturation magnetism ratio of 0.08). Xu et al. [89] synthesized an activated carbon with 5.2 emu·g⁻¹ and remanence and coercive forces.
equal to 0.30 emu·g⁻¹ and 63.84 Oe, respectively, confirming the super paramagnetic character of this carbon. It is worth mentioning that these values of specific saturation magnetization are comparable to or higher than others previously reported in the literature for magnetic activated carbon prepared by different synthesis procedures [104–107].

Figure 10. Magnetic hysteresis loop of magnetic activated carbon obtained by FeCl₃ chemical activation (reprinted from [60] with the permission of the RSC, 2019).

5. Applications

5.1. Adsorption

Probably the most well-known application of activated carbons is adsorption, and as a consequence, most of the studies in the literature about FeCl₃-derived carbons are devoted to adsorption processes, specifically aqueous-phase adsorption processes. This is due to the previously mentioned properties of these activated carbons, namely, well-developed porous texture, surface acidity, and superparamagnetic character. This latter property makes the separation of the activated carbon from the aqueous media using a magnet very simple (Figure 11). Among these studies, adsorption of dyes has attracted much attention, and among the dyes, many studies have analyzed methylene blue (MB) adsorption. This is probably due to the acidic surface of the FeCl₃-derived carbons (value of the pHₚₗ₃s lower than or around 5). When the pH of the solution is higher than the pHₚₗ₃s, the surface of the adsorbent becomes negatively charged, and therefore the positively charged MB molecules (pKₐ = 0.04) are more easily attracted to the surface, increasing the adsorption capacity. Chen et al. [60] studied the adsorption of MB on an eucalyptus wood-based FeCl₃-derived activated carbon. Maximum adsorption capacities of MB between 163 and 192 mg·g⁻¹ were obtained, increasing the saturation capacity with the adsorption temperature (25–55 °C). The authors concluded that the adsorption process was spontaneous and endothermic, and proceeded through the interaction of the N⁺ of the MB molecule and the -COOH surface groups of the activated carbon. Similarly, Theydan and Ahmed [64] confirmed that the adsorption of MB on activated carbon obtained by chemical activation of date pits with FeCl₃ was also spontaneous and endothermic. They reported a MB saturation adsorption capacity higher than 250 mg·g⁻¹, in the range of the values obtained when using other types of activated carbons as adsorbents [108–111]. Tian et al. [59] analyzed the adsorption of cationic MB and anionic Eriochrome Black T (EBT) dyes. As expected, the adsorption capacity of MB and EBT followed opposite trends to pH due to the changes in the attraction–repulsion interactions between the dye molecule and the carbon surface. Cazetta et al. [48] analyzed the adsorption of Acid Yellow 6 dye on magnetic activated carbon obtained from coconut shells at different impregnation ratios. The saturation capacity decreased...
with increasing pH due to the repulsive interaction between the negatively charged surfaces of the carbon adsorbent (pH\textsubscript{PZC} = 4.51) and the dye molecules at high pH values. Besides the electrostatic interactions, the authors concluded that hydrogen bonding and π–π interactions also have some influence on the adsorption properties. The maximum adsorption capacity was 22.3 mg·g\(^{-1}\).

Figure 11. Example of adsorption of methylene blue (MB) followed by removal of the magnetic activated carbon with a magnet (adapted from [112]).

Other organic compounds have also been tested in adsorption studies on activated carbons synthesized by chemical activation with FeCl\(_3\). In this sense, Ahmed and Theydan [63] studied the adsorption of p-nitrophenol on a microporous activated carbon synthesized by FeCl\(_3\) activation of date pits. The adsorption shows an optimum performance at pH equal to 5. At pH values higher than 5, the carbon surface becomes negatively charged, resulting in a decrease of the adsorption capacity due to the electrostatic repulsion with the anionic form of p-nitrophenol molecules (pK\(_a\) = 7.15) [113]. The maximum adsorption capacity was 185 mg·g\(^{-1}\), a value comparable to or higher than those obtained with other activated carbon obtained from biomass waste by other activation procedures [114–116].

Mojoudi et al. [74] analyzed the adsorption of phenol and phosphate using activated carbons from oily sludge obtained through physical and chemical activation. The carbon obtained by FeCl\(_3\) activation showed higher adsorption capacities than those physically activated or activated with ZnCl\(_2\) at similar values of surface area. It was suggested that the presence of Fe\(^{3+}\) on the carbon surface could be responsible for the high adsorption capacity of phosphate, since Fe\(^{3+}\) has a strong affinity for phosphorous species [117]. In the case of phenol, it was adsorbed through π–π interactions between the aromatic structures of the carbon and the aromatic ring of phenol molecule [118]. The maximum phosphate and phenol saturation capacities were 102 and 238 mg·g\(^{-1}\), respectively. The analysis of the adsorption thermodynamics revealed that the adsorption process is spontaneous and exothermic and proceeds through physisorption.

Several studies have analyzed the adsorption of emerging contaminants on FeCl\(_3\)-derived activated carbons. Fu et al. [65] studied the adsorption of cephalexin antibiotic on activated carbon from Arundo donax using different iron salts as activating agents, namely FeCl\(_3\), FeCl\(_2\), Fe\(_6\)H\(_5\)O\(_7\), and FeC\(_2\)O\(_4\). The activated carbon obtained by FeCl\(_3\) activation showed the highest adsorption capacity of cephalexin, at 286 mg·g\(^{-1}\). The work proposed different adsorption mechanisms: (1) Lewis acid–base, (2) electrostatic, and (3) hydrophobic interactions. At the adsorption pH (5.5), the amine group of the cephalexin molecule is protonated and can form a covalent bond with the O of a deprotonated carboxylate surface group of the carbon via Lewis acid–base interaction. Electrostatic interactions can also play a relevant role since at the adsorption pH of 5.5, cephalexin molecules are predominantly in zwitterion form (pK\(_{a1}\) = 2.56 and pK\(_{a2}\) = 6.88) and the surface of the carbon is positively charged (pH\textsubscript{PZC} = 5.70). Therefore, electrostatic interactions are expected to play a role in the adsorption
process. Finally, the hydrophobic nature of the surface of the activated carbons can also interact with the hydrophobic molecules of cephalexin. Bedia et al. [72] reported the adsorption of antipyrine, an analgesic, nonsteroidal anti-inflammatory and antipyretic compound, on activated carbons from FeCl₃ activation of Tara gum. The activated carbons were synthesized at different impregnation ratios and activation temperatures. It was concluded that adsorption capacity is directly related to the values of the total surface area of the carbons, although affected by the presence of oxygen surface groups, which enhanced the adsorption. An antipyrine saturation capacity of 275 mg·g⁻¹ was obtained, a value comparable to or higher than those reported for other emerging contaminants on different activated carbons [119,120]. Diaz et al. [68] analyzed the adsorption of sulfamethoxazole antibiotic on an activated carbon obtained through chemical activation of grape seed hydrochar with different chemical activating agents (KOH, FeCl₃, and ZnCl₂). Although the FeCl₃-derived activated carbon did not achieve the highest adsorption capacity, a significant saturation capacity close to 150 mg·g⁻¹ was reported.

Adsorption of heavy metals from water on FeCl₃-derived carbons has been also analyzed in the literature. Xu et al. [44] analyzed the adsorption of Cr(VI) at an acid pH of 2.0 on FeCl₃-activated carbon from waste cotton textiles. The work concluded that Cr(VI) adsorption proceeds through electrostatic interaction, reduction, and complexation. At the adsorption pH, the mainly negatively charged Cr(VI) species (chromate, CrO₂⁺, and hydrogen chromate, HCrO₄⁻) have a strong electrostatic attraction through the positively charged surface of the activated carbon (pH_PZC = 2.56). Moreover, in the positively charged surface of the carbon adsorbent, the adsorbed Cr (VI) is reduced to Cr(III) by the π electrons of the aromatic rings of the carbon [121,122]. Finally, complexation between Cr(VI) and carboxylate surface groups was also confirmed [123,124]. A similar adsorption mechanism of Cr(VI) was proposed by Feng et al. [61] when analyzing the adsorption on FeCl₃-modified lotus stem-based biochar. Finally, the removal of mercury using a FeCl₃-activated biochar was reported by Yang et al. [62]. The work proposed two active sites for the adsorption/oxidation of Hg₀, namely Fe³⁺ and oxygen-rich functional groups, especially the C=O groups. Siddique et al. [125] analyzed the adsorption of fluoride anions on an activated carbon obtained by FeCl₃ activation of Citrus limetta peels. The maximum adsorption capacity was close to 10 mg·g⁻¹, with the adsorption process being spontaneous and endothermic.

5.2. Catalysis

Fernandez-Ruiz et al. [73] reported the catalytic hydrodechlorination of chloroform on Pd-supported activated carbons obtained by chemical activation of lignin with different activating agents (H₃PO₄, ZnCl₂, FeCl₃, NaOH, and KOH). The aim of the study was to increase the selectivity of the reaction to ethane and propane. While the best results were obtained with NaOH-activated carbon, the surface chemistry of the FeCl₃-derived activated carbon resulted in the smallest mean Pd particle size and the highest metallic-to-electrodeficient Pd ratio, which opens new possibilities for the use of FeCl₃ derived carbon as catalyst or catalytic supports for different applications. Chemical activation with FeCl₃ yielded carbon with (1) a well-developed porous texture, and (2) stable and well-distributed iron species on the carbon surface (Figure 12). Due to these characteristics, several studies [56,57,70] have proposed these types of carbons as catalysts for water purification using catalytic wet peroxide oxidation processes (CWPO). Zazo et al. [56] synthesized highly stable Fe-loaded carbon catalysts by chemical activation of lignin with FeCl₃. One of the main drawbacks of Fe catalysts for CWPO is the iron leaching at the optimal reaction conditions (pH = 3). However, this study reported an almost negligible iron leaching even after 24 h of reaction, as can be seen in Figure 13, confirming the extremely high stability of this type of carbon for this reaction. Bedia et al. [70] synthesized Fe-loaded carbon catalysts by chemical activation of sewage sludge with FeCl₃. They obtained carbon catalysts with well-developed porosity (up to 800 m²·g⁻¹), with iron being stable and homogeneously distributed with Fe particle sizes in the range of 3–11 nm. The most promising sample achieved complete conversion of antipyrine with 70% of mineralization in 1 h at 50 °C. In the field of photocatalysis, activated carbons
are referred to for their use as supports of the active photocatalytic phase to improve the recovery of the photocatalyst from the aqueous medium. Peñas-Garzón et al. [126,127] studied the effect of different activating agents, namely KOH, ZnCl$_2$, H$_3$PO$_4$, and FeCl$_3$, in the chemical activation of lignin to prepare TiO$_2$/activated carbon heterostructures. The photocatalyst activated with FeCl$_3$ (TiO$_2$/Fe-C) showed the best performance in the photocatalytic treatment of different pharmaceuticals in aqueous solution under solar simulated light, which was attributed to a reduction in the band gap of the TiO$_2$/Fe-C sample.

![Figure 12. Scheme of FeCl$_3$ activation and main characteristics of the resulting activated carbons.](image)

**Figure 12.** Scheme of FeCl$_3$ activation and main characteristics of the resulting activated carbons.

![Figure 13. Comparison between the stability of the FeCl$_3$-derived activated carbon catalyst (FeC-800-2) and activated carbon with iron deposited by the incipient wetness procedure (Fe/AC) (reprinted from [56] with permission of Elsevier, 2012).](image)

**Figure 13.** Comparison between the stability of the FeCl$_3$-derived activated carbon catalyst (FeC-800-2) and activated carbon with iron deposited by the incipient wetness procedure (Fe/AC) (reprinted from [56] with permission of Elsevier, 2012).

5.3. **Energy Storage**

Batteries and supercapacitors are among the most employed energy storage devices in electronic apparatuses [15,128–130]. The electrodes used in batteries and supercapacitors are continuously being researched, with the aim of improving their performance. Nowadays, most of these electrodes are based on non-renewable carbon sources such as graphite. The search for alternative materials to be used for this application is of great interest. In this sense, Andrijanto et al. [58] analyzed the use of several biomass wastes (corncob, coconut husk, rice straw, and water hyacinth) as precursors for the synthesis of carbon electrodes using FeCl$_3$ as an activating agent. The effect of FeCl$_3$ is twofold, with on one hand the development of the porous texture, and on the other hand the partial graphitization of the carbon
materials, since Fe is a well-known graphitization catalyst \[131–135\]. FeCl_3 is also responsible for the reduction of carbon resistivity. Finally, Rufford et al. \[66\] synthesized electrochemical double-layer capacitors (EDLCs) from waste biomass by activation with FeCl_3, MgCl_2, and ZnCl_2. Among them, the FeCl_3-activated carbon supercapacitor prepared at 900 °C showed a specific capacitance of 57 F·g\(^{-1}\), retaining high capacitance value at high current loads. Moreover, the charge-cycling stability of this carbon was excellent.

6. Conclusions and Outlooks

Chemical activation with FeCl_3 has been revealed as a methodology to synthesize activated carbons with interesting properties and promise for different applications such as adsorption, catalysis, and/or energy storage. These carbons are characterized by a well-developed porous texture, composed mainly of micropores. The analysis of the surface chemistry revealed an acidic carbon surface (pH\(_{\text{PZC}}\) values lower than 5.0), the presence of different oxygen functionalities, and iron species predominantly in the form of Fe\(^{3+}\). These iron species are responsible for the superparamagnetic character of these carbons.

Research on this subject should be oriented towards the search for modifications of the synthesis procedure, an analysis of new carbon precursors, and the tailoring of the porosity and iron content of the final carbons. On this basis, the future applications of these carbons will be expanded, opening up new possibilities. Adsorption processes can be improved using well-developed porosity, a main composition of micropores, and surface chemistry of an acid nature for these types of activated carbons, making them ideal adsorbents for the removal and purification of both liquid and gas streams. Moreover, their superparamagnetic character facilities their separation from the liquid media, which constitutes an enormous advantage in relation to other activated carbons or adsorbents. FeCl_3-activated carbons are also promising candidates for catalytic applications, and as supports or as mass catalysts. The presence of well-distributed iron particles on the well-developed surface, as well as the high stability of Fe (which seems to be intimately attached in the carbon matrix during the synthesis stage), make these carbons promising materials for different catalytic applications. Some studies have already probed their high activity and stability in different catalytic reactions. Their use for energy storage applications is also favored by well-developed porosity and the presence of iron, which seem to produce a limited graphitization of the carbon structure and enhance carbon conductivity. Finally, researchers must find procedures for implementing these materials at the industrial scale, taking into account other aspects not yet analyzed such as the cost of the overall manufacturing process.

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