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New biochar from pecan nutshells as an alternative adsorbent for removing reactive red 141 from aqueous solutions

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A new biochar derived from pecan nutshell was prepared, characterized, and applied as an alternative and low–cost adsorbent for removing Reactive Red 141 (RR141) from aqueous solutions. The yield from raw pecan nutshell to biochar was approx. 30%. The biochar presented a micro/mesoporous structure with a surface area of 93 $m^2\ g^{-1}$, which is considered high for biomass derived materials. For both, raw pecan nutshell and its biochar, the RR141 adsorption was favored under acid conditions (pH of 2 and 3, respectively). The dye removal percentage was 85% using the biochar as an adsorbent, and was only 23% when raw pecan nutshell was used. The adsorption kinetics of RR141 on the biochar followed the pseudo –second order model. The equilibrium isotherms were well represented by the Freundlich model. The maximum adsorption capacity was approx. 130 mg g^{-1}. The adsorption was spontaneous, favorable, and exothermic ($\Delta H^0 = -56.42$ kJ mol^{-1}). These findings indicated that the new biochar prepared in this work is an alternative, low–cost, and eco–friendly adsorbent that can be used to remove dyes from colored effluents.

1. Introduction

Textile wastes dumped into the environment, especially the synthetic dyes, represents one of the main environmental problems currently, due to its great potential to pollute water bodies (Abbasian et al., 2017). Synthetic dyes are potentially toxic, carcinogenic, and non–biodegradable substances characterized by the presence of azo chromophores (–N=N–) or phthalocyanine chromophores (containing copper, nickel, or other metals) and aromatic rings (Vanaamudan and Sudhakar, 2015). The removal of these dyes from wastewaters is a major environmental challenge and, for this purpose, there is a constant search for effective and economically viable processes (Leechart et al., 2009).

Some chemical, physical, and biological treatment methods for dye removal from wastewaters include coagulation–flocculation (Saitoh et al., 2014), filtration (Kajekar et al., 2015), adsorption (Ausavasukhi et al., 2016), advanced oxidation processes (Collazzo et al., 2012), ion–exchange (Wu et al., 2008), biological treatment (Rodrigues et al., 2014), and magnetic separation (Pankaj and Joy, 2009). Among these methods, adsorption has been found to be promising compared with other techniques in terms of efficiency (Tang et al., 2017), low cost, ease of implementation and operation, high removal efficiency, and regeneration capacity. However, the high cost of preparation and regeneration of activated carbon (the main used adsorbent) limits the application of this technique (Ali et al., 2012).

New research has been conducted focusing on low–cost adsorbents. A low–cost adsorbent should be abundant in nature or a by–product or waste material from any industry. Then, adsorbents obtained from agricultural wastes are low–cost alternatives to activated carbon. In the South Region of Brazil, there are extended plantation areas of pecan trees (*Carya illinoensis*), native from North America. The kernel of the pecan nut is largely consumed in Brazil (Vaghetti et al., 2009). However, nutshell is a by–product with a complicated management. Pecan nutshells represent 49% of the pecan nut and have little or no economic value. Their disposal is costly and can cause environmental problems (Bansode et al., 2003). In this way, the reutilization of this waste, which is

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generated on a large scale, can be an alternative to obtain a new adsorbent to remove water contaminants. In this context, it is important to consider that pecan nutshells are vegetal wastes and it is possible that they contain cationic compounds with a significant effect on dyes adsorption (Aguayo–Villarreal et al., 2013). On the other hand, several characteristics, such as surface area, pore volume, and surface chemistry, can govern the adsorption capacity of an adsorbent (Leng et al., 2015). Li et al. (2017) reported the production of biochars by the pyrolysis of agricultural wastes for wastewater treatment. The biochar from pyrolysis aims to improve the properties of the adsorbent in comparison with the respective raw material as well as reduce the costs in comparison with the production of activated carbon, removing the activation step from the process. According to Aldana et al. (2015), the thermal pyrolysis of pecan nutshell occurs in two stages: The first stage is the hemicellulose decomposition and the second stage is the cellulose decomposition.

Some works reported the development of biochars from alternative materials, including sewage sludge (Leng et al., 2015), peanut shells (Georgin et al., 2016) and oil distillation residue (Li et al., 2017). These biochars were used for the removal of contaminants from aqueous media. Also, works reported the use of raw pecan nutshells as alternative adsorbents to remove metals (Vaghetti et al., 2009) and dyes (Aguayo–Villarreal et al., 2013) from aqueous media. From the best of our knowledge, there are no studies regarding to the preparation of a biochar from pecan nutshells and its application as an alternative adsorbent for removing a large dye molecules such as Reactive Red 141 from aqueous media. The development of a biochar from pecan nutshells and its application as adsorbent has a synergistic effect from the cleaner production viewpoint, contributing for the solid wastes management and for the treatment of liquid effluents.

Aiming to find a new and inexpensive adsorbent for dye removal as well as diminish the large amount of pecan nutshells, a new biochar was prepared, characterized, and applied for the removal of RR141 dye from aqueous solutions. First, the biochar was developed and characterized in detail. Then, the potential of biochar to adsorb RR141was compared with its precursor (pecan nutshells). The adsorption of RR141 on the biochar was finally studied from the kinetic, equilibrium, and thermodynamic viewpoints.

2. Materials and methods

2.1. Obtention and pretreatment of pecan nutshell

Pecan nutshell (*Carya Illinoinensis*) samples were obtained from a pecan–producing region in the South Region of Brazil. The samples were washed several times with deionized water, oven dried at 60 °C for 8 h. Then, pecan nutshell samples were ground in a Wiley mill and subsequently sieved. The fraction with diameter of particles lower than 710 μm was stored in closed bottles to be used in the biochar preparation.

2.2. Biochar preparation

The biochar was prepared from pecan nutshell via pyrolysis process. The sample was pyrolyzed in a bench reactor that operates in a batch system (Fig. 1). The system has an oven with a quartz reactor coupled internally. The reactor has the following dimensions: 981 mm length, 49 mm outside diameter, and 43 mm internal diameter. The useful length of the oven is 516 mm. The reactor is heated electrically by two resistors, each one with 1900 W. Two type K thermocouples are positioned inside the reactor. A cylindrical quartz reactor was charged with approximately 50 g of pecan nutshell (previously dried at 105 °C) and the system run under nitrogen gas (N_2) at 0.25 L min^{-1}. The heater temperature was increased at a rate of 10 °C min^{-1} until 800 °C, being held at 800 °C for 60 min and allowed to cool still under N_2 flow to room temperature. The pyrolysis vapors condensation was conducted in accordance with CEN BT/TF 143 standard (CEN Comité Européén de Normalisation, 2004), and ten bubblers were used. In each experiment, 100 mL of isopropyl alcohol were added in each

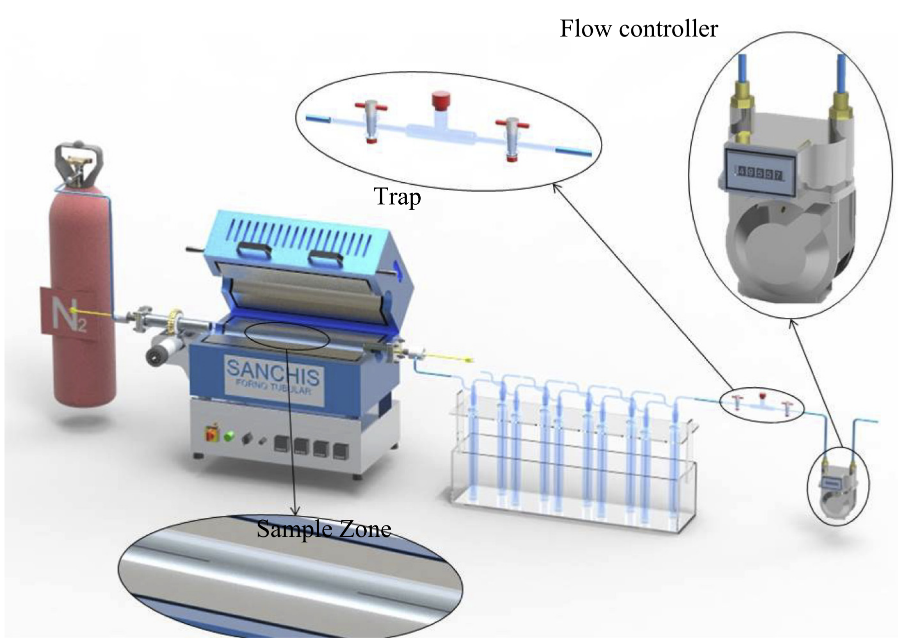

Fig. 1. Scheme for the biochar preparation.