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Activated Carbon from Almond Shells for Water Treatment: A Mini Review

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ABSTRACT

Activated carbon is a highly porous material that is gaining interest nowadays in different sectors due to its strong adsorption capacity. Although it can be manufactured from very diverse feedstock, vegetable carbon and coal have been the most widely used raw materials. The increasing market demand and the encouragement of practices for the transition to the circular economy have promoted the use of wastes for the manufacturing of activated carbon. A significant part of the activated carbon currently in the market is produced from coconut shells, but wastes from a variety of sources are the subject of intense research. The number and variety of agricultural wastes tested as precursors of activated carbon is enormous, especially due to their high lignocellulose content. This review is focused on the use of almond shells as feedstock for the production of high-quality activated carbon.

Key words: Agricultural wastes, Almonds, Biomass, Charcoal, Environmental remediation, Pyrolysis.

Activated carbon is a highly porous material composed of a carbon-rich skeleton chemically modified in its internal structure by reactive groups of oxygen, hydrogen and nitrogen (Marsh and Rodríguez-Reinoso 2006). It is manufactured from carbon-rich materials by activation at high temperatures. The manufacturing process involves the pyrolysis of the raw material under controlled conditions, accompanied by an activation step, which can be simultaneous or subsequent to the pyrolysis. This process allows the formation of internal porous of different sizes, mainly micropores, but also mesopores and macropores (Marsh and Rodríguez-Reinoso 2006). Thus, activated carbon has a large internal surface area, composed of a complex network of chemically activated pores of different sizes, which is responsible for its high adsorptive capacity.

Since its first application as a decolourising agent (Ostrejko, 1900), activated carbon has become an excellent solution for the elimination of pollutants from water bodies (Simate *et al*. 2016; Teodosiu *et al*. 2018), for gas purification in industry - such as removal of volatile organic compounds (VOCs) in the fossil fuel industry or mercury emissions in coal-fired power plants (Zhang *et al*. 2017,Yang *et al*., 2007), the removal of dyes in the wastewater of textile, food, beverages and other industries (Mezohegyi *et al*. 2012; Wong *et al*. 2018; Yagub *et al*. 2014) and other diverse applications in sectors such as medicine, cosmetics or pharmaceutics. More recently, due to its electrochemical performance, it has also been introduced as a component in new super-capacitor based batteries (Faraji and Ani 2015; Kalyani and Anitha 2013; Tang *et al*. 2017).

Social development in the last century has promoted the rapid growth of activated carbon market, especially in recent decades due to the increasingly stringent requirements in terms of environmental regulation, the need for new solutions for the storage of energy or the recovery of chemical substances with high added value in the industry. Recent market studies foresee a growth in the production of activated carbon worldwide, as well as an increase in the number of future applications at domestic and industrial scale (MRC Stratistics 2018).

To cope with the increasing global demand of activated carbon, intense research is currently focused on both the optimization of manufacturing process and the use of new feedstocks, mainly carbon-rich wastes. Among the huge variety of feedstocks, valorisation of agricultural wastes into activated carbon has been considered as most of the agricultural wastes are lignocellulosic rich materials, a kind of feedstock that has attracted the interest among scientific and producers of activated carbon (Danish and Ahmad 2018; Tan *et al*. 2017) due to the following properties: i) high carbon content, ii) low ash content iii) low degradation upon storage, iv) high strength and internal porosity and v) availability and low cost (Marsh and Rodríguez-Reinoso 2006). The lignocellulosic materials are composed mainly of cellulose, hemicellulose and lignin. The proportion of these components varies depending on the feedstock, being lignin the main responsible for the microporosity of activated carbon (Suhas *et al*. 2007). Lignin is a polymer very resistant to biodegradation that functions as a structural support for plants. In addition, lignin is the most abundant carbon source in nature after cellulose.

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A diversity of agricultural wastes has been tested as a precursor of activated carbon: stems, husks, bones, seeds, fibers, wood, or processing residues from the agroforestry industry (González-García 2018). Other valorisation strategies of agricultural wastes include their use in soil amendment (Akoijam *et al*. 2018), production of vermicompost (Barik *et al*. 2010) or production of charcoal (Nasar *et al*. 2019).

Among agricultural wastes, almond shells are the subject of a number of reports on the production of activated carbon, which, taken together, provides a set of knowledge in this field. In this review, a collection of the scientific literature related to the synthesis of activated carbon using almond shells as precursors is presented, as the results show that activated carbons obtained are a very promising solution in the field of water treatment. Based on the evidences presented, the information provided in this review has been summarized into the following items: i) synthesis parameters at lab scale - both by physical and chemical activation-ii) effect of biochemical composition of almond shells on final properties of the product and iii) absorption capacity of the activated carbons produced. In addition, a brief summary of the overall process for the synthesis of activated carbon is exposed previously to support and introduce the subject.

Synthesis of activated carbon

The process of synthesis of activated carbon involves two well-defined stages: carbonization of the precursor and activation of the carbon. Both processes can occur independently or simultaneously (Mohammad-Khah and Ansari 2009). The carbonization stage consists of the pyrolysis (combustion in the absence of oxygen) of the raw material, promoting the removal of the volatile substances and thus, generating a carbon skeleton with high internal porosity. The activation stage consists of activating the carbon at high temperature with an oxidizing agent, generating an increase in the porosity and the chemical modification of the internal surface. The production of activated carbon is carried out by two different methods: physical activation and chemical activation (Rodríguez-Reinoso 2001), although modifications and innovations on both methods are being studied, such as the use of microwaves (Ahmed 2016; Ao *et al*. 2018) or ultrasounds (Jiang *et al*. 2018; Zhang *et al*. 2019). The chemical activation is usually carried out in a single stage and involves the impregnation of the precursor with an activating chemical and subsequent incubation at elevated temperatures (400-800 ºC) in a controlled atmosphere (Yahya *et al*. 2015). The most commonly used activating substances are H_3PO_4, H_2SO_4, HNO_3, $ZnCl_2$, NaOH and KOH (Hayashi *et al*. 2000). A previous carbonization of raw material and a subsequent activation in the presence of the activating substance can also be carried out in a two-step chemical activation. In the physical activation, the activating substance is an oxidising gas, mainly CO_2, steam, air or a mixture of them. Generally, the precursor is previously carbonized in an inert atmosphere and subsequently activated in the presence of the oxidizing gas at a high temperature (700-1000 ºC), although direct activation can also be performed (Ioannidou and Zabaniotou 2007). The advantage of chemical activation versus physical activation is that higher yield and a higher specific surface can be obtained by using lower temperatures. The disadvantage is the necessity of washing the carbon to eliminate the activating agent (Yahya *et al*. 2015).

Synthesis of activated carbon from almond shells

The almond shells are good precursors of activated carbon as they have a high lignollelulosic content and a high hardness degree. Almond production is concentrated in four main regions: Western United States, the Mediterranean, central Asia and Australia (Yada *et al*. 2011) as it requires a Mediterranean-type climate. The composition of almond shell depends on the variety of the cultivated almond. In this review, we have recopilated data about almond shell composition depending on the country of origin (Table 1). In general, almond shells show properties suitable for the synthesis of activated carbon, as low ash content (0.7-3.4 wt % dry), high carbon composition (45.6-50.6%) or high lignin content (23.7-32.7 wt %). Accordingly,a significant number of reports shows their suitability in the synthesis of activated carbon at lab scale, a subject that is discussed below.

A compilation of data for the synthesis of activated carbon from almond shells in the scientific literature is summarized in Tables 2-4. Different studies focused on the effect of synthesis parameters in the properties of the activated carbon have been reported, including the characterization of the internal structure and the adsorbent capacity.Among the different studied parameters, the activating agent, the particle size of the precursor, the temperature of the carbonization/activation steps, the yield

Table 1: Chemical composition of almond shells.

Location	Ash content	Elemental composition					Biochemical composition			Reference
		C	H	N	S	O	Cell -ulose	Hemicell -ulose	Lignin	
Spain	-	-	-	-	-	-	37	32	27	(Caballero *et al*. 1996)
US	3.4	-	-	-	-	-	22.8	32.9	23.7	(Gong *et al*. 2011)
Iran	3.4	-	-	-	-	-	29.1	35.2	32.7	(Pirayesh and Khazaeian 2012)
Tunisia	-	45.6	6.2	< 0.5	< 0.5	45.4	-	-	-	(Elleuch *et al*. 2013)
-	1.65	47.8	6.3	0.44	0.028	43.6	32.3	30.1	31.2	(Molino *et al*. 2013)
Iran	0.7	49.5	6.3	0.2	0.03	43.97	33.2	24.5	25.2	(Hosseini *et al*. 2015)
China	-	-	-	-	-	-	38.47	28.82	29.54	(Li *et al*. 2018)
Spain	1.6	50.5	6.6	0.2	0.01	42.69	32.5	25.5	24.8	(Ledesma *et al*. 2018)

(-) Data not provided.

Table 2: Synthesis of activated carbon from almond shells by physical activation.

Activating compound	Particle size (mm)	Carbonization (T, °C)	Activation (T, °C)	Yield (%)	S_{BET} (m^2/g)	Reference
CO_2	3	900	875	15	1100	(González-Vilchez *et al*. 1979)
air	1.6 – 2	900/NO	300-400	17-33	11-635	(Linares-Solano *et al*. 1980)
CO_2	1.6 – 2	900/NO	750-900	6-24	388-1900	(Linares-Solano *et al*. 1980)
CO_2	1.2 - 2	750-900	825	22.0-25.5	236-1597	(Rodríguez-Reinoso and Molina-Sabio 1992)
CO_2	1.5 - 2	NO	850	8.6 - 22.3	621-1820	(Rivera-Utrilla and Ferro-Garcia 1987)
CO_2	0.13 - 0.49	NO	850	21.9	1103	(Ferro-Garcia *et al*. 1988)
CO_2	0.49 - 1.0	NO	850	-	1246	(Ferro-García *et al*. 1990)
CO_2		NO	800	30	-	(Rodríguez-Reinoso and Molina-Sabio 1992)
CO_2	2.0	700	800	7	349	(Toles *et al*. 1997)
CO_2	1.5 - 2	275/850	755-800	15.8-26.3	1005-1218	(Marcilla, Garcìa-Garcìa, *et al*. 2000)
CO_2	1.5 - 2.0	850	780	18-28	870-1060	(Iniesta *et al*. 2001)
CO_2	1 - 3	600	700	12 - 19	526 - 1090	(Plaza *et al*. 2010)
CO_2	2 - 4	400	700/800	-	364-1138	(Nabais *et al*. 2011)
CO_2	1 - 2	450	600-900	-	1310	(Omri *et al*. 2013)
CO_2	1 - 5	500-1200	500-1200	-	322-385	(Hashemian *et al*. 2014)
CO_2	0.841 - 2.0	800	800	14-23	197-560	(Toles *et al*. 2000b)
H_2O	1.0 - 3.0	NO	700	10.5-14.4	188-398	(Gergova *et al*. 1992)
H_2O	1.0 - 3.0	NO	700	17.2	574	(Gergova *et al*. 1994)
H_2O	0.84-2	700	850	-	549-587	(Thomas Klasson *et al*. 2010)
H_2O	0.841 - 2.0	700	800	7 - 21	425 -673	(Toles *et al*. 2000b)
H_2O	1-2	600	850	24.61	601	(González *et al*. 2009)
H_2O	0.23	400	600	-	143	(Flores-Cano *et al*. 2016)

(-) Not available; S_{BET}: surface area calculated by the N_2 adsorption isotherm method BET (Brunauer, Emmett and Teller 1938).

and the specific surface area are summarized in this review. As both physical and chemical activation have been reported for the production of activated carbon from almond shells, two sets of data, one for physical activation and other one for chemical activation, are presented and analysed separately.

Physical activation of almond shells

The first report on the use of almond shells for the synthesis of activated carbon at lab scale describes the two-step physical activation using CO_2 (González-Vilchez *et al*., 1979). The authors demonstrated the feasibility of using almond shells for the synthesis of activated carbon with high adsorbent capacity. The production of activated carbon from physical activation of almond shells was later confirmed and further characterized by other researchers. Activated carbons with high degree of microporosity (Linares-Solano *et al*. 1980; Rodriguez-Reinoso, *et al*. 1982; Rodríguez-Reinoso *et al*. 1984) and high adsorption capacity of heavy metals have been obtained by physical activation of almond shells with CO_2 (Ferro-Garcia *et al*. 1988; Ferro-García *et al*. 1990; Rivera-Utrilla and Ferro-Garcia 1987; Toles *et al*. 1997). Although CO_2 is the most used activating agent among researchers, steam has also been reported for the activation of almond shells. Activated carbons with the ability to absorb pharmaceutical substances (Flores-Cano *et al*. 2016) and solvents (Klasson *et al*. 2010) have been obtained through physical activation of almond shells with steam.

Overall, reports on physical activation with CO_2 show activated carbons with higher S_{BET} values than physical activation with steam (Table 3). Activation with CO_2 produces activated carbons with a maximum value of 1820 m^2/mg, compared to the maximum value of 673 m^2/mg for activated carbons obtained by activation with steam. The number of reports for activation with steam is significantly lower than that for activation with CO_2, thus explaining the lower maximum value of surface area reached, as the temperature range tested is also narrow. Consequently, it is not possible to conclude that CO_2 is more efficient than water as an activating agent of almond shells. Better results for steam activation are possible to obtain if further research is conducted and improvement of the process is possible. In fact, both substances has been compared under the same conditions and show similar results in terms of surface area and yield values for the final product (Toles *et al*. 2000b).

Research on physical activation both with CO_2 and steam has been focused mainly in the effect of thermal regime on different properties of activated carbon. Several studies have been focused on the effect of carbonization temperature on density and reactivity (loss of mass) of the activated carbon obtained by two-step physical activation with CO_2 (Iniesta *et al*. 2001; Marcilla *et al*. 2000a; Marcilla *et al*. 2000b). These studies concluded that density of activated carbon depends directly on thermal regime during the carbonization step, due to the influence of both temperature and incubation time on the amount of volatile substances produced, the fluidity of the carbon and both mass contraction and cross-linking processes. Furthermore, a two-stage thermal regime during carbonization has been shown to produce a carbon with higher reactivity, density

Table 3: Synthesis of activated carbon from almond shells by chemical activation.

Activating compound	Particle Size (mm)	Carbonization (T, °C)	Activation (T, °C)	Yield (%)	S_{BET} (m^2/g)	References
$ZnCl_2$	-	NO	500-800	30-40		(Rodríguez-Reinoso and Molina-Sabio 1992)
$ZnCl_2$	1-1.25	NO	750-850	33	736	(Aygün *et al*. 2003)
H_3PO_4	2.0	NO	170/450	33-38	955-1207	(Toles *et al*. 1997)
H_3PO_4	0.841 - 2.0	NO	170/450	34-39	822-1458	(Toles *et al*. 2000a)
H_3PO_4	-	NO	170/450	-	733	(Mohan *et al*. 2011)
H_3PO_4	2-4	NO	850	-	1358	(Chayande, Singh and Yenkie 2013)
H_3PO_4	0.2 - 1	NO	400-800	67.3-74.8	502-1128	(Izquierdo *et al*. 2011; Martínez de Yuso *et al*. 2013)
H_3PO_4	0.2 - 1	NO	400-600	66.7 - 83	789-1408	(Martínez de Yuso *et al*. 2014)
H_3PO_4/H_2O	0.23	400	800	-	103	(Flores-Cano *et al*. 2016)
H_2SO_4	0.4 - 1.0	NO	600	48	500	(Brudey *et al*. 2016)
NaOH	2 - 3	300	800	-	2054	(Ait Ahsaine *et al*. 2018)
KOH	2.0 - 3.0	300	800	-	1391.0	(Zbair *et al*. 2018)

(-) Data not available; S_{BET}: surface area calculated by the N_2 adsorption isotherm method BET (Brunauer *et al*. 1938).

and mechanical strength than a single-stage thermal regime based on heating at low speed (Iniesta *et al*. 2001), thus highlighting the importance of thermal regime during carbonization step on the internal structure of activated carbon from almond shells. A most recent research has corroborated and describe the effect of carbonization temperature on the specific surface area of activated carbon (Hashemian *et al*. 2014). The authors tested different carbonization temperatures in the range 200-1200°C, showing that surface area of activated carbon increased in the range 200-700ºC, decreased in the range 700-1200°C, concluding that the optimum carbonization temperature was 700°C. Other reports on the physical activation of almond shells with CO_2 show that carbonization at temperatures below 700°C also produces activated carbon with good adsorbent properties, high mechanical resistance and high internal surface with microporous structure, independent from the activation conditions (Nabais *et al*. 2011; Omri, Benzina and Ammar 2013; Plaza *et al*. 2010).Physical activation with steam has been also tested in order to investigate the effect of thermal regime. As shown in (Gergova *et al*. 1992; Gergova *et al*. 1994), yield and surface area of activated carbons from almond shells were dependent on temperature and duration of thermal treatment. Steam activation of almond shells at 700°C produces activated carbons showing a wide pore size distribution with a predominantly meso- and microporosity (Gergova *et al*. 1994). Yield and surface area of activated carbons from steam activation of almond shells are inversely related and depend on thermal regime (Gergova *et al*. 1992).

Different authors have also compared direct activation to the two-step process (carbonization followed by activation). Different reports on physical activation of almond shells demonstrate that two-step physical activation yield activated carbons with similar properties than that of one-step physical activation. In fact, the specific surface values for activated carbons obtained from one-step activation and two-step CO_2 activation are in the range 621-1820 m^2/mg and 197-1597 m^2/mg, respectively (Table 2). The surface area values range between 188-574 m^2/mg and 425-673 m^2/mg for one-step and two-step steam activation (Table 2).

Chemical activation of almond shells

A number of reports show the successful production of activated carbons by chemical activation. Different activating agents have been tested (Table 3). The first attempt to chemically activate almond shells was carried out with $ZnCl_2$ as activating substance (Rodríguez-Reinoso and Molina-Sabio 1992). Afterwards, a number of works on the use of H_3PO_3 were reported and recently, other activating agents have been tested, such as H_2SO_4, NaOH and KOH. Most of reports on almond shell chemical activation are performed by direct activation (one-step). Only the most recent reports include a carbonization step previous to activation (Ait Ahsaine *et al*. 2018; Flores-Cano *et al*. 2016; Zbair *et al*. 2018).

Much of the work on chemical activation of almond shells has been carried out using phosphoric acid as activating substance by direct activation, obtaining activated carbons with high specific surface values (Toles *et al*. 2000a; Toles *et al*. 1997). Different authors have tested the effect of chemical dosage and thermal regime on the structure and yield of activated carbon. For $ZnCl_2$, it has been found a direct dependence on the level of porosity of the final activated carbon and the concentration of chemical agent used (Rodríguez-Reinoso and Molina-Sabio 1992). For chemical activation with H_3PO_3 surface area depends greatly on the impregnation ratio in a defined range (Izquierdo *et al*. 2011). An inverse relationship between the impregnation ratio and temperature of activation is observed for almond shells activated with phosphoric acid; for intermediate degrees of impregnation, lower temperatures are needed and for very low degrees of impregnation, higher temperatures are needed to obtain high specific surface values (Izquierdo *et al*. 2011). These results suggest that chemical activation allows high flexibility in the distribution of pores by modifying concentration of the activating substance or the impregnation ratio. During chemical activation, the activating substance is introduced into the precursor, producing physicochemical changes in its internal structure, which reduces the need for high temperature to develop the porosity, thus allowing higher yields by reduction of the burn-off. In fact, as observed in Table 3, certain authors have achieved the production of activated carbon from almond shells by using activation temperature values around 400°C with specific surfaces above 1000 m^2/g and maintaining overall higher yields to that obtained by physical activation. Under the same experimental conditions, activated carbons obtained by chemical activation with phosphoric acid showedhigher surface area and higher yield than those obtained by physical activation with CO_2 (Toles *et al*. 1997) Additionally, it has been demonstrated that the activation in the presence of oxidizing atmosphere allows greater flexibility in the internal structure of the final product. Martínez de Yuso *et al*. 2014 obtained activated carbons with mainly microporous internal structure (70-80% microporosity) and better adsorption capacity for activation with phosphoric acid in the presence of O_2. Likewise, the activation with phosphoric acid an oxidizing atmosphere in the presence of water vapour produces activated carbons with low specific surface areas and mainly mesoporous structure (Flores-Cano *et al*. 2016).The most recent research on chemical activation of almond shells is focused on evaluating different activating agents to obtain activated carbons as absorbent of aquatic pollutants. Activated carbons obtained by activation of almond shells with sulphuric acid (Brudey *et al*. 2016), potassium hydroxide (Zbair *et al*. 2018) and sodium hydroxide (Ait Ahsaine *et al*. 2018) show high specific surface area and good absorbent properties.

Effect of lignocellulosic composition on activated carbon properties

The effect of lignocellulosic composition on carbon structure has been studied using physical activation of almond shells. Different authors have analysed the effect of thermal regime on the internal structure of almond shells both for CO_2 and steam activation. Early reports on direct activation with CO_2 (Rodríguez-Reinoso and Molina-Sabio 1992) showed that three temperature-dependent phenomena affect the carbon

structure, namely: loss of water occurs at 30-200ºC; evolution of gases and tars and formation of the basic structure of the carbon occur between 200-500ºC, accompanied with a great loss of mass and the consolidation of the carbon structure takes place at 500-850ºC, with minimal loss of material. Later, Omri *et al*. 2013 demonstrated for CO_2 physical activation of almond shells subjected to different thermal regimes, that the elimination of volatile substances coming from the decomposition of cellulose and hemicellulose takes place in the temperature range 600-800ºC, with a loss of mass depending on the temperature. They also showed that above 800°C, the yield remained almost constant due to the thermal resistance of the lignin. These results on physical activation with CO_2 are comparable to steam activation. A comparative analysis on steam activation of different lignocellulosic precursors showed that the dynamics of the formation of porous structure and the final structure of activated carbons were dependent on the raw material (Gergova *et al*. 1992). Lignin and cellulose contents were demonstrated to be responsible for the effect of thermal regime on the final structure of activated carbons (Gergova *et al*. 1994). These findings were further confirmed by (González *et al*. 2009). The authors studied the correlation between lignocellulosic composition and the thermal behaviour by comparing different raw materials under the same thermal treatment in a two-step steam activation process. They showed that solid and liquid yields were proportional to the lignin andcellulose+hemi -cellulose contents of the precursor during carbonization, respectively. During activation, the loss of material was due to devolatilization and loss of fixed carbon resulting from the activation reaction. The high rate of initial thermal decomposition observed for almond shells were due to their high content of hemicellulose, which is responsible for the production of activated carbons with high density and microporosity (González *et al*. 2009). These set of result points out that the rapid volatilization process of almond shells, due to their relative cellulose and hemicellulose content, is responsible for the low yield values obtained in general for physical activation, which are below 30% (Table 2). In fact, proximate analysis of almond shells reflects a high percentage of volatile matter, in the range 73-81% (Hosseini *et al*. 2015; Lahijani *et al*. 2013; Ledesma *et al*. 2018; Molino *et al*. 2013).

The overall results on physical activation of almond shells show a good relationship between the original texture of the precursor and the final microstructure of the activated carbon. Thermal regime plays a crucial role in the development of porosity for almond shells activated with CO_2 or steam. By contrast to physical activation, which involves an inverse relationship between surface area and product yield, for chemical activation yields have not a direct relationship with the development of porosity and it is possible to obtain activated carbons with high surface areas and high yields (Izquierdo *et al*. 2011). Overall results on chemical activation of almond shells suggest that the activating substance, together with original structure of precursor, plays a significant role in the pore size distribution, allowing more flexibility than physical activation in the production of activated carbons with different properties.

Table 4: List of substances tested for adsorption by activated carbon from almond shells.

Type of activation	Type of tested substance	Compound	Reference
Physical (CO_2)	Heavy metals	Cobalt	(Rivera-Utrilla and Ferro-Garcia 1987)
Physical (CO_2)	Heavy metals	Copper	(Toles *et al*. 2000b)
Physical (CO_2)	Heavy metals	Lead	(Ferro-García *et al*. 1990)
Physical (CO_2)	Heavy metals	Zn, Cd, Cu	(Ferro-García *et al*. 1988)
Physical (CO_2)	Organic solvents	Benzene, toluene, 1,4-dioxane, acetonitrile, acetone, methanol	(Toles *et al*. 2000b)
Physical (CO_2)	Organic solvents		(Omri *et al*. 2013)
Physical (CO_2)	Pharmaceutical compounds	Metronidazole, dimetridazole, ditriazoate	(Flores-Cano *et al*. 2016)
Physical (H_2O)	Organic solvents	Tricloroetileno	(Thomas Klasson *et al*. 2010)
Chemical (H_2SO_4)	Heavy metals	Lead	(Brudey *et al*. 2016)
Chemical (H_3PO_4)	Explosives	Trinitrophenol	(Mohan *et al*. 2011)
Chemical (H_3PO_4)	Organic compounds	Phenol	(Aygün *et al*. 2003)
Chemical (H_3PO_4)	Heavy metals	Copper	(Toles *et al*. 2000a)
Chemical (H_3PO_4)	Organic solvents	Toluene, hexane	(Martínez de Yuso *et al*. 2013)
Chemical (H_3PO_4)	Organic solvents	Benzene, toluene, 1,4-dioxane, acetonitrile, acetone and methanol	(Toles *et al*. 2000a)
Chemical (NaOH)	Organic dyes	Methylene blue, Crystal violet	(Ait Ahsaine *et al*. 2018)
Chemical/physical	Pharmaceutical compounds	Metronidazole, dimetridazole, ditriazoate	(Flores-Cano *et al*. 2016)

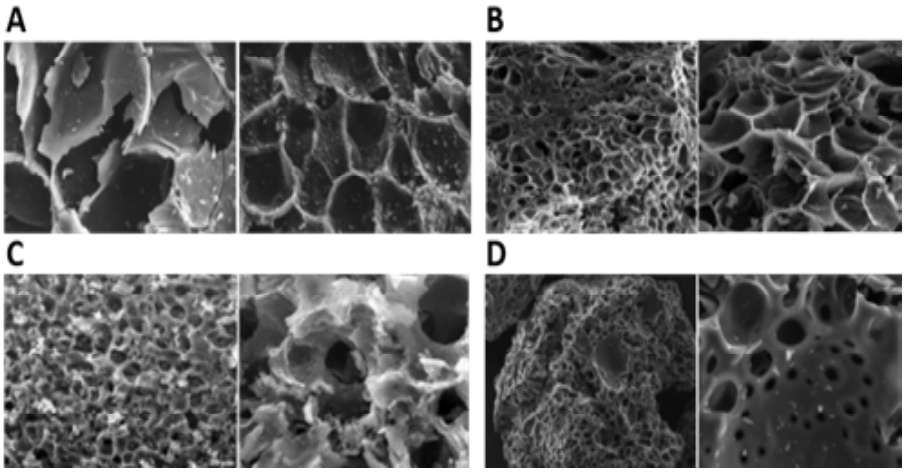


Fig 1: SEM images of almond shells activated carbons obtained under different treatments. A) Two step physical activation with CO_2 (Marcilla *et al.* 2000). B) Two step physical activation with CO_2 (Hashemian *et al.* 2014). C) Two-step chemical activation with KOH (Ait Ahsaine *et al.* 2018). D) Direct chemical activation with sulphuric acid (Brudey *et al.* 2016). Magnification is different for each image. A fragment of the original image is shown.

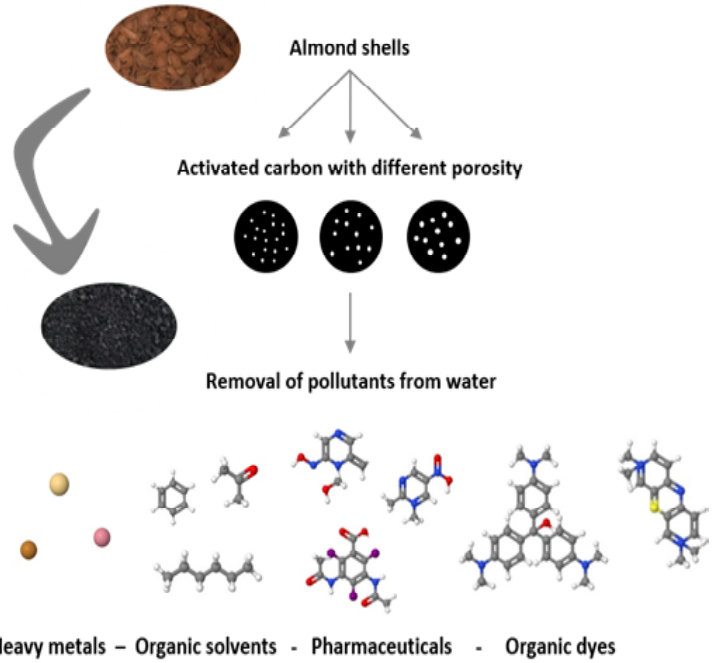


Fig 2: Schematic representation of the reviewed topic. Chemical compounds are represented by 3D models.

Independent from activation treatment, the relative hardness of almond shells, provided by the high lignin content, is manifested in the internal structure of the activated carbons (Fig 1), which display the cell structure typical of the precursor.

Potential of almond shell activated carbons to remove aquatic pollutants

Table 4 shows a compilation of substances that have been tested to study the adsorption capacity of the activated carbons produced from almond shells. Compounds with different chemical structures and sizes are adsorbed by activated carbons obtained from almond shells (Fig 2). Many reports have demonstrated the synthesis of highly microporous activated carbons with the ability to absorb small compounds, such as heavy metals and organic solvents. Other reports show the synthesis of activated carbons with ability to absorbed more complex compounds with exhibit higher sizes, such as pharmaceutical compounds. Finally, organic dyes, which require the development of mesopores, are also absorbed by almond shells activated carbons. Most of the compounds tested are substances that can produce toxic effects in the environment and usually appear in concentrations above the permitted levels in aquatic ecosystems, demonstrating the potential of almond shells in environmental remediation.

CONCLUSION

Almond shells are a very promising feedstock to be used in the industrial manufacturing of activated carbon.The properties of activated carbon obtained from almond shells in terms of surface areas, porosity and adsorption capacity are similar to that of commercially available products. From the first proof of concept (González-Vilchez *et al*. 1979), the technology of activated carbon production from almond shells has been validated at lab scale. The high flexibility in the parameters of synthesis allows the design of industrial strategies aimed to reduce costs and energy. Currently the technology of removing aquatic pollutants with activated carbon produced from almond shells has reached a technology maturation state of TRL4. Further research, both at lab scale and pilot scale, is necessary to bring the technology to a more advanced maturation state. The use of almond shells as a feedstock for the production of activated carbon will contribute to the transition to a circular economy, as involves the valorisation of agricultural organic wastes into a renewable and high valuable product, which, in turns, has a strong potential to solve current global environmental concerns, such as climate change and water/ atmospheric pollution.

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