WALAILAK JOURNAL

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Activated Carbon for Food Packaging Application: Review

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Received: 4 July 2017, Revised: 18 October 2017, Accepted: 25 November 2017

Abstract

Recently, several types of food packaging have been developed which are able to prolong shelf-life of, and maintain the quality and safety of, products. Many kinds of material have been applied to food packaging, in the forms of film, sachets, or pads, to protect, eliminate, or inhibit undesirable changes in food. Based on the increasing concern about environmental sustainability, there have been many attempts to develop a natural biodegradable food packaging. Activated carbon as a multifunctional material is an interesting alternative choice. Apart from its ability to naturally degrade, non-toxicity, and low cost, it possesses remarkable adsorption potential. Its abilities are versatile, and could be used in various application purposes. Thus, its ability strongly depends on its pore structure and surface chemistry. Although it has been known for its effect on hydrophobic substances, the modification of pore size and surface property of activated carbon could improve its affinity to hydrophilic substances. Two means of activated carbon applications in food packaging were classified, according to its adsorption and releasing ability. The first mean is the application of activated carbon for the emission of antimicrobial agents in the vapor phase and nanoparticles inside food packaging. The second mean is the application of activated carbon for scavenging of factors affecting food quality inside packaging, such as water vapor, oxygen, ethylene, and odor. In this paper, the adsorption-releasing mechanism of activated carbon on some of the antimicrobial agents and vapor phase substances are discussed. Additionally, the potential role of activated carbon in food packaging is summarized.

Keywords: Activated carbon, food packaging, food quality, adsorption, releasing

Introduction

Activated carbon (AC) is a porous carbonaceous material that has long been used as an adsorbent and carrier in medical, cosmetic, and environmental applications. According to its multifunctional adsorption properties, it is able to remove a broad spectrum of substances. Utrilla *et al.* (2001) found that modified granular-activated carbon could remove pathogenic bacterial, such as *E.coli*, from aqueous [1]. Cermakova *et al*. (2017) revealed that it could eliminate harmful toxins, like cyanobacterial toxin, from water [2]. Furthermore, Diban *et al*. (2008) proved that normal activated carbon could recover an aroma compound from processed effluent [3]. Also, many researchers have reported that it could be used to adsorb color [4], organic compounds [5], and various pollutants from the environment [6,7].

As a useful, low cost, and non-toxic material, the interest in activated carbon in food applications is increasing rapidly. As the latest trend, activated carbon has been added into various types of food products as a food additive, such as bakery goods, ice-creams, and beverages, in order to improve the food texture, color, and health benefits [8]. Moreover, it has been used in several food processing sectors. The researchers found that activated carbon could be used to recover benzaldehyde, which is an aroma in coffee [9]. It was also able to remove brown compounds from soy sauce [10] and separate bioactive tripeptide from milk casein hydrolysate [11]. However, it still has many hidden advantages that are very challenging to find and apply to food packaging.

Due to increasing consumer pressure regarding food safety and quality, manufacturers try to fulfill consumer requirements and survive tough competition. They provide more focus on food management and strategies to maintain food safety and quality, along with lowering expenses. Consequently, the demand for multi-functional food packaging which is able to maintain freshness, retard spoilage, and inhibit microbial growth in food has been dramatically increasing.

Several researches have established that the present of one or more vaporous substances in food packaging can influence the chemical mechanisms, physical mechanisms, microbiological mechanisms, and quality of food products. Many vapor phase substances or volatile compounds, including gases, food aromas, odors, smoke, alcohol, and moisture, are associated with food safety and quality. For instance, the safety and quality of food can depend on the presence of oxygen, carbon dioxide, and moisture or relative humidity in packaging. Oxygen has been considered to be the cause of oxidative rancidity, enzyme browning and metabolism of food, and oxidation of pigment that leads to changes in quality characteristics, like color, freshness, and organoleptic properties, while moisture is the major cause of spoilages from microbial growth, chemical deterioration, and changes in physical properties affected by non-enzymatic browning and enzymatic activity [12,13]. Various available technologies have been widely developed to control and eliminate vaporous substances in food packaging. Meredith *et al.* (2014) examined the effect of the modified ratio of CO_2, O_2, and N_2 gases in food packaging on the quality of chilled poultry fillets, and found that the modified atmosphere packaging (MAP) technique could help control the growth of microorganisms and prolong the shelf-life of food [14]. Another research from Haute *et al.* (2017) found that, using vacuum technique to remove gases from packaging could help prevent spoilage from microorganisms and off-odors [15]. In 2007, the ethylene scavenger from Pd-zeolite was developed by Terry *et al.* to eliminate ethylene produced by climacteric fruit, and this resulted in delay in ripening of fruits such as avocados, bananas, and strawberries [16].

Alternatively, from the mentioned techniques, one application presently used to control vapor phase substances are absorbents. The adsorption of gases and vapor through various types of absorbents has been incorporated into food via silica gel, chitosan, natural clay zeolites, and activated alumina [17,18]. Among those various renewable, biodegradable adsorbents, activated carbon in particular is an interesting multifunctional material. Many experiments have reported that activated carbon can act as a substance carrier. It can carry antimicrobial volatile compounds, such as ethanol [19] and natural extracts [20], and expose those volatile compounds to food to inhibit microorganism. Furthermore, Biswas *et al.* (2016) reported that it can carry metal nanoparticles, such as silver, and let the particle migrate to the food surface [21]. Indirectly, several researchers indicated that it also has high potential in scavenging atmospheric gases, moisture, and other substances, which can result in the interruption of microorganism growth factors. Dastgheib *et al*. (2004) proved that activated carbon could adsorb oxygen by chemisorption at low pressure (0.001 - 5 mmHg); however, at high pressure, the oxygen would be adsorbed by physisorption [22]. Puchalska *et al*. (2017) examined the ability of activated carbon in up taken carbon dioxide, and found that carbon dioxide adsorption in activated carbon could be improved by mineral acid activation [23]. Yao *et al*. (2014) confirmed that activated carbon could adsorb water vapor, and also generated a model to predict water adsorption in activated carbon [24]. Additionally, Sohn *et al*. (2009) revealed that activated carbon could be used to eliminate off-odor in food packaging [25]. However, its role in food packaging has not been promoted, and only a few applications are available on the market.

In order to support the potential use of activated carbon in food packaging applications, this paper presents an overview of activated carbon and its potential, which would lead to the understanding and acknowledgment of activated carbon vapor adsorption in food packaging.

Activated carbon

Activated carbon is the oldest kind of adsorbent in human history, from normal carbonized wood in the ancient Egyptian periods over 5700 years ago, until the activated carbon fiber used in the present day. The first charcoal, or what is technically known as porous carbon, was first produced from wood to use as a fuel. It took centuries later for the Egyptians to realize the antimicrobial and adsorption properties of carbon. Recently, activated carbon has been improved on, and has become a well know adsorbent. More than a million tons of activated carbon are produced and consumed each year. As it can efficiently remove a broad spectrum of substances, both organic and inorganic [26,27], from air, liquid, and soil by adsorption, it has been used in various fields, such as chemical engineering, pharmaceuticals, the environment, purification, and food and beverage applications.

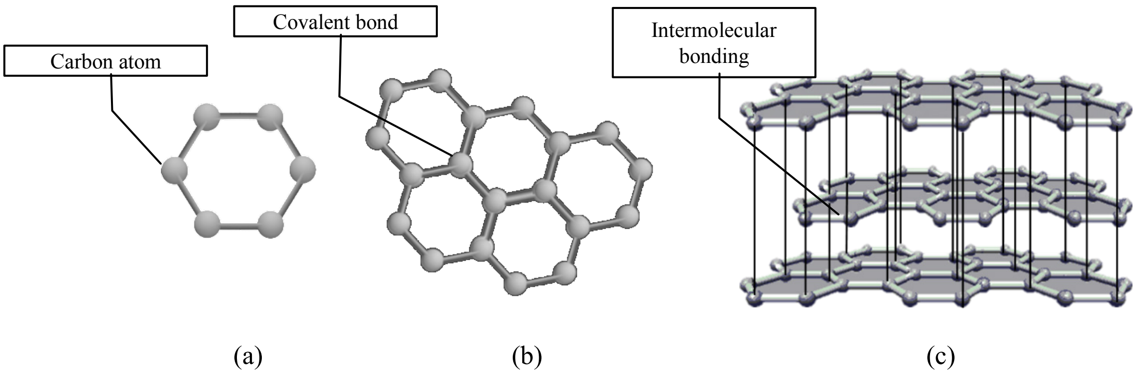


Figure 1 Hexagonal carbon atom (a), microcrystalline carbon layer (b), and activated carbon structure (c).

Activated carbon, as defined by Marsh and Reinoso in 2006, is a porosity enclosed by carbon atoms produced from a variety of carbonaceous materials for different purposes [28]. It is a black, non-toxic, rigid, amorphous microcrystalline adsorbent, distinguished by its high degree of porosity, large surface area (ranges from 500 to 2900 m^2/g), and high adsorptive capacity [29,30]. It is composed of hexagonal carbon atoms (**Figure 1a**) that covalently bond together into microcrystalline carbon layers (**Figure 1b**) which gives its surface a non-polar or hydrophobic property. The intermolecular bonding between the microcrystalline layers of activated carbon gives its structure interlayer spaces that develop into porosity (**Figure 1c**). Moreover, the bonding between functional groups, such as oxygen and hydrogen, at the edge of the carbon layer affects its surface property, pore size, and makes less ordered layers, so it is considered to be non-graphite.

Basically, it is derived from natural raw materials, both renewable materials like plant base materials such as wood [29], coconut husk [31], bamboo [32], sugarcane, rice husk [30], and wheat, and non-renewable materials, like bismuth, coal, and lignite. However, agricultural bio-waste, such as rice stem, corn crop [33], rice straw, almond shell, sewage sludge, sunflower shell, and bagasse [34], also is also used as activated carbon starting material. The production of activated carbon involves 2 steps, the carbonization process, at temperatures lower than 800 °C in the absence of oxygen, and the activation process, which plays an important role in the development of the surface area and pore volume of activated carbon. The activation process can be divided into 2 different methods; physical activation, such as being activated by a heated stream of carbon dioxide, and chemical activation, which uses chemicals, such as $ZnCl_2$, HNO_3, and NaOH, in the processing [35,36]. This makes activated carbon cheap, environmental friendly, non-chemical, and available in mass quantities. Furthermore, it can be regenerated, which can reduce the cost of products.

Characteristics of activated carbon

Many characteristics of activated carbon involve the adsorption efficiency of activated carbon. Fletcher *et al.* (2006) studied the adsorption behavior of hydrophilic and hydrophobic vapors on activated carbon, and found that the adsorption of substances is related with the activated carbon pore structure and functional group concentration, adsorptive structure, and adsorption mechanism [37].

According to activated carbon physical characteristics, many researches have developed various forms of activated carbon by using different materials and methods for specific purpose application, as presented in **Table 1**.

Table 1 Classification and application of activated carbon.

Types of AC	Shape/Particle size	Application	References
Powder AC (Fine powder)	Pulverized carbon / less than 0.18 mm	Recovery of liquid and gas	Nasehi *et al.* [38]
Granular AC (Coarse particles)	Irregular shaped/ 0.6 - 4.0 mm	Recovery, separation of liquid and gas	Rodriguez-Illera *et al*. [39]
Extruded AC (Cylindrical particles)	Cylindrical shaped/ large than 4.0 mm	Natural gas storage, off-gases from wastewater control	Duan *et al*. [40]
Activated carbon fiber (Threadlike piece)	Fabrication flexibility/ narrower pore size distribution	Removal of volatile organic compound	Das *et al*. [41]
Activated carbon cloths	Fabrication flexibility/ uniform microporosity	Removal of volatile organic compound	Ramos *et al*. [42]

However, the 2 most importance characteristics of activated carbon, which have the greatest effect on the application of activated carbon in food packaging, are pore size structure and surface chemistry.

Pore size of activated carbon

The pore size of activated carbon is the main important factor that should be determined before application of activated carbon in the adsorption process. The pore size distribution of activated carbon is directly related to the adsorption surface area. The higher the porosity, the larger the surface area of activated carbon. This can be confirmed by Sethia *et al.* (2016) who found that the activated carbon could adsorb more hydrogen when the porosity increased [43]. According to the IUPAC classification, the pore structure of activated carbon can be classified into 3 types: macropore, with a pore size larger than 50 nm, mesopore, ranging from 2 - 50 nm, and micropore, which is smaller than 2 nm (**Figure 2**) [44]. Each type of activated carbon contains different pore size distributions, according to the natural structure of the starting material and activation process. Correa *et al.* (2017) reported that the type of biomass used in activated carbon production plays a major part in the pore size distribution and surface area of activated carbon. Biomass rich in cellulose gives the largest surface area of activated carbon when compared with biomass from xylan and lignin [45]. Generally, powder-activated carbon, which is a fine particle diameter of less than 0.2 mm, mainly contains more micropore, but no macropore, while granular-activated carbon contains a mixture of all pore sizes in different ratios.

The selective adsorption of adsorbate molecule on the internal porous structure of activated carbon is controlled by the pore size. The adsorbate molecules have to be able to pass through the certain pore size of activated carbon before adsorption process occurs. Li *et al.* (2002) examined the effect of pore size distribution of activated carbon on the adsorption of organic compounds, and reported that, in order to perform the most effective adsorption, the target adsorbate diameter has to be 1.3 to 1.8 times smaller than the pore diameter [46]. For instance, water and metal ions, which have molecular sizes of around 2 -

6 angstroms, are able to pass through the micropore, while bacterial cells, which have molecular sizes larger than 10^4 angstroms, could not pass through the mesopore, and would clog at the pore wall entrance.

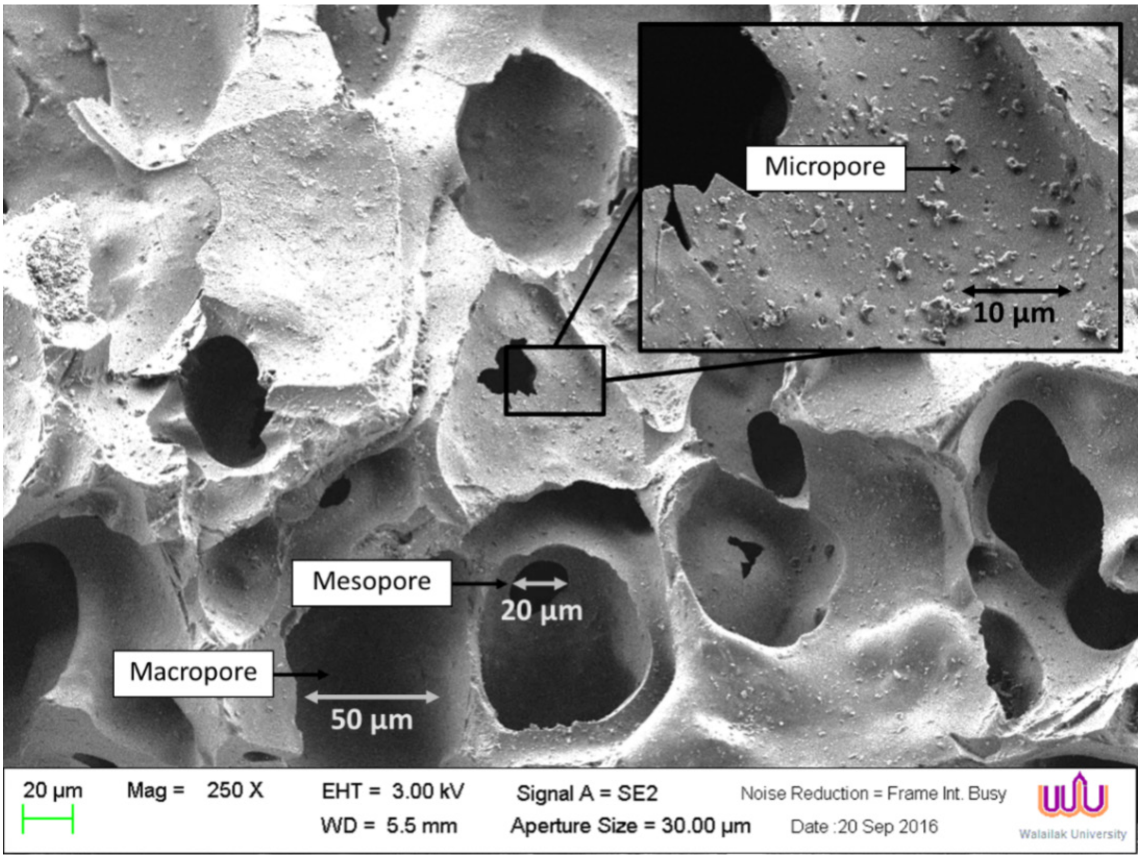


Figure 2 Pore structure of stream-activated granular bituminous coal-based activated carbon.

Moreover, as related to the size of the adsorbed molecule, the macropore is suitable for aqueous phase adsorption, and the micropore suitable for gas phase adsorption, while the mesopore is suitable for both aqueous and gas phase adsorption. The adsorption in the micropore is normally a pore-filling process, in which the adsorption capacity is controlled by the volume of the pore. For the mesopore, the adsorption process is generally due to physical interaction between the molecule and pore surface; accordingly, the mono and multilayer adsorption mostly occurs at the mesopore surface, followed by pore-filling. For the macropore, due to its vast pore space, the adsorption only happens at the pore wall surface, which is considered negligible since the adsorption area is very small compared to the mesopore, while the macropore acts like a channel for molecules to be transported into the mesopore and micropore. Therefore, using the wrong pore size could result in low adsorption capacity in activated carbon.

Surface structure of activated carbon

The adsorption of molecules into activated carbon takes place at active sites on the activated carbon pore surface. The effect of the surface chemistry of activated carbon on adsorption ability has been well recognized. Even the surface functional groups of activated carbon might be originated from the starting material; many experiments tried to modify the original surface structure of activated carbon which contained only carbon atoms and had non-polar or hydrophobic properties by using several types of chemical agents, such as zinc chloride ($ZnCl_2$) [47], phosphoric acid (H_3PO_4) [35], sodium hydroxide (NaOH) [35], potassium hydroxide (KOH), and ammonia (NH_3) [48] and physical processes, in order to enhance the adsorption capacity of the adsorbed organic or inorganic substances.

Normally, activated carbon causes 2 types of adsorption: physical adsorption and chemical adsorption. The adsorption of activated carbon is mainly physical adsorption, which is caused by weak molecular interaction, such as hydrogen bonding, Van der Waals forces, hydrophobic bonding, or dipole bond force, in which the adsorption energy is lower than 40 kJ/mol. This interaction can happen rapidly at low temperatures, and its equilibrium can easily reverse at high temperatures.

However, the presence of surface functional groups results in chemical adsorption with firmly covalent bonds. Chemical adsorption is caused by electron or atom transfer from the adsorbate molecules to the surface functional groups of activated carbon. It usually takes place at high temperatures and is generally an irreversible adsorption. Hyun Pak *et al*. (2016) established that a chemical activation process with 10 % sulfuric acid could enhance the adsorption capacity of organic compounds like benzene and toluene on activated carbon, at 18 and 47 %, respectively [49]. Another study on inorganic compound adsorption by Krishnan *et al*. (2017) revealed that the adsorption capacity of perchlorate in drinking water could be enhanced by chemical activation of activated carbon with organic acid solutions such as phosphoric acid and hydrochloric acid, which increase the adsorption capacity of the activated carbon from 3.5 mg g^{-1} to 9.8 and 9.7 mg g^{-1}, respectively [50]. The adsorption capacity enhancement of activated carbon by using chemical activation not only increases the porosity or the surface area of the activated carbon, but also results in the presence of heteroatoms from the surface functional groups on the edge of the microcrystalline carbon layers, which could increase bonding with the adsorbate molecules. Oxygen-containing and hydrogen-containing functional groups are the predominate functional groups, which might influence the acidic, basic, or neutral surface properties. For instance, the acid activated carbon (AAC) which is formed by increasing the carbon-oxygen groups, such as carboxylic, lactonic, and phenolic groups, would result in increases in the polarity or hydrophilic properties. On the other hand, Truong *et al.* (2002) confirmed that basic activated carbon which contains carbon-oxygen groups, like carbonyl, pyrone, and benzopyranyl, or nitrogen-containing groups, such as ammonia, nitrogen monoxide (NO), pyridinic, pyrrolic, and quaternarynitrogen groups, is more hydrophobic than acid activated carbon [51]. The selectivity adsorption of activated carbon is dependent on their surface functional groups, which give firm interactions with the selective compounds, and is irreversible. For example, Bian *et al.* (2015) reported having oxygen-containing groups on the activated carbon, due to its surface carbon-oxygen resonance structure, resulting in increases in hydrophilic properties and improvements in ion-exchange capacity, which meant activated carbon could play an important role in metal adsorption, such as Cd (II) ion adsorption [52]. Contrarily, basic treated activated carbon would result in the enhancement of hydrophobic organic substance adsorption. For instance, Mohammed *et al.* (2015) stated that the adsorption of benzene and toluene into KOH activated coconut shell-based carbon could be increased when treated with NH_3 [48]. Also, Shafeeyan *et al.* (2010) reviewed the effect of surface modification on the adsorption of carbon dioxide into activated carbon, which could be enhanced by nitrogen functional groups, such as amide groups, imide groups, and pyridinic groups [53].

Application of activated carbon in food packaging

The safety and quality of food in packaging involves the presence of gaseous molecules like oxygen, carbon dioxide, and moisture or relative humidity in the packaging system. These factors influence the deteriorating effects of enzyme reaction, chemical reaction, physical change, microbiological growth, respiration, the ripening process, sensory properties, and shelf-life on food products, especially fresh food that still has respiration. To maintain or control gaseous conditions in the packaging, the application of activated carbon into food packaging is a multifunctional method. Since activated carbon could act as both releaser and absorber, it could be used to expose the volatile compound, and also adsorb the gaseous molecules. As in the earlier mentioned studies, activated carbon could be particularly modified to be used in specific adsorption purposes, so it can selectively eliminate the dominant gas molecules that greatly affect the quality and safety of individual foods in packaging systems.

Contrarily, it also can release antimicrobial compounds, such as ethanol and sulfur dioxide, to prevent the growth of microorganisms that might lead to food poisoning or food spoilage. In order to describe the possible potential of activated carbon in food packaging, the application of activated carbon has been classified into 2 means, based on the adsorption and release of the substance.

The release of antimicrobial compounds from activated carbon

The adsorption-release of antimicrobial agents on activated carbon can be divided into 2 types. The first is the adsorption of liquid antimicrobial agents that could be released out of activated carbon by volatilization, such as ethanol and natural extracts. The released antimicrobial vapor could be diffused in the packaging atmosphere and accumulate on the food surface before antimicrobial activity happens. The second one is the adsorption of metal nanoparticles, such as silver nanoparticles, on the surface of activated carbon, which needs surface contact to transfer the nanoparticles from the activated carbon surface to the food surface.

Release of volatile antimicrobial compound by activated carbon

Of general antimicrobial substances that are used worldwide, ethanol and essential oils are known as volatile organic compounds that have antimicrobial ability and have been applied in many foods, for example, in ethanol pads, seen mostly in bakery packaging, and as an essential oil coating on many types of fruit.

Essential oil vapor has recently become famous for its excellent antimicrobial activity in the medical field. However, it is unfamiliar for application in the field of food, because of its limitation on the application method, and its service life that needs to be improved. A study from our laboratory, the Innovation of Essential Oil for Food Safety and Packaging, at Walailak University, showed that the activated carbon can be adsorbed and release essential oil vapor. Moreover, the released essential oil vapor still has antifungal activity against several types of post-harvest pathogenic molds, such as *Penicillium*, *aspergillus flavus*, *aspergillus niger*, and *Rhizopus spp*. In **Figure 3**, the antifungal activity of peppermint oil vapor released from activated carbon against *A. flavus* is shown. It can be seen that there is no mycelium growth presence in **Figure 3b**, which was exposed to the peppermint oil vapor, while in **Figure 3a**, mycelium growth can be observed.

(a) (b)

Figure 3 Antimicrobial activity of peppermint oil vapor released from activated carbon against *A. Flavus*.

Another volatile antimicrobial compound is ethanol. The adsorption and desorption ability of ethanol on activated carbon had been examined by Albero *et al*. (2009). They found that activated carbon could adsorb ethanol, and 98 % of the adsorbed ethanol could be easily released at room temperature in the vapor phase [54]. For the interaction between activated carbon and ethanol molecules, it has been reported that the adsorption of ethanol molecules, which are polar molecules, on activated carbon could be achieved by physical adsorption of van der Waals force, hydrophobic-bound force, or hydrogen bonds that could be easily broken at room temperature. This could be proven by the adsorption energy (ΔE) of ethanol on activated carbon, which is less than 40 kJ/mol (ranging from 5 - 5.5 kJ/mol). Moreover, they found that the adsorption capacity of ethanol on activated carbon could be increased by increasing oxygen surface functional groups, but the interaction between the oxygen groups and ethanol on activated carbon would result in the decrease of the releasing ability of ethanol (to approximately 91 %) [54]. The adsorption and releasing ability of ethanol on activated carbon was confirmed by Uddin *et al*. (2014) and Bouzid *et al*. (2016), who generated an adsorption model of ethanol onto activated carbon [55,56]. However, there have been no studies on the effect of the released ethanol on antimicrobial activity.

Release of nanoparticles by activated carbon

Another example is the release of metal nanoparticles from activated carbon to inhibit bacterial growth. The effectiveness of metal nanoparticles on antimicrobial activity has been recognized. Many works have tried to study the antimicrobial activity of activated carbon coated with various types of nanoparticles, as shown in **Table 2**.

Table 2 Antimicrobial activity of metal nanoparticle-impregnated activated carbon.

Source of AC	Activation agent	Metal nanoparticle	Inhibited microbial	Ref.
Corncobs	H_3PO_4	AC/Ag	*E.coli*	Altintig *et al*. [33]
Chestnut shells	$ZnCl_2$	Ag-AC	-	Altintig *et al*. [36]
Activated carbon	-	Ag-NP	*E.coli*	Biswas *et al.* [69]
Coconut shell	Physical activation	Ag/AC	*E.coli*	Zhao *et al.* [70]
Fishtail palm seed	H_2SO_4	Pb-AC Zn-AC Ag-AC	*E.coli,* *S.aureus,* *C.albicans, P.aeruginosa* and *S. epidermidis*	Saravanan *et al*. [57]

The results revealed that activated carbon was able to release the nanoparticles and exhibit antimicrobial activity against many kinds of microbials in both solid and aqueous phase applications in the form of granular activated carbon, powder activated carbon, or activated carbon fiber.

The vapor phase molecule scavenging of activated carbon

Food products in food packaging can be divided into 2 types, according to its respiration behavior, which are respiring food, such as fresh fruits and vegetables, and non-respiring food, such as grains, meat, and processed food. The surrounding gaseous conditions in the food packaging system have different influences on the food quality and safety. For respiring products, oxygen is an important factor needed for the respiration process, in which carbon dioxide, ethylene, and water vapor are produced as byproducts. Low oxygen content in food packaging reduces respiration rate, and that results in the retardation of the ripening process and the senescence of fruit and vegetables. Also, the removal or inhibition of ethylene in storage environments plays a key role in maintaining quality and prolonging of the postharvest life of many fresh products. Ivanov *et al*. (2005) stated that ethylene content of only 20 μL/L (ppm) is enough to trigger unwanted ripening processes in climacteric fruits [58]. So, removal of ethylene could prolong the shelf-life of fruit and vegetables. Activated carbon has been applied to reduce the level of ethylene and to maintain the quality of many fruits and vegetables during storage, such as tomatoes and broccoli [59,60].

On the other hand, for non-respiring products, the quality and safety of food products largely depends on oxygen and water vapor content (moisture content). High oxygen content accelerates oxidation reaction, resulting in off-odor, color change, and nutrition loss. Moreover, it provides suitable conditions for aerobic spoilage microorganisms which cause food spoilage and food illness. Also, high levels of moisture content provides free water molecules that could be used in enzymatic reactions, chemical reactions, and microbial growth, causing product degradation, spoilage, and reduction in product quality. Furthermore, it affects the texture of food, which becomes soft or shriveling.

Accordingly, in order to maintain the quality and safety of the product in food packaging, the levels of oxygen, ethylene, and relative humidity or water vapor should be reduced or controlled. Additionally, in some products, the odor of the food is an important factor that is used to indicated the quality and sensory characteristics of the product. In this review, a case study of activated carbon in release and adsorption of the factors affecting food quality and safety in the packaging is discussed, as per the following.

Adsorption of oxygen by activated carbon

There are many techniques used to control the level of oxygen in fruit and crop storage in order to maintain or improve fruit and crop quality. Using oxygen absorbers is one of the methods that can remove oxygen, or residual oxygen, from the storage conditions, resulting in the minimization of quality change. A variety of materials can be used for oxygen adsorption. Usually, commercial oxygen absorbers are based on oxidation reactions of the chemical, like iron powder bases or ascorbic acid bases, or enzyme reactions, like glucose oxidase/catalase bases, which can absorb and reduce oxygen to less than 0.01 %. However, chemical absorbers have a potential hazard. They are non-edible and cannot be used with liquid products. Alternatively, as an inexpensive, versatile, durable, non-toxic, natural, safe, and effective adsorbent, activated carbon has a high potential to be applied to oxygen removal in agricultural crop packaging.

Activated carbon has a high potential to be applied to oxygen removal in food packaging. Actually, activated carbon has a hydrophobic surface, which is attractive to and physically adsorbs non-polar molecules, including oxygen. Due to unsaturated carbon atoms at the edge of the graphite-like layers, activated carbon can rapidly form a stable covalent bond with oxygen, as shown in **Figure 4**, resulting in weak interaction with carbon-oxygen functional groups like the carbonyl and hydroxyl groups.

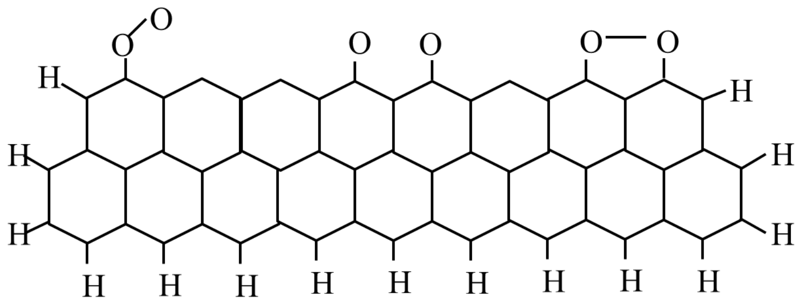


Figure 4 Different forms of oxygen adsorption at the edge of the activated carbon layer (Adapted from Truong *et al.* [51])

However, Dastgheib *et al.* (2004) revealed that the chemisorption of activated carbon normally occurs at low pressures, while physisorption generally occurs at higher pressures [61]. Additionally, they showed that the chemisorption of activated carbon could be influenced by the surface functional groups and porosity of activated carbon. Correspondingly, Phillips *et al.* (1998) found that activated carbon could adsorb high amounts of oxygen in the present of nitrogen gas at 25 °C by using adsorption energy of around 125 kcal/gmol O_2 which is very high, and considered to be a chemically-bound force (≥ 19 kcal/gmol) [62]. Moreover, Aroua *et al.* (2008) reported that oil palm shell-based activated carbon could adsorb oxygen of around 0.51 cm^3/g, but the adsorption capacity could be increased to 8.30 cm^3/g by chemical impregnation with polyethyleneimine (PEI) [63].

For the effect of porosity on oxygen adsorption in activated carbon, in fact, oxygen molecular weight is approximately 32 g/mol, and its molecular diameter is about 300 pm, which is able to penetrate through the micropore, which has a 7 - 8 times larger diameter [64]. So, for the adsorption of oxygen in the air, using powder-activated carbon, which has more micropore distribution, might give higher efficiency than using granular-activated carbon. To support this, Dastgheib *et al.* (2004) revealed that the results from a comparison of the adsorption capacity between 2 types of activated carbon that mainly contained mesopore (mesoporous AC) and macropore (macroporous AC) structure.

The results showed that, even though mesoporous AC has less pore volume, it exhibits more surface area and can adsorb more oxygen than macroporous AC, as shown in **Table 3**.

Table 3 Pore volume and surface area of macroporous and mesoporous granular-activated carbon.

AC	Pore volume (cm^3/g)	Surface area (m^2/g)
Macroporous	0.868	1251
Mesoporous	0.700	1332

However, Zhou *et al.* (2005) said that the pellet-activated carbon that was made from pressed powder-activated carbon can be used to enhance oxygen storage in an oxygen tank better than powder-activated carbon since, as at the same given volume, the pellet has more bulk density than the powder-activated carbon, it can adsorb more oxygen than the powder form. Thus, the volume of adsorbed oxygen using pellet-activated carbon increased approximately 2 times. A lot of information about oxygen adsorption on activated carbon at different temperatures (118 - 313 K) and pressures (0 - 10 MPa) has been developed by Zhou *et al.* (2005). This showed the possibility of activated carbon to be applied in a wide range of agricultural crop conditions, from cold room storage to normal ambient temperatures [65].

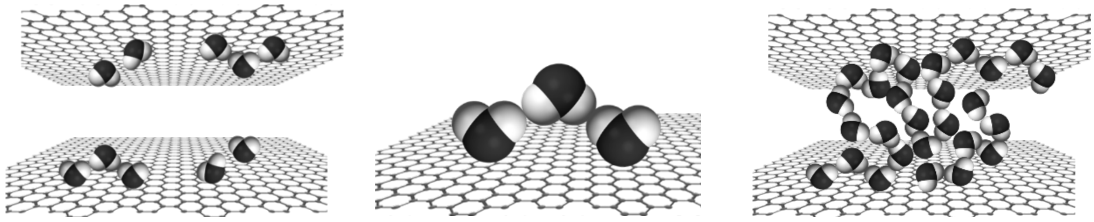
Adsorption of ethylene by activated carbon

Cao *et al.* (2015) developed an ethylene scavenger that used activated carbon as a supporter [59]. Activated carbon was chosen because it is cheap and has high adsorption capacity. To support the adsorption capacity of the ethylene on activated carbon, Bailén *et al.* (2006) compared the adsorption capacity of ethylene between granular-activated carbon and powder-activated carbon [66]. The results of this study showed that granular-activated carbon (GAC) could adsorb more ethylene than powder-activated carbon (PAC). The reason why GAC had higher adsorption capacity than PAC could be explained by the diffusion of ethylene through the activated carbon particle. Granular-activated carbon contained a mesopore and macropore, which allowed a higher diffusion of air containing ethylene to pass through the particle into the internal surface of the activated carbon in which the adsorption of ethylene occurred. Even the ethylene adsorption capacity of activated carbon was very low when compared to another adsorbent, such as potassium permanganate ($KMnO_4$), zeolites, or clays, but its adsorption capacity could be improved by impregnating it with metal particles, such as palladium (Pd) or copper (Cu), which act as catalysts and have influence on the ethylene oxidation mechanism.

The studies from Cao *et al*. and Bailén *et al*. showed that the removal of ethylene by activated carbon based ethylene scavengers in broccoli and tomato storage conditions not only retarded the loss of chlorophyll content that leads to the yellowing of the broccoli and loss of redness in tomatoes, but also enhanced the firmness of tomatoes and prolonged the shelf-life of both broccoli and tomatoes.

Adsorption of water vapor by activated carbon

Naturally, activated carbon by itself as a hydrophobic adsorbent has a very low affinity to polar molecules like water vapor, and exhibits negligible moisture adsorption, as shown in **Figure 5a**. However, the application of activated carbon to adsorb water vapor could be improved by modification of activated carbon surface functional groups, in order to decrease its hydrophobicity. Wang *et al.* (2013) found that the adsorption of water vapor depended on the amount of surface acidic functional groups in low humidity (low pressure), and pore size distribution in high humidity, conditions [67]. The modification of activated carbon with chemical, oxygen, carbon dioxide, or steam during the activation process could create an acidic surface by interaction with carbonyl, hydroxyl, or carboxyl functional groups. The increase in oxygen-carbon bonding (acidic group) will reduce the hydrophobicity of the activated carbon, and lead to ability in water adsorption. Muller *et al*. (1996) expressed that the water adsorption mechanism on activated carbon contained 2 mechanisms; firstly, at low pressure, only a few molecules of water could be adsorbed in the activated site (surface functional group) of the activated carbon surface by intermolecular force (**Figure 5a**). Then, the adsorbed water molecules would form extended water-water hydrogen bonds that acted as a bridge to chemically bind more water molecules (nucleation sites) (**Figure 5b**) and result in the increase of pressure in the pore. Capillary condensation in the pore of activated carbon then occurs by the formation of water clusters, as shown in **Figure 5c** [68].



(a) (b) (c)

Figure 5 The configuration form of water molecule on activated carbon pore surface at low pressure (a) at the nucleation site (b) and at high pressure (c) (Adapted from Müller *et al.* [68]).

However, at moderate humidity (50 - 60 % RH) the interaction between water vapor and activated carbon could be strengthened by nitrogen basic sites, as shown in **Table 4**. Moreover, at high relative humidity, activated carbon can uptake more water vapor than at low relative humidity, since, at high %RH, more water molecules can interact with each other, and cause a strong water-water force that promotes adsorption. Accordingly, modified activated carbon shows high potential as a moisture adsorbent to apply in food packaging.

Table 4 Modification of activated carbon for water adsorption.

Raw material	Modification method	Improving ability	References
Bamboo	Oxidation with HNO_3	Improve water vapor adsorption capacity (0.05 - 0.2 g H_2O/g) especially at low %RH	Wang *et al*. [67]
	Ammonization with NH_3	Improve water vapor adsorption capacity (0.01 - 0.8 g H_2O/g) especially at high %RH	
Cattle manure compost	Zinc chloride activation	Maximum water vapor adsorption capacity approximately 0.8 g H_2O/g at 100 %RH	Qian *et al*. [47]

Adsorption of odor by activated carbon

Off-odor is one of the critical aspects that are used to indicate the quality of food products. For consumers, an off-odor is undesirable. This unpleasant smell is a mixture of low molecular volatile organic compounds with hydrophobic properties, which occur from degradation of food by microorganisms or chemical reactions like lipid oxidation. Activated carbon has long been known for its ability to eliminate off-odor. Nowadays, it is used to eliminate bad smells in home refrigerators. Also, it is suitable for application in food packaging. Sohn *et al*. (2009) reported that the application of powder-activated carbon in irradiated ground beef packaging could eliminate off-odor that happened through the irradiation process [25]. Moreover, from sensory evaluation, most consumers prefer irradiated ground beef that is kept with activated carbon to normal beef. As can be seen in **Table 5**, some major volatile components of odors in packaging containing activated carbon is decreased, in both non-irradiated and irradiated samples.

Table 5 Odor preference and major volatile compounds of ground beef with treatments.

Compound	Non-irradiated raw meat		Irradiated raw meat	
	Without AC	With AC	Without AC	With AC
Pentane	42.50	31.87	84.47	66.00
3-Methylbutanal	25.37	-	72.23	50.07
2-Methylbutanal	28.77	-	55.17	45.73
EthanolBenzene	31.23	15.67	-	-
Hexanal	222.07	227.10	297.33	384.33
Total volatile	551.13	565.04	747.93	738.71
Odor preference	2.25b	4.75a	3.25b	6.00a

Future perspectives

From the case studies, this review attempts to present the possibility of activated carbon being applied in food packaging. Activated carbon has several advantages over other materials. It is durable and has high mechanical strength. It is well known for its high capacities of adsorption. Moreover, it is made from renewable materials, and is natural, eco-friendly, able to be reused, and is a low price. It could be locally produced by using waste organic material. It is non-toxic, edible, and odorless. Particularly, it is multifunctional. In packaging containing food and activated carbon, activated carbon could release adsorbed antimicrobial agents into the packaging to inhibit pathogenic or spoilage bacteria. Meanwhile, after the activated carbon releases the antimicrobial agent out, free carbon atoms on the activated carbon surface could adsorb gaseous molecules such as oxygen, water vapor, ethylene, or odor, which are factors affecting both food quality and food safety. Such processes could occur by using only activated carbon. This idea leads to efficiency in food quality and safety control by using material that can be locally produced, which results in the sustainable improvement of local manufacture and local economy.

Conclusions

The adsorption ability of activated carbon greatly depends on the pore size and surface chemistry of activated carbon. The modification of activated carbon pore size and surface chemistry makes activated carbon able to adsorb various specific types of substances. According to its ability, activated carbon has high potential to be applied in food packaging to maintain food quality and control food safety. Its antimicrobial emission ability gives it advantages for inhibiting the growth of bacteria on food in food packaging. On the other hand, its adsorption capacity makes it able to eliminate factors affecting food quality, such as oxygen, water vapor, and ethylene, which are the cause of food deterioration and senescence. This causes shelf-life extension of food products in packaging systems containing activated carbon.

Acknowledgements

The author would like to thanks the Thailand Research Fund (TRF) through Research and Researcher for Industries (RRI) (Grant. No. PHD58I0040), Timber Engineering of Krabi Co.,Ltd., and Walailak University, for financial support.

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