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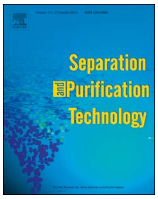

Review

Bio-regeneration of activated carbon: A comprehensive review

Maisa El Gamal[a], Hussein A. Mousa[b], Muftah H. El-Naas[c,*], Renju Zacharia[c], Simon Judd[c]

[a] College of Natural and Health Sciences, Zayed University, P.O. Box 144534, Abu Dhabi, United Arab Emirates
[b] Chemical and Petroleum Engineering Department, UAE University, P.O. Box 15551, Al-Ain, United Arab Emirates
[c] Gas Processing Center, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

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ABSTRACT

The use of microorganisms to regenerate activated carbon (AC), bio-generation, can avert costly and logistically challenging ex-situ steam regeneration of carbon normally required to recover its adsorptive capacity. Bio-regeneration employs microbial metabolism in which the microbes use the available organic substrates (contaminants) to generate energy. During this process, they generate equivalent protons and electrons, which are transferred to the substrates to finally break them down to simpler molecules or ions, such as CO_2, methane and Cl^-. The optimal microbial conditions depend on the temperature, available nitrogen and phosphorus levels, dissolved oxygen levels, and microbe/substrate stoichiometric ratios and the residence time of the AC particles within the reactor. In this review, the authors highlight the most recent development in bio-regeneration including the regeneration mechanism, the relationship between the reversibility of adsorption and the efficiency of bio-regeneration, the general aspects affecting bio-regeneration, the principle and target compounds for bio-regeneration, different established methods for quantifying the bio-regeneration and the efficiency of bio-regeneration. Few case studies of bio-regeneration of activated carbon loaded with different contaminants are presented. Research on microbiology regeneration has gained considerable attention in recent years, but it still needs more contribution from other disciplines including process engineering, biochemistry and material sciences for optimizing the process performance.

1. Introduction

Activated carbon is a carbonaceous material that is processed to have high specific surface area, large pore-volumes, and small pore diameter predominantly between 8 and 100 Å [1]. It is often described as the best adsorbent to capture inorganic, organic, and toxic metal ions that contaminate water resources [2]. Waste materials such as fruit wastes, coconut shell, scrap tires, sawdust and other wood type materials, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes, blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, and minerals have been used as adsorbents or adsorbent precursors [3]. The development of inexpensive adsorbents from waste materials were successfully applied for the removal of water pollutants, using adsorption technology including batch processes and column operations [4]. Nanomaterials as adsorbents have been effectively used for the removal of metal ions, anions, and organic and biological species from water. These particles rapidly remove pollutants even at low concentration, under different conditions of pH and temperatures [5].

Owing to the high specific surface areas and micropore volumes of AC, it has been extensively used as an adsorbent and support for chemical reactions. In physical activation, the precursor is initially pyrolyzed and the carbonaceous residue is subsequently activated by thermal treatment in the presence of CO_2 or steam. On the other hand, in chemical activation, the precursor is impregnated with porogens such as ZnO and KOH and the impregnated biomass is pyrolyzed to produce the AC. As different precursor materials and activation methods produce ACs with different properties, the selection of the raw material and the activation routes depend on the end-use or design specifications. ACs are commercially available in numerous forms: powders, granular in various mesh size ranges, and shaped or molded products extruded into rod-like shapes and monoliths, the dimensions of which commonly range from 0.8 to 6 mm (diameter) by 3 to 10 mm (length) [1].

The synthesis of low-cost adsorbents from inexpensive and commonly available carbonaceous waste materials has taken a substantial amount of effort [6–8]. As an adsorbent, the AC has been effective in many applications, particularly for the removal of organic and inorganic pollutants from wastewater [9]. A major reason that AC is used is the flexibility stemming from its heterogeneous porous structure,

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[*] Corresponding author.
E-mail address: muftah@qu.edu.qa (M.H. El-Naas).

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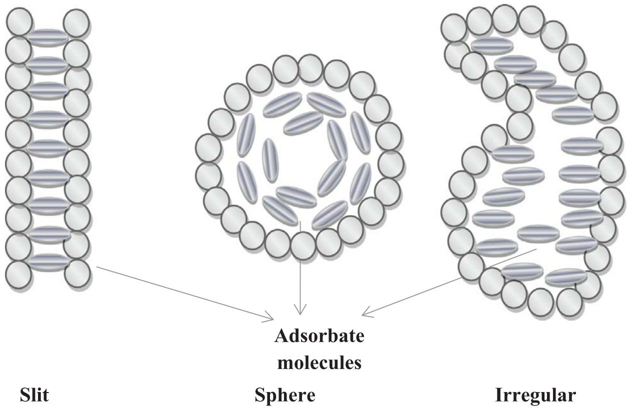

Fig. 1. Mechanism of surface coverage, adapted from [12].

high specific surface area, wetting characteristics and adsorption capacity, all of which can be adjusted by controlling the chemical and physical activation steps. To overcome the high cost of available commercial ACs, numerous studies focus on developing new low-cost ACs with properties comparable to that of commercial ones [10,11].

The volume of the adsorption pores in ACs can be measured using the Brunauer-Emmett-Teller (BET) method. The total pore volume is usually estimated to be larger than 0.2 ml/g, while the pore-width varies from 3 Å to several thousand angstroms, and the internal specific surface area is typically more than 400 m^2/g. In addition to different diameters, the pores usually have different shapes. In their cross-section, the pores can to be cylindrical, rectangular or irregular shapes. There are some pores which are open only to the smaller molecules while blocking larger ones. A simple illustration of different pore shapes in ACs containing adsorbate molecules is presented in Fig. 1 [12]. Pores may also have constrictions or bottlenecks. Macropores depend mainly on the nature of the carbonaceous raw material employed and the preliminary manufacturing process. They usually contribute only very little to the total specific surface area of AC. Their major function is to serve as transport arteries that make the internal parts of the carbon granules readily accessible to the molecules being adsorbed. The transitional pores account for about 5%, and the micropores for about 95% of the internal surface area. The micropores are largely the result of the activation process [13].

2. Types and properties of activated carbon

For broad application purpose, ACs are generally classified based on their physical appearance into:

(i) Powdered AC (PAC), which has a particle size below 100 mm and a diameter from 15 to 25 µm. It has high specific surface area and higher diffusion resistance of adsorbed molecules.
(ii) Granulated AC (GAC), which is larger in particle size, lower in specific surface area and lower gas/liquid diffusion resistance compared to the PAC. It is therefore preferred for many industrial applications.
(iii) Spherical AC, which is made up of small spherical particles, and has higher mechanical strength and lower diffusion resistance compared to PAC or GAC.
(iv) Impregnated AC, where, the porous carbon is impregnated with elements such as iodine or cations of Ag, Al, Mn, and Zn. Such elements or ions are used for the removal of specific contaminants that are not predominantly adsorbed by the carbon.
(v) Polymer coated carbon [14], where the surface of the porous carbon is coated with biocompatible polymers. They can be applied in homoperfusion [15].

3. Application of activated carbon

The adsorption capacity of ACs depends on both their physical and chemical properties of AC [16]. Recently, the effects of surface functional groups on the adsorption phenomenon were investigated [14,17–19]. The surface chemical structure and functional group play important role in the extent of substrate adsorption from the liquid phase. For example, the oxygenated functional groups improved the adsorption and removed methylene blue from wastewater [20]. Functional groups such as carboxylic act as centers of water vapor adsorption, they are thus used in humidity removal [21]. It has been shown that the selectivity of ACs for adsorption is dependent on their surface chemistry. The distribution of functional groups changes the structure of AC and hence modifying the AC surface functional groups to induce changes on the AC's surface structure by creating or eliminating certain interactions. For instance, the presence of sulfur-philic functionalities improves the adsorption of volatile sulfur containing molecules [16,22,23]. Likewise, the surface functional groups of ACs can be tailored to enhance the removal of volatile organic compounds [24].

4. Methods of regeneration of activated carbon

Although AC is used in the industrial application, its cost is a major barrier to its more widespread application. Once AC is saturated with the adsorptive species, the carbon is mostly discarded in the landfills. Regeneration of saturated AC is indispensable to minimize the operational costs and product wastage [25]. Regeneration allows stabilization of the exhausted AC which in turn reduces the amount of solvents and adsorbents used in the process [26]. Several methods have been developed to regenerate AC. These include chemical [27,28] supercritical carbon dioxide [29], electrochemical [30], microwave [31] and thermal [32]. Usually an appropriate technique is selected depending on the nature of the contaminant, the recovery cost and process conditions.

4.1. Steam regeneration

Steam regeneration of AC has been shown to be effective and economical [33]. It has been used for the regeneration of adsorbents in industry for years [34]. In steam regeneration, the steam rapidly heats up the bed be , allowing a faster desorption of the contaminant from the adsorbent; the desorbate, however, is only removed out of the bed when the latter is hot enough such that at least some steam remains in gaseous form and can satisfactorily remove the adsorbate. During the steam regeneration of consumed GAC from a wastewater treatment plant, five steps take place: the thermal decomposition of AC, oxidization of AC with steam, vaporization of adsorbate, thermal decomposition and carbonization of the contaminants, and the oxidative decomposition of carbonized waste matter with the steam [35].

4.2. Thermal regeneration

Thermal regeneration involves the use of rotary kilns, fluidized-bed/fixed-bed furnaces, etc. In thermal oxidation using kilns, extensive amounts of CO_2, contaminants in partially oxidized and reactive states and particulate matter are released into the environment. The process includes drying at 105 °C, pyrolysis under inert atmosphere, and gasification of the organic contaminants using an oxidizing gas. Some low-volatilty hydrocarbons are thermally decomposed [36]. Furthermore, some AC undergoes oxidation and is lost in the process. Thermal regeneration can also affect the mechanical strength of ACs.

High temperature regeneration of spent AC is characterized by complex physical and chemical processes that depend on many parameters. The processes directly affect carbon regeneration efficiency, thereby affecting the ability of AC to regain its adsorbing capacity. The adsorption of different chemical compounds and their mutual reactions