Environmental Chemistry for a Sustainable World

Grégorio Crini · Eric Lichtfouse *Editors*

Green Adsorbents for Pollutant Removal

Innovative materials

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Editors
Grégorio Crini
Laboratoire Chrono-environnement,
UMR 6249, UFR Sciences et Techniques
Université Bourgogne Franche-Comté
Besançon, France

Eric Lichtfouse
CEREGE, Aix Marseille Univ, CNRS, IRD,
INRA, Coll France
Aix-en-Provence, France

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Preface

> A further aspect of water pollution control is the treatment methods by which this control is to be achieved. The term BATNEEC is now used and means Best Available Technology Not Entailing Excessive Cost. It is likely that adsorption will find its way into this group of water treatment technologies. (Gordon McKay 1995)

Over the past three decades, there has been an increasing interest in the phenomenon of contaminant sequestration by nonconventional green adsorbents using oriented-adsorption processes. This phenomenon has a high potential for applications in water and wastewater treatments. Liquid-solid adsorption using green adsorbents can be simply defined as the removal of contaminants from solutions using products and by-products of biological, agricultural, and industrial origin. Green adsorbents represent cheap filter materials often with high affinity, capacity, and selectivity to interact with contaminants. They are abundant and already available in most places in large quantities. The list of green adsorbents is extremely extensive, including carbons from agricultural solid wastes and industrial by-products; agro-food wastes; industrial by-products; natural products, e.g., clays, hemp, flax, and cotton; and biological materials such as dead biomass, living plants, algae, biopolymers, and fungi.

Cultivation of *Lepista nuda*, named “blue foot” in French, an edible mushroom, on a composted substrate. (Copyright: INRA, Jacques GUINBERTEAU 2018)

This book is the second volume of two volumes on *Green Adsorbents for Pollutant Removal* published in the series *Environmental Chemistry for a Sustainable World*.

Written by 80 international contributors coming from 23 different countries who are leading experts in the adsorption field, these two volumes show a typical selection of green materials used in wastewater treatment, with emphasis on industrial effluents. The first volume provides an overview of fundamentals and design of adsorption processes.

This second volume focuses on innovative materials. The first chapter by Nadia Morin-Crini et al. presents hemp-based materials for metal removal. The second chapter by Leticia B. Escudero et al. describes the biosorption of metals and metalloids on various materials. In Chap. 3, Ioannis Anastopoulos et al. present the use of leaves for metal removal. Then, Anita George Varghese et al. discuss the recent advances in cellulose-based adsorbents used in environmental purposes in Chap. 4. Ramonna Kosheleva et al. (Chap. 5), Liliana Giraldo et al. (Chap. 6), and Viraj Gunarathne et al. (Chap. 7) review activated carbons from food wastes, aerogels and bones, and municipal solid waste biochar as efficient materials for pollutant removal, respectively. Biosorption of dyes onto microbial biosorbents is presented by Uttariya Roy et al. in Chap. 8. In Chap. 9, Shweta Kulshreshtha discusses the use of mushroom biomass to remove pollutants. A detailed review of green adsorbents for removal of antibiotics, pesticides, and endocrine disruptors is given by Akeem Adeyemi Oladipo et al. in Chap. 10. In Chap. 11, Prashant Pandey and Vipin Kumar Saini review the use of pillared interlayered clays as innovative materials for pollutant removal. Finally, in Chap. 12, Dharmendra K. Gupta et al. discuss the use of green adsorbents for radioactive pollutant removal from natural water.

The audience for this book includes students, environmentalists, engineers, water scientists, and civil and industrial personnel who wish to specialize in adsorption technology. Academically, this book will be of use to students in chemical and environmental engineering who wish to learn about adsorption and its fundamentals. It has also been compiled for practicing engineers who wish to know about recent developments on adsorbent materials in order to promote further research toward improving and developing newer adsorbents and processes for the efficient removal of pollutants from industrial effluents. However, the book is not meant to be an extensive treatise on adsorption and adsorbents. For example, particular aspects on modeling or biosorption are not considered because the reader can find abundant information on these topics in the literature. The book will serve two main functions: a readable and useful presentation not only for undergraduate and postgraduate students but also for the water scientists and engineers and a convenient reference handbook in the form of numerous recent examples and appended information.

The editors extend their thanks to all the authors who contributed to this book for their efforts in producing timely and high-quality chapters. The creation of this book would not have been possible without the assistance of several friends deserving acknowledgment. They have helped by choosing contributors, by reviewing chapters, and in many other ways. Finally, we would like to thank the staff at Springer Nature for their highly professional editing of the publication.

Besançon Cedex, France — Grégorio Crini
Aix-en-Provence Cedex, France — Eric Lichtfouse

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Chapter 5
Activated Carbon from Food Waste

Ramonna Kosheleva, Athanasios C. Mitropoulos, and George Z. Kyzas

Contents

Abstract Activated carbons are considered to be the most successful adsorbent materials due to their high adsorption capacity for the majority of pollutants, e.g. dyes, heavy metals, pharmaceuticals, phenols. They possess large surface area, and different surface functional groups, which include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers. Therefore, they are regarded as good adsorbents both in liquid and gas phases. The most widely used carbonaceous materials for the industrial production of activated carbons are coal, wood and coconut shell. These types of precursors are quite expensive and often imported, in many places; hence making it necessary, particularly for developing countries, to find a cheap and available feedstock for the preparation of activated carbon for use in industry, drinking water purification and wastewater treatment. In order to reduce the synthesis cost of activated carbons, some green final products are recently proposed, using several suitable agricultural by-products (lignocellulosics) – i.e. including olive-waste cakes, cattle-manue compost, bamboo

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R. Kosheleva · A. C. Mitropoulos · G. Z. Kyzas (✉)
Hephaestus Advanced Laboratory, Eastern Macedonia and Thrace Institute of Technology,
Kavala, Greece
e-mail: amitrop@teiemt.gr

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materials, apple pulp, potato peel – as activated carbon precursors. In this chapter, special attention is given to activated carbons based on some of agricultural wastes from the Mediterranean region, which can be characterized as green.

5.1 Introduction

With the growth of mankind, society, science, technology our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem. Environmental pollution is the contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected. The introduction of contaminants into the environment causes harm or discomfort to humans or other living organisms damaging the environment. Environmental pollution is categorised in three main groups; air, water and soil pollution. In general, any human activity releases pollutants, with the most severe being sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone, volatile organic compounds, insecticides and herbicides, food processing waste, pollutants from livestock operations, heavy metals, chemical waste and others. With the rapid push of globalization, wide application of new technologies and the increasing pressure from resource and environment, it has been realized that the natural environment is irreversible and critically important for urban development, thus is the call for urban transition towards greening (McGranahan 2015). Green technology, also referred to as environmental technology or clean technology, is an encompassing term. It deals with using science and technology in order to protect the environment. A lot of techniques fall under this term such as the use of green chemistry, environmental monitoring, and more. Specifically, Green Chemistry is defined as the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances (Sheldon 2008), governed by 12 principles. One of them is the usage of renewable feedstock for material synthesis (Anastas and Eghbali 2010). The major renewable feedstock on the planet both for material and energy is bio-mass, the material available from living organisms. This includes wood, crops, agricultural residues, food (Kamm et al. 2000; Fornasiero and Graziani 2011). Research of the past two decades have shown that bio-mass as feedstock has many applications including transport fuel production (McKendry 2002), chemicals (Tong et al. 2010), electricity generation (Chaudhuri and Lovley 2003) as well as materials production for usage in many industrial applications (Agbor et al. 2011).

According to Environmental and Energy Study Institute, a list of some of the most “common” bio-mass feedstocks is comprised of (i) grains and starch crops (sugar cane, corn, wheat, sugar beets, industrial sweet potatoes), (ii) agricultural residues (corn stover, wheat straw, rice straw, orchard pruning), (iii) food waste (waste produce, food processing waste), (iv) forestry materials (logging residues, forest thinning), (v) animal byproducts (tallow, fish oil, manure), (vi) energy crops (switchgrass, hybrid poplar, willow, algae) and (vii) urban and suburban wastes (municipal solid wastes, lawn wastes, wastewater treatment sludge, urban wood wastes, disaster debris, trap grease, yellow grease, waste cooking oil). Biomass derived from plants, the so-called lignocellulosic bio-mass, is the most abundant and bio-renewable bio-mass on earth (Isikgor and Becer 2015). The major components of woody plants, as well as grasses and agricultural residues are three structural polymers; lignin (10–25%), hemicellulose (20–30%) and cellulose (40–50%) (Pérez et al. 2002). Apart of these three components, which vary regarding the source, there are also some minor non-structural components such as proteins, chlorophylls, ash, waxes, tannins (in the case of wood) and pectin (in most of fibers). Among the three fractions of the lignocellulosic materials, lignin has been identified as the main component in lignocellulosic bio-mass responsible for the adsorption process (Mohamad Nor et al. 2013). Specifically, lignocellulosic wastes are a low cost natural carbon source for the production of various materials including activated carbon. In addition, lignocellulosic precursors and biomass sources have become important materials to produce activated carbon because their use creates many benefits, mainly environmental. Nowadays, it is possible to find numerous research papers devoted to the synthesis characterization and applications of novel precursors to produce activated carbon. Except from the treatment conditions, the biomass source determines many of the properties of the final material. In fact, although the lignin is considered to be the major contributor for activated carbons production, properties such as the mean pore size versus the specific porous volume are effected by all precursor's components whatever is its weight contribution (Cagnon et al. 2009).

Activated carbon is a well-known material used in an increasing number of environmental applications; namely water and waste water treatment, gas filters, green gases capturing. High surface area, a microporous structure, and a high degree of surface reactivity make activated carbons versatile adsorbents, particularly effective in the adsorption of organic and inorganic pollutants from aqueous solutions ref. In recent years, scientific interest on lignocellulosic precursors for activated carbon production used as storage material of several gases as well as catalytic reactor has been increased (Fiuza et al. 2015; Ruiz et al. 2017), leading to replacement of less cost effective materials such as metal organic frameworks (Llewellyn et al. 2008; Kuppler et al. 2009; Sumida et al. 2012) or less eco-friendly (in sense of production of raw material or activation treatment) such as fly ash (Lu and Do 1991).

Activated carbon is the generic term used to describe a family of amorphous carbonaceous adsorbents with a highly crystalline form and well developed internal pore structure. Any organic material can be the starter material (precursor) of activated carbon production after being subjected to carbonization and activation of its organic substances (Bansal and Goyal 2005). Traditionally, typical precursors for activated carbon production were coal (Teng et al. 1998), peat (Veksha et al. 2009), and lignite (Shrestha et al. 2013). Mainly due to economical as well as environmental issues, the replacement of those raw materials with low-cost and environmental friendly precursors is mandatory. To this end, in recent years there has been a growing interest in the production of activated carbons from agricultural and forestry wastes (Dias et al. 2007). In the context of the present chapter, as agricultural wastes are considered residues of agricultural by products (not for consumption) i.e. peels, stems and fruit core. The following sections describes the treatment and activation processes of carbonaceous materials of various precursors. Furthermore, comparison of final properties regarding treatment conditions as well as the source is provided too. Related industrial applications are discussed.

5.2 Activated Carbon from Lignocellulosic Biomass

The production of activated carbons from lignocellulosic materials is a two phase process; it involves carbonization at low temperatures (700–800 K), in the absence of oxygen, to eliminate volatile materials, and subsequent activation at higher temperatures (1100–1300 K) to increase the porosity and the surface area of the solid. The process of activation can be carried out through different ways: (i) with chemical agents (e.g. KOH, H_3PO_4, $ZnCl_2$), known as chemical activation; (ii) with CO_2, air or water vapor for physical or thermal activation or; (iii) these two methods combined (Marsh and Rodríguez-Reinoso 2006). Although physical activation is a low-cost process with a lower environmental impact, chemical activation of is preferred because of porosity improvement (adsorption capacity) of the final material (Rodríguez-Reinoso and Molina-Sabio 1992).

Recent studies have shown that extraction of valuable solutions from agricultural by product could also act as reagents of biochar activation, minimizing further the cost and the impact to the environment (Treviño-Cordero et al. 2013). To this end, the pre-treatment process of biomass should follow (among others) the following criteria: (i) affordable with low energy and resource consumption, (ii) low water and chemical consumption in order to minimize or even eliminate liquid waste stream, (iii) low operation risk and safe to operate as well as (iv) low cost of the construction materials in order to be considered cost effective and eco-friendly. It is worth to mention that the challenge is to develop adsorbents which are not only cost effective and environmentally friendly, but also possess high efficiency, selectivity and regeneration δrate and cycles (Ince 2014). There is numerous literature about the influence of preparation conditions of carbonaceous materials on the physicochemical properties of the produced material e.g. surface area, pore size distribution. Another critical factor is physicochemical properties of the precursors itself; depending on weather conditions, harvesting methods and even on the season that it is collected, agricultural precursors' properties such as initial moisture, oxygen content, and derived components fraction of cellulose, hemicellulose, lignin may vary (Huggins et al. 2011; Balan 2014).

5.3 Lignocellulosic Precursors for Activated Carbons Process

Activated carbons have a highly developed porosity and an extended interparticulate surface area. As it was already mentioned, preparation involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800 °C in an inert atmosphere and the activation of the carbonized product. Thus, all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the conditions of the carbonization and activation processes.

Carbonization of bio-mass has a number of advantages over common biological treatments regarding time and required equipment. Also, high process temperatures can destroy pathogens and such potential organic contaminants as pharmaceutically active compounds that could be present (Libra et al. 2011). On the other hand, the preparation of activated carbon is usually conducted at relatively high temperatures, consequently there is also a considerable risk of overheating, leading to complete combustion of the carbon (Foo and Hameed 2011). Besides of pyrolysis in furnaces, there have been developed other carbonization technologies; to name a few of the most promising technologies there is hydrothermal carbonization, microwave heating. When compared to fermentation and anaerobic digestion, hydrothermal carbonization is referred to as the most exothermic and efficient process for carbon fixation. In addition, some feed stocks are toxic and cannot be converted biochemically. Microwave technology is gaining importance as a promising technology for research and industrial applications. Microwave heating offers a potential means of cost reduction as it is capable of reducing the heating period, energy consumption, and gas consumption. Additionally, microwave irradiation may promote rapid and precise temperature control and compact equipment size. However, application of microwave technology for carbonization process has not been implemented until recently, hence there are very few studies that report its use for preparation of activated carbon (Foo and Hameed 2011; Thue et al. 2016).

Physical activation of carbonized material involves the implementation of hot gases or water vapor steams (Román et al. 2008; Zhang et al. 2014; Vivo-Vilches et al. 2015). This generally is carried out by using one or a combination of carbonization in the presence of an inert gas to convert this organic precursor to primary carbon, which is a mixture of ash, tars, amorphous carbon, and crystalline carbon, and activation/ oxidation where high temperature in the presence of carbon dioxide, steam is required. Undesirably, in the step of carbonization, some decomposition products or tars are deposited in the pores (Rodríguez-Reinoso and Molina-Sabio 1992; Maciá-Agulló et al. 2004).

Chemical activation on the other hand, prohibits the formation of tar; in this way a carbonized product with a well-developed porosity may be obtained in a single operation (Lozano-Castelló et al. 2001; Kalderis et al. 2008). Chemical activation takes place prior to carbonization wherein the agricultural waste is impregnated with certain chemicals, which is typically an acid such as H_3PO_4, a strong base such as KOH, and NaOH or a salt such as $ZnCl_2$. Then the agricultural precursor is carbonized at lower temperatures (450–900 °C). Number of studies conducted, indicate that the carbonization/activation step proceeds simultaneously with the chemical activation (Milenković et al. 2009; Ludwinowicz and Jaroniec 2015). It is also believed that the chemical incorporated to the interior of the precursor particles reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way the conversion of the precursor to carbon is high, and once the chemical is eliminated after heat treatment, a large amount of porosity is formed (Kumar and Jena 2016; Shamsuddin et al. 2016). Chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating the material. The chemical activation method presents many advantages over the physical activation method and therefore it has been employed enormously in many studies when the preparation of activated carbon from agricultural wastes is concerned. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation (Aygün et al. 2003; Valix et al. 2004). On the other hand, from the economical point of view, chemical activation requires the use of agents that rise the total cost of the production process (Zhang et al. 2004; Dias et al. 2008).

As it was mentioned in previous section, the suitability of an activated carbon for different applications is matter of many parameters. Although carbonization/activation conditions play the most important role in adsorbent's efficiency, they are not the only major contribution towards porous structure of activated carbon; the original nature and structure of the precursor also is significant. The proximate analysis along with ultimate analysis of the precursor are common properties investigated in the related literature. Proximate analysis involves the determination of moisture content, volatile matter, fixed carbon and ash content of the raw material (Jin et al. 2012; Koay et al. 2013).

From the economical aspect, biomaterials are promising precursors for adsorbents because of their abundance. To preserve their cost effective treatment, especially regarding large scale applications, the source should be taken into account. For instance, although some agricultural wastes (i.e. coconut shells (Shrestha et al. 2013; Nandeshwar et al. 2016), hazelnut husk (Imamoglu and Tekir 2008; Milenković et al. 2009; Kwiatkowski and Broniek 2017), rice husk (Foo and Hameed 2011; Menya et al. 2018; Rwiza et al. 2018) and others) are acknowledged as highly efficient precursor, in many cases it has to be imported, resulting in an increase of cost. Therefore, agricultural/household residuals, including fruit and vegetable peels are considered as good alternatives. Moreover, regions such as Mediterranean, can take advantage of residuals produced from regional commodities like olive or peach stones. Properties of such agricultural wastes are collected

Table 5.1 Surface area of various agricultural wastes abundant in Mediterranean region

Precursor	Surface area (m^2/g)	Reference
Orange peels	1090	Fernandez et al. (2014)
Orange peels	1477	Xie et al. (2014)
Olive stones	1031.5	Román et al. (2008)
Olive stones	790.25	Kula et al. (2008)
Cherry stones	1200	Lussier et al. (1994)
Peach stones	608	Duranoğlu et al. (2010)
Potato peels	904–1041	Kyzas et al. (2016)

form recent studies. Table 5.1 summarizes some of the most investigated agricultural wastes as activated precursors; only obtained surface is presented because properties such as pore size, contaminant uptake and are omitted because such characteristics depend mainly on process conditions. Effect of process conditions will be discussed in a following section.

5.4 Characterization of Lignocellulosic Based Activated Carbons

As it was mentioned, characterization of adsorbents derived from lignocellulosic based materials should be comprised of both physicochemical analysis of precursors and textural analysis after processing. Analysis of raw material determining moisture, percentage of main polymeric structure as well as density and other compounds presence is required. Proximate analysis conducted prior to carbonization phase and ultimate analysis after that provide important information about the final product properties (Wilkins et al. 2001; Fu et al. 2013; González and Pliego-Cuervo 2013; Kumar and Jena 2016). The impact factor of those measurements on the understanding of effects that treatment processes have is discussed in depth through literature.

Given an example is the work by Sentorun and his associates (2006), where it was found that the initial sulfur content influenced the obtained porosity properties and surface area of the final material. One interesting outcome of the specific study is the effect of raw material treatment on the final properties (after activation). Here, the apricot stones were dried under two different environments prior activation process; sun-dried and SO_2-dried apricot stones. As it is illustrated in Figs. 5.1 and 5.2, the two pre-treatment methods resulted with very different materials regarding porosities and internal microstructure. Investigation of the effect of process variables such as activation temperature, soak time, and particle size range on microstructural characteristics of the adsorbent was studied as well. The highest BET surface area carbon (1092 m^2/g) was obtained from the low sulfur content (0.04%) apricot stone with a particle size range of 1–3.35 mm at the activation conditions of 800 °C for 4 h.

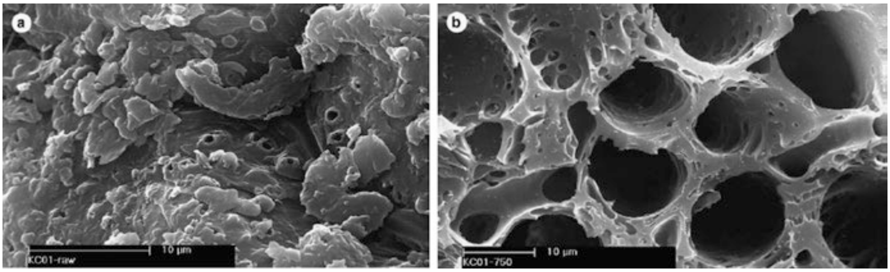


Fig. 5.1 Scanning Electron Microscopy (SEM) micrograph of sun-dried apricot stone (**a**) prior activation, (**b**) after activation; prior activation the sun-dried raw material presents almost no porosity and a thick wall structure while after activation a wide porosity is observed. (Reprinted with permission by Elsevier (Şentorun-Shalaby et al. 2006))

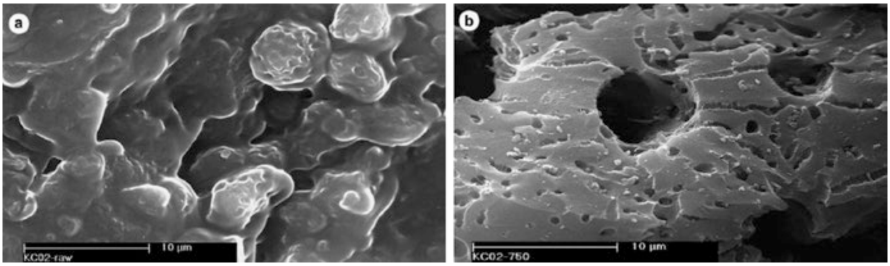


Fig. 5.2 Scanning Electron Microscopy (SEM) micrographs of SO_2-dried apricot stone (**a**) prior activation, (**b**) after activation; high ash and Sulphur content of the precursor leads to the appearance of anon-porous cloudy surface (**a**) while activated material does not present a well-developed porous network compared to sun-dried material (Fig. 5.1). (Reprinted with permission by Elsevier (Şentorun-Shalaby et al. 2006))

Temperature during carbonization phase plays significant role in the final material's properties. Biochar yield increases with a decrease in pyrolysis temperature, an increase in the residence time, and a preferable low heating rate (Tripathi et al. 2016). The highest treatment temperature is regarded to have the greatest effect on the physical properties of biochar produced (Mukome et al. 2013). In a recent study, Palanisamy et al. reported that biochar of *C. vulgaris* prepared at higher temperatures (450–600 °C) contained a higher proportion of organic matter (C, H and N) than those produced at lower temperatures.

Kyzas et al. (2016) conducted experiments involving potato peels for metal ion removal. In this work, potato peels were cleaned and dried for 24 h for moisture reduction. The activation agent used was H_3PO_4. All conditions kept same (amount of dried material, activation agent) and three samples were produced at different heating temperature (400, 600, 800 °C). Comparison of the samples regarding, among others, the surface area of the material, revealed that the higher surface area resulted for the sample treated at 600 °C, while at higher temperature the surface area of the sample was less than 1 m^2/g. Size distribution analysis confirms the

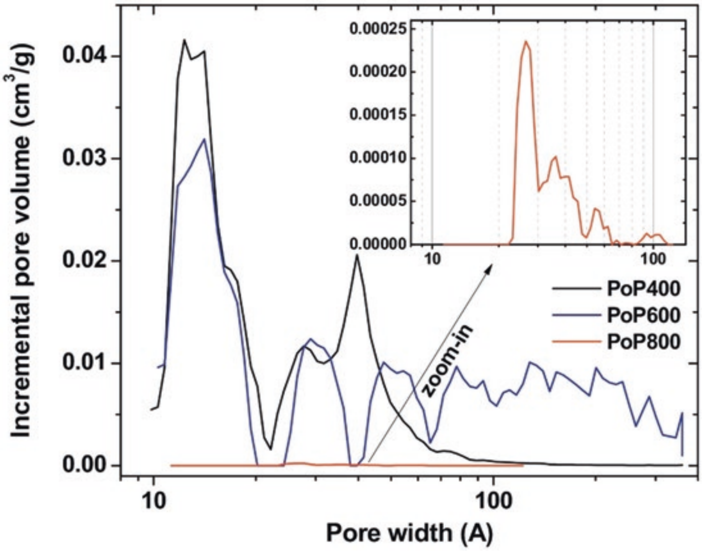
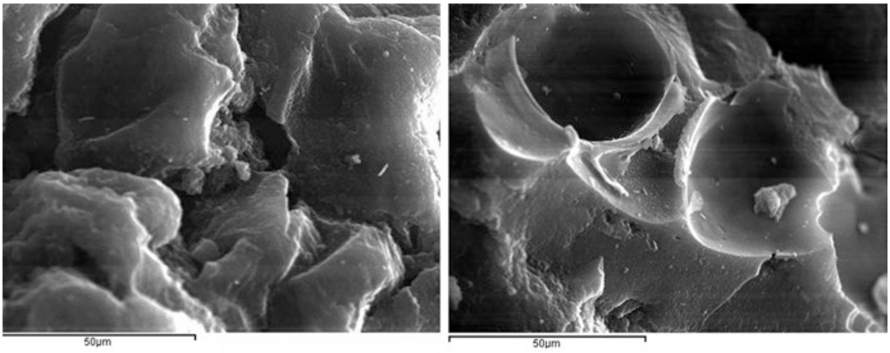


Fig. 5.3 Pore size distribution curves of potato peels (denoted as PoP in the graph) carbons activated at 400 °C, 600 °C and 800 °C. PoP400 is defined by micro-meso porosity while PoP600 curve shows a structure combined of all three groups of pores. (Reprinted with permission by Elsevier (Kyzas et al. 2016))



(a) (b)

Fig. 5.4 Scanning Electron Microscopy (SEM) micrographs of surface morphology of potato peels samples; (**a**) potato peels treated at 400 °C, (**b**) potato peels treated at 600 °C. (Reprinted with permission taken by Elsevier (Kyzas et al. 2016))

aforementioned results as it is shown in Fig. 5.3. This last observation may be attributed to overheating of the sample leading to precursor's combustion.

The two samples were further examined by means of SEM (Fig. 5.4). As it is obvious from Fig. 5.4 (taken by Kyzas et al. 2016), potato peels treated at 600 °C perform larger porous. Relevant studies have been conducted including many different lignocellulosic materials and the influence of treatment conditions on the produced activated carbons.

Köseoğlu and Akmil-Başar (2015) reported the effect of treatment temperature on orange peel activation. Chemical activation using zinc chloride ($ZnCl_2$) and potassium carbonate (K_2CO_3) was performed. The activation temperatures and impregnation ratios were selected at the range of 500–1000 °C and 1:1, respectively. The carbon content of activated carbons resulted 70% while BET surface area of activated carbons prepared with K_2CO_3 and $ZnCl_2$ activation is 1352 and 1215 m^2/g, respectively. An increase in the temperature for both K_2CO_3 and $ZnCl_2$ led to a decrease in the yields of the activated carbons. The overall yield of material, estimated to be greater for activated carbons by $ZnCl_2$ than those activated by K_2CO_3, although it does not play any role in performance.

Besides, the activation temperature, the time and heating rate are important preparation variables for obtaining activated carbon with specific characteristics (Yorgun and Yıldız 2015). According to the literature review, chemically activated carbons have developed surface areas ranging from very poor surface area to as high as 3000 m^2/g, a broad range of pore size distribution from a few nm to a few micrometers and pore volume from 0.1 to 2.5 cm^3/g. From released scientific reviews, it is possible to note that activation with alkaline agents produces the highest surface area values. Secondly, treatment with acids and acid salts supplies also high surface areas; for instance, impregnation of Chinese fir using H_3PO_4 yields to 2518 m^2/g, impregnation of lignin with H_2SO_4 produces 1946 m^2/g, the use of $FePO_4$ on peach stone provides 2160 m^2/g, use of $CaHPO_4$ on pistachio shell supplies 1919 m^2/g, and the use of K_2CO_3 on wasted tea yields 1722 m^2/g. Finally, activation of coconut shells with $ZnCl_2$ and with a mixture $ZnCl_2/H_2O_2$ yields to 2450 and 2050 m^2/g, respectively. Additionally, depending on the activation agent, the carbon surface exhibits numerous functional groups, mainly acidic, which favor specific interactions allowing it to act as an ionic interchanger (Toles et al. 2000; Bharathi and Ramesh 2013). Physical activation of lignocellulosic chars with steam or CO_2 causes different effects on the development of microporosity. In early stages of activation process, CO_2 develops narrow micropores, while steam widens the initial micropores of the char. At high degrees of burn-off, steam generates activated chars which exhibit larger meso- and macropore volume than those prepared by CO_2 (Liou 2010). As a result, CO_2 creates activated chars with larger micropore volume and narrower micropore size than those activated by steam. At this point is possible to note that physically activated carbons have smaller surface area values than those obtained from chemical (i.e H_3PO_4, KOH, NaOH and $ZnCl_2$) activation. However, there have been reported high surface area adsorbents from lignocellulosic precursors activated physically (Maciá-Agulló et al. 2004). On the other hand, oxidizing treatments using water steam and CO_2 atmospheres, yield average surface area values, comparable with those obtained from the activation using acid salts; such as K_2CO_3 or $CaHPO_4$. In this sense, water steam of date pits yields surface area of 1467 m^2/g and CO_2 activation of olive stones yields 1355 m^2/g (Román et al. 2008). Other option to design activated carbons with controlled porosity and larger surface areas is the combination of both, chemical and physical activations, simultaneously or by step (Şentorun-Shalaby et al. 2006). For instance, simultaneous physical and chemical activation process have been described a few years ago to improve the mesoporosity in activated carbons from lignocellulosic materials, such as coconut shells and palm stones. According to the authors, $ZnCl_2$ and KOH can be used as chemical activating agent coupled with CO_2. However, the use of $ZnCl_2$ has two advantages of higher mesoporosity and much higher yield of activated carbon. But, the emission of heavy metallic zinc may cause serious environmental problem. KOH/CO_2 activation has a significant contribution to the development of microporosity as well as mesoporosity. In their work, $ZnCl_2/CO_2$ activation of coconut shells yields surface area of 2191 m^2/g whereas the KOH/CO_2 activation of palm stones yields 2390 m^2/g.

5.5 Activated Carbon for Water Purification and Wastewater Treatment

Various industrial processes such as mineral processing, metal mining, tanning in the leather industry, dyeing in textile industry and pigment manufacture, contribute in the discharge of pollutants which can be classified as inorganic (heavy metals, sulphates, nitrates), organic (dyes, phenols, pesticides) and biological (viruses, bacteria).

There have been developed many processes that have been utilized to remove chemical pollutants from different aqueous matrices include, but not limited to, membrane filtration, precipitation, ion exchange, solvent extraction and adsorption (Fu and Wang 2011). Some of the drawbacks associated with these processes include: low removal efficiencies, high cost of regeneration, deposition of sludge, high energy demand, and high reagent requirements, amongst others. Multiple researches lend credence to the postulation that adsorption still remains one of the preferred techniques for pollutant removal from aqueous media since it is safer and easier to use (Cooney 1998).

Over the years, the literature has been enriched with various applications which are based on the adsorption techniques for the removal of pollutants from aqueous waste streams. This amount of knowledge has shown that agricultural-based adsorbents are promising alternatives to the conventional treatment techniques because of their inherent advantages such as minimization of chemical or biological sludge, high efficiency for dilute solutions, no additional nutrients requirements, ease of operation, possibility of adsorbent regeneration,and ultimately, the fact that these materials are non-hazardous to the environment contributes to their growing popularity (Yu et al. 2000; Celik and Demirbaş 2005; Demirbas 2008). This insistence for the use of adsorption as a technique for decontamination of aqueous environments is mainly due to the availability of biomaterials/biomass used as adsorbents, high adsorption capacities and the almost zero cost.

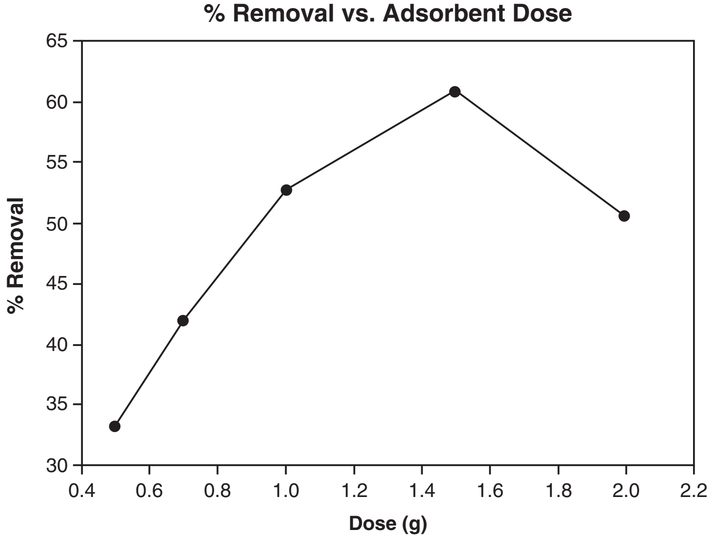


Fig. 5.5 Effect of adsorbent dose on dye removal efficiency. (Reprinted with permission by Springer (AbdurRahman et al. 2013))

5.5.1 Dyes Removal

Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, to color their products. As a result, they generate a considerable amount of colored wastewater. Besides aesthetic issues, dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration. Among side-effects, there are allergic dermatitis, skin irritation, cancer, mutation.

AbdurRahman et al. (2013), studied the removal of various dyes from textile wastewater by adsorption on orange peels. Obtained results indicate that the adsorption of dyes onto orange peels is influenced by pH values, amount of adsorbents and contact time. Also, the adsorption of dyes onto orange peels follows the Langmuir isotherm model. Additionally, it is reported that for higher removal of dyes from textile effluents adsorbent dose of 1.5 g was favorable (Fig. 5.5). The uptake of the dye increased with increasing contact time and the optimum contact time was obtained at 2 h. Also, the adsorption was found to be higher for pH 7 (Fig. 5.6). Authors concluded that even though the removal efficiency of orange peels is not much higher than other bio-adsorbents, it is preferred for its available.

Another work has been conducted for removal of methylene blue from an aqueous solution (Amela et al. 2012) by biosorption on banana and orange peels waste. Kinetic study is also carried out to observe the effects of various process parameters. The maximum values of adsorption capacities for activated banana peel was 19.671 and 18.647 mg/g for natural banana peel at pH 4–8, 20 °C. The results follow kinetic of pseudo second-order rate equation (Fig. 5.7). The suitability of the

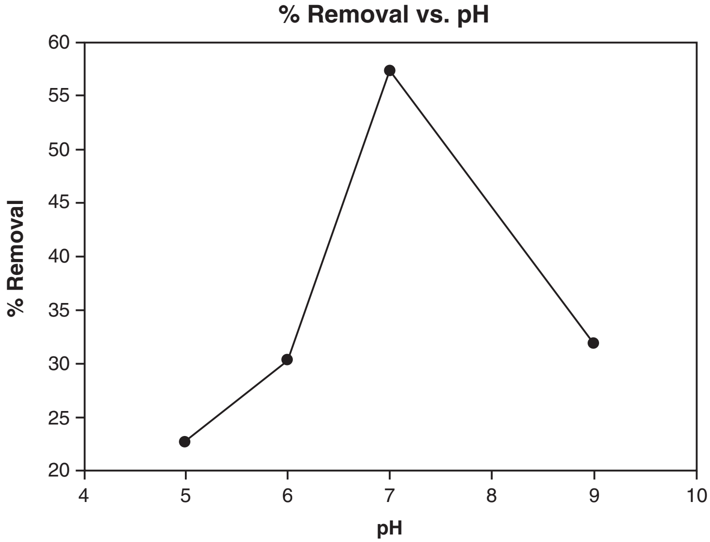


Fig. 5.6 Effect of pH on dye removal; the adsorbent dosage was 1.5 g (previously found) for 90 min of contact time. (Reprinted with permission by Springer (AbdurRahman et al. 2013))

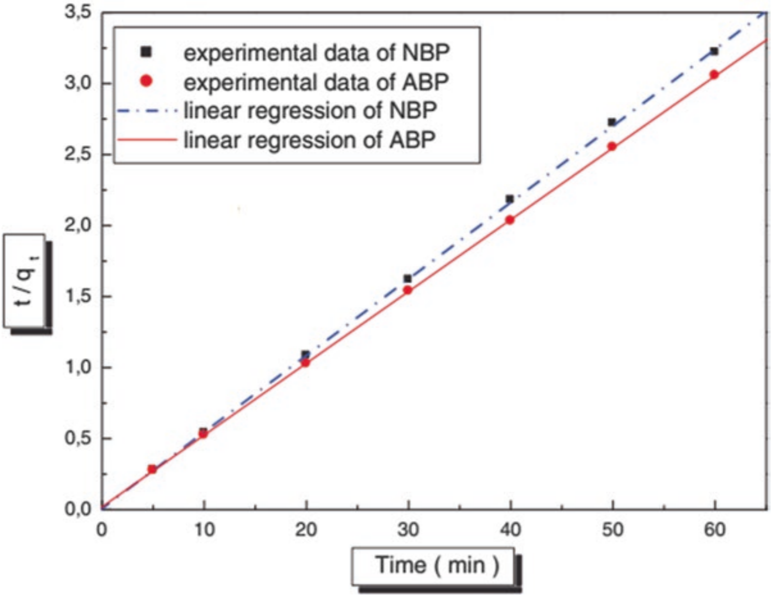


Fig. 5.7 Kinetics of Methylene blue ions onto banana peels (activated and natural –ABP, NBP respectively) test for pseudo second order equation. (Reprinted with permission by Elsevier (Amela et al. 2012))

adsorbent was tested by fitting the adsorption data with four isotherms, namely Freundlich, Langmuir and Temkin. The characteristic parameters for each isotherm have been determined. The Freundlich equation represented the best fit of experimental data for activated banana peel than the other isotherm equations, and Langmuir equation described the adsorption of natural biosorbent.

Namasivayam et al. (1998), examined the adsorption of direct red and acid brilliant blue by waste banana pith. Varying the agitation time, dye concentration, adsorbent dose and pH results were obtained; adsorption capacity was 5·92 and 4·42 mg dye per gram of the adsorbent for direct red and acid brilliant blue, respectively. Adsorption of dye followed first-order kinetics. An acidic pH was favorable for the adsorption of both dyes. An alkaline pH was favorable for desorption of the dyes.

Removal of ultramarine blue dye from aqueous solution using yam peels waste was investigated in the study conducted by Owamah et al. (2013). The effect of adsorbent concentration, dye concentration, time and pH were evaluated. Maximum adsorption occurred at pH of 10. A general increase in adsorption with increase in adsorbent concentration, dye concentration, time and temperature, respectively was also reported. The pseudo second order model with R^2 of 0.98 indicates that adsorption occurred mainly by intra-particle diffusion. The Freundlich and Langmuir isotherms were found suitable for describing the adsorption.

Valorization of olive stones as an agricultural waste into an efficient granular activated carbon for the removal of Methylene blue in batch and fixed bed modes from aqueous solutions was proposed by Benallou Benzekri et al. (2018) The activated carbon preparation was carried out in two steps: an impregnation with 50% phosphoric acid at 170 °C for 2.5 h followed by physical activation using steam at 750 °C. Activated carbons resulted in specific surface areas of 1031.5 and 1029.2 m^2/g, respectively. The Langmuir model was found to describe correctly the isothermal adsorption of Methylene blue for both adsorbents and resulted in adsorption capacities of 107 and 121 mg/g for the commercial one.

Chemically modified olive stones investigated regarding the sorption efficiency towards cadmium and safranine removal from their respective aqueous solutions. Treated Olive stones material was prepared by treatment of olive stones with concentrated sulfuric acid at room temperature followed up by a subsequent neutralization with 0.1 M NaOH aqueous solution. Results indicated that treated olive stones exhibited efficiency in terms of sorption capacities toward the two pollutants (128.2 and 526.3 mg/g for cadmium and safranine, respectively).

In order to valorize olive stones and to show its potential use in the sorption of two dispersed dyes, it was transformed in activate carbon and characterized by Hemsas et al. (2014). The adsorption capacity of activated carbon for the dyes removal was found to be affected by the solution’s pH. Acidic pH was found the favour disperse dyes removal. Over 95% removal was achieved for both the dyes at pH 3. The equilibrium time for both dyes was 30 min. Both Langmuir and Freundlich isotherms could be used to describe the adsorption of the dyes. Freundlich adsorption model succeeded in fitting the adsorption isotherms of dyes on olive stones activated carbon in single-solute systems, and prediction of the competitive adsorption behavior of dyes with the Freundlich-based Sheindorf-Rebuhn-Sheintuch model gave acceptable results.

Uğurlu et al. (2007) studied the removal of a reactive dye from aqueous solution by adsorption onto activated carbon from olive stone. Different amounts of activating agent ($ZnCl_2$) and adsorbent particle size were studied to optimize adsorbent surface area. The adsorption experiments were conducted at different process parameters such as adsorbent dose, temperature, equilibrium time and pH. The experimental results showed that at equilibrium time 120 min, optimum pH ranged between 3 and 4, and adsorbent dosage was 2.0 g per 200 mL. While the kinetic data support pseudo-second order, a pseudo-first order model shows very poor fit. In addition, the thermodynamic parameters such as isosteric enthalpy of adsorption $(\Delta H_{ads})_y$, isosteric entropy of adsorption $(\Delta S_{ads})_y$ and free energy of adsorption ΔG0ads were calculated. BET surface area measurements were made to reveal the adsorptive characteristics of the produced active carbon. The surface area of the activated carbon produced with 20% w/w $ZnCl_2$ solution was 790.25 m^2/g.

Survey on the feasibility of the biosorption of two acid dyes (Acid blue 113 and Acid black 1) from aqueous solution using biomass prepared from potato peel waste was attempted by (Hoseinzadeh et al. 2014). Adsorption isotherms were constructed and the kinetics of dye adsorption were studied. Langmuir and Freundlich isotherms, pseudo-first-order, and pseudo-second-order kinetic models were studied. The maximum biosorption was observed at a pH of 2 and 3 for Acid blue 113 and Acid black 1, respectively. The biosorption of two dyes increased with increasing contact time and reached equilibrium after two hours, approximately. Pseudo-second-order kinetic and the Langmuir isotherm model was shown to have better fit for the adsorption of Acid blue 113 and Acid black 1 on used potato peel waste.

Interesting findings are also provided by Atttia et al. (2008), in their work of activated carbon production from peach stones. The acid used for activation was H_3PO_4 at constant temperature but at different concentrations. The obtained results of the materials characteristics such as porosity, surface area reveal that impregnation ratio effects positively the process. On the other hand, increase of temperature conditions and post heat treatment effect negatively the same properties. Equilibrium adsorption of methylene blue proved good uptake of the bulky dye, which improved considerably with impregnation concentration that was related to enhanced porosity. Increased impregnation ratio improved column performance, as well as forcing N_2 pyrolysis or extra heat-treatment. Activated carbon impregnated with 70% H_3PO_4 and carbonized at 500 °C exhibited the best properties which prevailed upon raising treated dye concentration to 150 and 200 mg/L, although degraded its capacity due to the limited mass of adsorbent and to the short contact time.

5.5.2 Heavy Metals Removal

The release of heavy metals into our environment is still large. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise toxic to human beings and ecological environments, include chromium, antimony, copper, lead, mercury, cadmium, manganese. Studies on heavy metal adsorption by activated carbon from agricultural wastes have shown remarkable removal efficiency even compered to commercial ones (Babel and Kurniawan 2004; Kołodyńska et al. 2017). Among others, most common metals constituting in water pollution are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg) and their ions. Related studies are presented for heavy metals adsorption by activated carbons from various fruit and vegetable peels as well as stones that can be found abundant in Mediterranean region.

According to Khalfaoui and Meniai (2012), orange peels can efficiently remove copper ions from aqueous solutions. In fact the use of orange peels without any pretreatment leads at the most a copper retention percentage of the order of 75%, whereas percentages over 99% could be achieved by means of chemical activations with sulfuric acid, caustic soda, methanol and acetic anhydride. Remarkably, results showed that saturation was reached after 10 and 5 min, for the cases of no pretreatment and the chemical activation of the orange peels, respectively. The pH study indicated that a value between 4 and 6 seemed to be the most adequate. The results did also show that the copper initial concentration value did have an influence on the retention capacity for the natural solid support. The sorption kinetic study showed that the process could be considered of a pseudo-second order, whereas the obtained equilibrium data were best fitted to the Freundlich model.

Liu et al. (2013) have conducted experiments of cysteine-modified orange peel for the removal of Cu(II) from aqueous solutions compared to diethylenetriamine-modified orange peel. Both materials were systematically evaluated via their capabilities for adsorbing Cu(II), including the key influential parameters such as initial pH, contact time and initial Cu(II) concentration. This work suggests that the sorption of Cu(II) onto both materials fits well with the pseudo-second-order equation, and the corresponding sorption isotherm can be classified to a Langmuir. The maximum capacities of both materaials for adsorbing Cu(II) were found to be 95.23 and 83.68 mg/g, respectively, about three times higher than that of unmodified orange peels. The sorption efficiency of cysteine-modified orange peel drops by merely about 3% after five cycles, implying a promising usage in the removal of Cu(II) from wastewater in practice.

The performance of a microporous activated carbon prepared chemically from olive stones for removing Cu(II), Cd(II) and Pb(II) from single and binary aqueous solutions was investigated by Bohli et al. (2015). Adsorption kinetic rates were found to be fast and kinetic experimental data fitted very well the pseudo-second-order equation. The adsorption isotherms fit the Redlich–Peterson model very well and maximum adsorption amounts of single metal ions solutions follow the trend

Pb(II) > Cd(II) > Cu(II). In another work, Bohli et al. (Bohli and Ouederni 2016) modified surface structure of activated carbon from olive stones using ozone (O_3) in the gaseous phase and in liquid phase using nitric acid (HNO_3) were examined. The activated carbon parent exhibits a high surface area of 1194 m^2/g and shows a predominantly microporous structure. They also revealed that acidic treatment lead to fixation of high amount of surface oxygen functional groups, thus making the carbon surface more hydrophilic. The obtained data from Co(II), Ni(II), and Cu(II) heavy metal ions removal were well fitted to the Redlich-Peterson and Langmuir equation. Further investigation on ability to remove metal ions from binary systems presented an important maximum adsorbed amount as compared to single systems.

Potato peels charcoal (PPC) was investigated as an adsorbent of Cu(II) from aqueous solutions by Aman et al. (2008). Study of the effects of various parameters such as temperature, pH and solid liquid ratios concluded to an optimum pH value found to be 6.0. The thermodynamic parameters such as standard Gibb’s free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated by applying the van’t Hoff equation. The equilibrium data at different temperatures were analyzed by Langmuir and Freundlich isotherms.

Although there is a great amount of literature for lignocellulosic activated carbons used efficiently in aqueous solution, development of such adsorbents for gas phase applications is in immature level. The main drawback for gas phase applications of lignocellulosic based activated carbon was considered the low surface area of produced material. Nowadays, research on surface modification of activated carbon from agricultural precursors has open the way for efficient application in air pollution control (Mohamad Nor et al. 2013). The potential use of those adsorbents as catalysts for flue gas, gas storage material of CH_4, CO_2 and other has attract scientists’ interest for further study. Reports for efficient CO adsorption (Grigor’ev et al. 2003), CO_2 capture (Fiuza et al. 2015) and other flue gas compounds (H_2S, NO_x) (Ghouma et al. 2017).

Among the various harmful gases, nitrogen oxides (NO_x) have a negative impact through the smog and acid rain formations as well as the decrease of the superior ozone layer (Wilkins et al. 2001; Blondeau et al. 2005). The most recent work for NO_x adsorption from automotive gas exhaust was conducted by Ghouma et al. (2017). In this study, adsorption of NO_2 at room temperature and very low concentration was performed onto three different activated carbons. The importance of textural and surface properties was realized. The results obtained during the different experiments indicate that both of these properties are responsible of NO_2 uptake and reduction to NO. The reduction rate of NO_2 is found to be very high when the activated carbon is prepared by H_3PO_4 activation. Adsorption capacity was found to be higher for one of the subjected activated carbons, attributing this fact to the presence of high amount of basic groups. The difference observed for the breakthrough curve of NO_2 for AC-CO_2 and AC-H_2O is explained by the mesoporous structure of the AC-H_2O sample, which enables a better diffusion of NO_2 inside the activated carbon particles. The particular study is considered to be the only that examines NOx adsorption onto lignocellulosic based activated carbon.

Ahmed et al. (2015) tested nanofibers for lead removal from wastewaters. Here, activated carbon was used as substrate for nanofibers growth. Pb^{2+} was the target pollutant of the study. After experiments of pH, contact time, adsorbent dosage and agitation speed, optimal conditions for sorption were determined. Specifically, the best performance was obtained when the dosage of adsorbent was 0.25 g/L at solution pH 5.5 and 200 rpm for 60 min of contact.

At this point, it will be good to just report some cases of organic components removal. Organic compounds are another severe source of water pollution. Polycyclic aromatic hydrocarbons (PAH) were efficiently removed from water samples by solid phase extraction. Razmi et al. (2016) proposed a new nanocomposite of graphene quantum dots and eggshells for extract PAH. Effect of initial pH of the solution, adsorbent amount within the column as well as the flow rate of the sample on the total extraction efficiency was investigated. Characterization by SEM revealed that although eggshells examined separately presented an irregular crystal structure when mixed with graphene quantum dots a uniform distribution was achieved resulting in an effective contact of the effluent. This study concluded that taking into consideration both the ease of preparation and well adsorption desorption performance, graphene quantum dots-eggshell nanocomposite can be considered suitable for extraction of various aromatic hydrocarbons from water.

Also, in a review article for nitrogen and phosphorous containing pollutants removal, several adsorbents are presented by Prashantha Kumar et al. (2017). Among adsorbents such as zero-valent metal, metal oxides/metal hydroxides, there is a reference to carbon based materials too. Specifically, carbon nanotubes and chitosan based nanocomposite present high uptake values compared to other carbon based materials including graphene (Prashantha Kumar et al. 2017). From all carbon based materials, carbon nanotubes have gained a great attention the past decade. Due to their versatility, carbon nanotubes find many applications including water desalination (Hebbar et al. 2017).

5.6 Conclusions

Activated carbons are considered to be the most successful adsorbent materials due to their high adsorption capacity for the majority of pollutants (dyes, heavy metals, pharmaceuticals, phenols). Their large surface area, and different surface functional groups, which include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers. Numerous agro-food wastes as summarized in this Chapter regarding their adsorption potential to many pollutants. The most important conclusion is that some basic characteristic of adsorption as capacity and kinetics are directly influenced by the structural characteristics of the prepared materials. It is mandatory to note that the system of adsorbent-adsorbate is unique and therefore to make a safe comparison, the adsorption conditions must be exactly the same. Otherwise, the comparison is faulty.

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