Active carbons and their functional applications in water purification – an overview

Liliya Manoilova[1,*] and *Kamelia* Ruskova[2]

[1]Department of Fundamentals of Chemical Technology
University of Chemical Technology and Metallurgy 8 Kl. Ohridski, 1756, Sofia, Bulgaria
[2] Department of Chemistry, Faculty of Electronic Engineering and Technologies,
Technical University of Sofia, 8 Kl. Ohridski, 1000, Sofia, Bulgaria

Abstract. The activated carbons (ACs) represent the cost-effective approach to ecosystem remediation. They are one of the most used and popular adsorbents for most pollutants, due to its high absorption capacity and high surface area. The potential application of AC is determined by the source of material, the technology, and the production conditions. An advantage of ACs is that they could be obtained from any carbon-containing feedstock, so based on their nature and characteristics, various adsorbents are used for the purpose of water treatment. They can be used for different applications: removal of volatile organics, toxic agents, petroleum hydrocarbons, chlorinated solvents, heavy metals, pesticides etc.

1 Introduction

Water pollution has become a huge problem for the modern world and represents a global issue for the planet’s survival. Since the beginning of the industrial revolution, factories have been dumping waste products into rivers, lakes, and seas. Many enterprises: tannery, textile, mining metallurgical and petrochemical released toxic metal ions such as copper, zinc, chromium, and cyanide from electroplating. Apart from the industry, pollution also comes from people's daily life and agriculture’ pesticides and fertilizers. This is harmful not only for local flora and fauna, but it’s also a problem for plants and animals hundreds of kilometers away. Water pollution represents an undesirable change in physical, chemical, and biological properties of water that may have detrimental effect on any living organism.

Fig.1. Pictures of contaminated drinking and industrial water (Photographer L. Manoilova).

Active carbons are the most used adsorbents for industrial and drinking water decontamination, due to its high surface area and its ability to adsorb different contaminations, such as petroleum hydrocarbons, chlorinated solvents, heavy metals, pharmaceutical residues, volatile organics, and total organic carbon. It is also used to remove pesticides, to improve water taste, to remove odor and toxins blue-green algae.

1.1 Pollution resulting from industrial activity and agriculture fertilizers

The main source of water nitrate pollution is the agricultural sector, which accounts for 45% of the total nitrogen pollution. Agriculture fertilizers used to increase the agriculture yield, seep directly from the soil into groundwater and drinking water. These chemicals sometimes cause toxic effects to humans and all living organisms. The effect of toxic pollution often has an direct impact on flora and fauna’s life.

Mining enterprises and geological exploration released industrial water that is characterized by increased acidity or alkalinity, high hardness, and turbidity due to the presence of petroleum products sometimes. This water is contaminated with solid colloidal rock and mineral particles, enriched with chemical substances containing bacterial and organic contaminants. Metal ions such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, Se^{2+}, As^{5+}, Mn^{2+} are the main pollutants from electroplating and metallurgy. In aim to deactivate this wastewater, concentration of different contaminants and heavy metal ions needs to be reduced through effective technologies for purification, precipitation, and filtration.

*Corresponding author: lili_manoilova@abv.bg

1.2 Adsorption methods for water purification

Adsorption methods for industrial wastewater purification are widely used nowadays. They are based on adsorption processes and represent an adsorption of dissolved solids and gasses from a liquid or gaseous medium. They can be used for deep purification of wastewater from dissolved organic substances, phenols, surfactants, pesticides, heavy metal ions, etc. Besides ACs, synthetic sorbents (zeolites), natural mineral sorbents (clays), etc. are also used as adsorbents.

ACs, characterized by relatively low cost and good regeneration possibilities appear to be the most used among the variety of adsorbents. They have certain properties that correspond to the increasing requirements for the purity of drinking water. Their application as adsorbents is determined by its appropriate combination of physicochemical properties, such as: developed specific surface and porous structure, presence of functional oxygen groups on the surface and excellent adsorption capacity with respect to various substances. The additional requirements and advantages of ACs are weak interaction of the hydrophobic carbon surface with water molecules, good interaction with organic substances and molecules; well-developed mesoporosity, performing transport functions and providing good access to micro- and supermicropores; as well as high selectivity and ability to be regenerated.

For the water treatment ACs need to have good mechanical strength and particle composition of certain size. Fine-grained fractions with a particle size of 0.25 ÷ 0.50 mm or highly dispersed carbons with a particle size of ≤ 40 μm are preferred and commonly used [1].

2 Main concepts and bases of adsorption

Adsorption is an effective method for removal of many soluble contaminants, where the pollutants - molecules or ions are removed from contaminated aqueous solution by adsorption onto the solid surface of adsorbent. The base concepts of adsorption theory are given in Fig.2.

The solid base material which provides the adsorption surface is referred to as adsorbent and the species adsorbed at the surface are called adsorbate. This process is known as adsorption or sorption process [2].

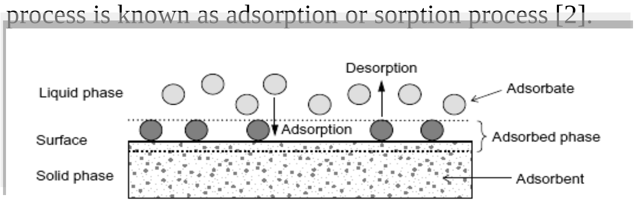

Fig. 2. Main concepts and bases of adsorption (Worch, 2012).

Usually it is a reversible process, where the reverse process is called desorption. One of the main advantages of ACs is the possibility to be regenerated. Changing the properties of the liquid phase, for example temperature or pH, allows the absorbed substances to be removed from the surface and so the activated carbon to be regenerated.

Adsorption is a mass transfer process that is a phenomenon of sorption of gasses or solutes by solid or liquid surfaces. The adsorption on the solid surface occurs when the molecules or atoms on the solid surface have residual surface energy due to unbalanced forces [3].

Different kind of adsorption forces determine the adsorption process into two categories: physical adsorption and chemical adsorption. Physical adsorption is due to the interaction of intermolecular forces (i.e. van der Waals forces), for example gas adsorption from AC. Chemical adsorption process includes the destruction and formation of new chemical bonds [3]. Physical and chemical adsorption are not isolated processes and often occur together.

3 Activated carbon as a sorbent

Activated carbons are defined as a porous (micro-, micro-mesoporous, mesoporous or meso-macroporous) materials. Although they always contain different pore sizes (Fig. 3), the dominant pore types determine the choice of ACs for any specific applications. By the structure, AC belongs to the group of graphite materials with porous texture and highly developed surface area. In this non-uniform texture (characterized by a turbostratic structure), consisting of graphite crystallites and amorphous carbon, pores with sizes of the order of 10^{-10} ÷ 10^{-8} nm to 1 μm appear between the individual particles.

Mass transfer takes place through this pore system for all processes occurring in the inner surface of the carbon material. Micropores are pores sizes up to 2nm. Pores with a size < 0.7 nm are called ultra-micropores, and those with a size > 0.7 nm and < 2.0 nm, supermicro pores, according to the IUPAC classification. Pores with a radius between 2 and 50 nm are named mesopores, and pores with radii larger than > 50 nm - macropores.

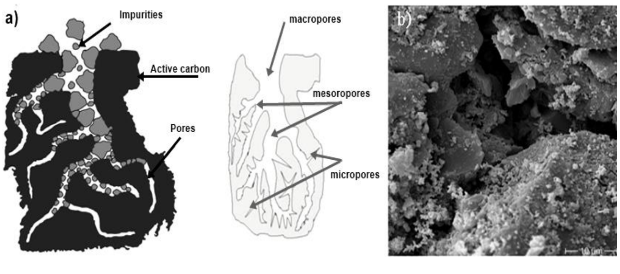

Fig. 3. Porous structure of activated carbon and SEM of AC.

The adsorption mainly occurs in the micropores and only to a small extent in the mesopores. The macropores serve only as channels for the passage of the adsorbent to the inner surface of the mesopores and micropores. The AC's pores' sizes and their distribution depend on the type of source raw material and the production technology. Increasing the internal surface of AC, increases the rate of adsorption and determines its exceptional efficiency in absorbing process of various substances. The most widely used activated carbon has a surface area in the range of 800 to 1500 m^2/g.

3.1 Characterization of activated carbon used as metal ion sorbent

When studying the sorption capacity of the AC towards a wide range of different ions, it is established that the magnitude of sorption from aqueous solution differs significantly. However, it can be noted that many transition metal ions, under static conditions adsorb much greater than the ions of alkali metals. This refers with some approximation to the process of dynamic conditions [4]. According to the absorbed ability on the carbon surface, applied both to static and dynamic conditions, the cations can be presented in the following order:

$NH^{4+}<Cd^{2+}<Ca^{2+}<Zn^{2+}<Fe^{2+}<Ni^{2+}<Cr^{3+}<Be^{2+}<Cu^{2+}<Fe^{3+}$

To compare the ions' sorption capacity in real conditions it is more difficult, since it depends on many factors as: pH, ions concentration, presence of different metal ions that tend to be absorbed at the same time, as well as the kinetic parameters of carbons. It is established that the high sorption capacity of AC to the metal ions in aqueous solution is mainly related to the presence of oxygen functional groups on their surface [5].

Depending on the method and conditions of their production, ACs usually contain chemically bonded oxygen, which form chemical compounds on the surface of basic or acidic type. Eight types of oxygen surface compounds, according to Boehm [6] can be identified on the carbon surface, having different importance for the ions sorption from aqueous solution. The specificity of the AC's texture results in individual interaction of metal ions with the carbon surface. In this sense the interaction AC- metal ion is different and depends on metal ions nature.

3.2 Oxidative modified activated carbon for contaminated water purification

There is a tendency to increase the sorption capacity of AC to specific water pollutants (metal ions for example) using different methods for surface modification or using different chemical agents. Oxidizing and non-oxidizing methods for chemical modification are currently broadly used. Among non-oxidative methods, the main importance is the impregnation method. The term impregnation can be defined as distribution of fine chemicals or metal particles in the pores of activated carbon [7,8]. Activated carbon impregnated with "Prussian blue" has an increased sorption capacity to Tl^{1+} ions in water treatment [9]. Water purification from metal ions is of great concern due to the high toxicity of metal compounds, especially those of Thallium. Tl^{1+} ions can be a by-product of various chemical processes or components of some chemical compounds used against insecticides in contaminated water [10].

The increased sorption capacity of the oxidizing activated carbon to the metal ions, is due to the surface of the oxidizing carbon, which is more negatively charged than the non-oxidizing AC, because of presence of surface acid groups, which increases electrostatic adsorption interactions with metal cations [11].

It is important to note that not all surface acid groups, not even all carboxyl groups are involved in the adsorption process of metal ions. This is due to the fact that one part of the metal ions is absorbed on the carbon surface and electrostatically eject other metal ions into the solution or block their access to the surface acidic groups located in the porous texture of the oxidated activated carbon [7].

3.3 Powdered and granulated AC for water treatment

The potential application of AC is determined by the source of material, the production technology, and the conditions of generation. An essential advantage in terms of raw material is that ACs can be obtained practically from any carbon-containing raw material. Activated carbon is usually used in water treatment in the form of granules in bulk or powdered carbon (Fig.4). When the absorbent properties of activated carbon are depleted, it can be regenerated by burning the organics. AC is also used in water decontamination in powdered form without regeneration. Such an application, however, is usually limited to water treatment where negligible amounts of carbon adsorbent is used.

Fig.4. Picture of granulated activated carbon and powdered AC.

Granular activated carbon (1.2 mm to 1.6 mm) is mainly used for the adsorption of gasses and vapors. It is also used in liquid media to dechlorinate tap water, to decolorize solutions and to separate different components.

Powdered carbon (with an average diameter between 0.15 and 0.25 mm.) is most often used for adsorption from aqueous solutions, for removal of organic compounds in wastewater treatment, enrichment of sediments, decolorization of food and chemical products.

The choice between powdered and granular form depends on the frequency of use and the required doze. The powdered AC is dozed in water as a liquid powder mixture and can be separated during the next stages of purification together with the other impurities. Its use is limited when using water purification with filter systems.

Granular AC is used for the water taste and odor controlling. It is commonly used in fixed beds or placed in pre-existing filters by replacing their content, for example with sand or granules of similar size. It is used much more efficiently, with the effective consumption of carbon for a certain volume of water. To achieve the same extent of treatment is significantly easier than when using powdered type of carbon. The service life of the granular carbon layer depends on the capabilities of the carbon and the contact time between it and the water, determined by the water flow. This time is usually 5-30 minutes. The capabilities of the granular filter are highly dependent on certain organic substances, which can have a very serious impact on its service life.

4 Conclusion

The content of various nitrites, metal ions and other pollutants in the wastewater from the chemical, mining and processing enterprises exceeds the maximum permissible norms and is a serious source of pollution for surface and underground water. This requires reducing the concentration of these ions to acceptable levels by appropriate methods. One of the successful and cheap method for cleaning industrial wastewater can be adsorption, based on activated carbon.

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