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Review

Preparation of activated carbons from date (*Phoenix dactylifera* L.) palm stones and application for wastewater treatments: Review

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ABSTRACT

Adsorption on activated carbons from lignocellulosic biomass has been a cost-effective technique for elimination of environmental pollution. Date stone can be considered as one of the best candidate among the agricultural wastes due to its quite availability and high carbon content. This article provided an overview of the different techniques that so far have been applied for conversion of date stone to carbon adsorbent. The effects of temperature, time, impregnation ratio, and type of activator on pore characteristics and yield of carbons were reviewed. According to collected data, the surface areas of date stone-carbons were in the range from 490 to 1282 m^2/g and yields from 17 to 47% with highest values obtained by chemical activation. Application of date stones-carbon for adsorption of organic and inorganic pollutants has also been reviewed. Low-cost carbons derived from date pits biomass have demonstrated maximum capacities of 612.1, 359.1, 238.1, and 1594.0 mg/g for dyes, phenols, pesticide, and heavy metals, thus solving environmental problems of waste disposal and pollution control.
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1. Introduction

The generation of bioenergy in terms of liquid, gaseous, and solid fuels from biomass wastes has been an important field in the area of research and development (Bulushev and Rossa, 2010). Low-cost, quite abundance, renewability, and high lignocellulosic content of agricultural biomass make them promising precursors for cost-effective activated carbons (Chayid and Ahmed, 2015; Gupta et al., 2015a). Fruit stones are of particular interest for their generation as by-products from food processing industries, in amounts sufficient for obtaining good adsorbing carbons with appreciable hardness and better porous structure (Heschel and Klose, 1995; Mechati et al., 2015). Peach stones (Torrellas et al., 2015; Uysal et al., 2014; Maia et al., 2010), apricot stones (Depci et al., 2014; Djilani et al., 2015; Petrova et al., 2010), olive stones (Hazzaa and Hussein, 2015; Obregón-Valencia and Sun-Kou, 2014; Berrios et al., 2012), cherry stones (Nowicki et al., 2015a; Angin, 2014; Olivares-Marín et al., 2012), grape stones (Okman et al., 2014; Jimenez-Cordero et al., 2014; Al Bahri et al., 2012), and date stones (Sekirifa et al., 2013a; Reddy et al., 2012a; Alhamed, 2009; Yamina et al., 2013; El-Sharkawy et al., 2007) have been effectively utilized as precursors for production of activated carbons with high surface areas and pore volumes.

Among all the agricultural wastes, date pits can be considered as one of the best candidates for the production of activated carbon due to its high carbon content, low price, and quite availability, especially in Mediterranean countries (Ahmed and Theydan, 2014a; Amor and Ismail, 2015). It is estimated that the number of date palms worldwide is about 105 million. The world production of date fruits has been considerably expanded over the last decade where the production has moved from 6 to 7 million tons in 2004 and 2009, respectively (FAOSTAT, 2010). About 10% of the fruit is waste in the form of seeds, making them the largest agricultural by-product in palm growing countries with an approximately amount of 700 thousand tons (Briones et al., 2011; El-Naas et al., 2010a). Date processing plants producing pitted dates, date syrup and date confectionery are the main sources of date stones (Basuny and Arafat, 2014). Hence, from an economical consideration, these wastes are desirable to be used as good precursors for activated carbon.

The applicability of agricultural biomass in their original state has been found to be constrained by their relatively small surface area, inadequate pore size distribution, and leaching of some organics into the process stream (Chowdhury et al., 2012). In this context, physical, chemical and physicochemical techniques have been adopted for conversion of these wastes to activated carbons (Nowicki et al., 2015b; El-Sheikh et al., 2004). Physical activation involves carbonization of a raw material followed by activation of resulting char in the presence of an activator such as CO_2 or steam (Nowicki et al., 2010a). In chemical activation, the raw materials are impregnated with activators such as $ZnCl_2$, H_3PO_4, KOH, etc., and heated under inert atmosphere (Li et al., 2010). Chemical activation is preferred over physical due to higher yield, single treatment step, lower temperature, shorter time, and good development of porous structure (Sudaryanto et al., 2006; Chen et al., 2013). Physical and chemical activations can be performed simultaneously after step of carbonization under the name of physiochemical activation. The utilization of chemical and physical activators together can produce carbon with specific surface properties (Mohd Din et al., 2009).

Various methods, like coagulation, ion exchange, biodegradation, oxidation, solvent extraction, adsorption, and electrolysis have been applied to control water pollution (Bhatnagara and Sillanpääb, 2010). Among these methods, adsorption is an effective separation process because of its simple design, flexibility, suitability for batch and continuous processes, possibility of regeneration and reuse, low capital cost, and capability to remove wide range of pollutant concentrations (Ahmed and Theydan, 2014b; Gupta et al., 1998, 2011, 2012, 2013; Mittal et al., 2009a,b, 2010a,b; Gupta and Nayak, 2012; Jain et al., 2003; Saleh and Gupta, 2012). Activated carbon has the advantages of exhibiting a high adsorption performance for pollutants due to its high surface area, well-developed porous structure, and favorable surface properties (Ahmed and Theydan, 2013; Saleha and Gupta, 2014; Gupta et al., 2015b,c). Activated carbons from fruit stones have been effectively utilized for adsorptive removal of heavy metals (Alslaibi et al., 2013a; Duranoğlu et al., 2010; Bouhamed et al., 2012a), synthetic dyes (Ramírez-Montoya et al., 2014; Uğurlu et al., 2008; Demirbas et al., 2008), pesticides (Ioannidou et al., 2010; El Bakouri et al., 2010), and phenols (Aygün et al., 2003; Beker et al., 2010; Arana and Mazzoco, 2010). Preparation of porous carbon from biomass wastes and its application for pollution control has been reviewed by number of articles (Yahya et al., 2015; Alslaibi et al., 2013b; Foo and Hameed, 2009; Demirbas, 2009; Nor et al., 2013; Abdullah et al., 2011). Ahmad et al. (2012) provided a review on the preparation of activated carbon from date palm wastes and its application for wastewater treatment. However, the present review focuses on preparation of activated carbon from date stone biomass with detailed explanation for effects of preparation variables on pore structures and yields of date stone carbons which have not been addressed before. The adsorption behavior of various contaminants on prepared carbons was also discussed in details.

2. Origin and properties of date palm

Date palm *Phoenix dactylifera* L. is the most important fruit tree of the *Arecaceae* family that found in arid, tropical, and subtropical regions of the world specifically those stretching from North Africa to the Middle East (Ahmad et al., 2012). An adult date palm tree (Fig. 1) has a trunk or stem of 15–25 m high and fronds or leaves that look like feathers with 3–5 m long. There are about 150 leaflets in each frond which can be up to 30 cm in length and 2 cm in breadth. The full span of the crown of the palm tree is about 6–10 m height. The date fruit contains an edible pericarp and seed which is about 2–2.5 cm long, 6–8 mm thick, and approximately 10–15% of date fruit weight (Al Harthi et al., 2015). Thus, date pits represent the largest agricultural wastes in palm growing countries compared to other date palm by-products such as fronds, leaflets, fruit bunches, fruit wastes, and trunks (El may et al., 2012).

The date fruits are traditionally used to prepare a wide range of date products such as paste, syrup, honey, jam, and

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