

# The utilization of oxidized biochar obtained of palm tree fibers for caffeine removal

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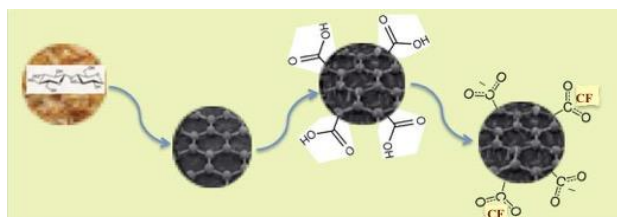
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**The present work investigates the adsorption of caffeine (CF) by oxidized biochar obtained from palm tree fibers (OPT).** Caffeine (CF) (or 1,3,7-trimethylxanthine) is a natural chemical compound which belongs to the family of alkaloids. It is the most common psychostimulant in the world, that is why it is consumed by most people.<sup>[1],[2]</sup> 3% of a person's caffeine intake is excreted unchanged in the urine, as this is the path that enters the sewage.<sup>[3]</sup> Based on many studies, CF has been detected in many aqueous matrixes from wastewater plants (WWTPs), groundwater, rivers and lakes, and seawater..<sup>[4]</sup> The presence of CF in wastewater is increasing, which leads to pollution of the environment. Regardless of its concentration CF affects the cellular stress of mussels,<sup>[5]</sup> reduces the stability of the lysosomal membrane of bivalve mussels and generally affects health of aquatic.<sup>[6]</sup> Various adsorbents have been used to remove caffeine from wastewater, such as metal-organic frameworks (MOFs),<sup>[7]</sup> carbon xerogels,<sup>[8]</sup> graphene nanoplatelets GNPs,<sup>[9]</sup> luffa cylindrica,<sup>[10]</sup> pine needles<sup>[11]</sup> and others. In addition, recently biochar has been used for wastewater treatment. Biochar-based materials are economical, environmental friendly in terms of reduced by-product production, have a large specific surface area, porous structure, and active functional groups. These characteristics make them suitable for the adsorption and removal of pollutants from polluted waters.<sup>[12]</sup>

The present study focuses on the use of oxidized biochar prepared from palm tree fibers (OPT) as an adsorbent material for CF. Palm trees are a tree species that consist of many varieties and species (~1.100 different species) depending on the location they are found. A palm stem is a long, cylinder tube, usually without branches consisting of fibers.<sup>[13]</sup> Carbonization and following oxidation of these fibers, leads to a very stable tubular/porous material with increased surface area and number of active sites (e.g. carboxylic moieties), which are negatively charged for pH > 3 resulting in an increased affinity for the positively charged caffeine molecule in the near neutral pH region.<sup>[14, 15]</sup> (**Fig. 1**)



**Fig. 1.** Conversion of palm tree to oxidized palm tree biochar.

Batch equilibrium experiments were carried out and the effect of adsorption parameters such as pH, contact time, temperature, ionic strength, and adsorbent amount have been investigated and discussed in detail. Maximum adsorption efficiency was observed at pH 3.0 (10.55 mg/g) and the adsorption of CF onto OPT reached equilibrium after 120 min. The kinetic experimental data followed the pseudo-second-order kinetic model and the equilibrium adsorption data were fitted well to both *Langmuir* and *Freundlich* isotherm models (**Table 1**). Temperature did not significantly affect adsorption. Increasing ionic strength up to 1 M results in a dramatic decrease of the adsorption efficiency. Thermodynamic studies showed that the adsorption of CF onto OPT was spontaneous ( $\Delta G^0 = -24.4882, -23.7302$  and  $-24.9104$  kJ/mol at 298, 313 and 323 K, respectively, exothermic ( $\Delta H^0 = -20.77$  kJ/mol) and with increasing randomness ( $\Delta S > 0$ ) at the solid/solution interface. Increasing the adsorbent amount results in the decrease of the adsorption capacity of CF onto OPT. Based on

FTIR studies, the adsorption of CF is mainly based on electrostatic interactions and the formation of outer-sphere complexes, which agrees with the effect of ionic strength.

**Table 1**

Parameters evaluated applying the *Langmuir* and *Freundlich* models to CF adsorption at 298, 313 and 323 K.

<b>Isotherm</b>	<b>Parameter</b>	<b>298 K</b>	<b>313 K</b>	<b>323 K</b>
Langmuir	$q_m$ (mg/g)	21.0	24.0	22.7
	$b_L$	0.101	0.047	0.055
	R	0.994	0.981	0.985
Freundlich	$K_F$	3.225	2.045	2.109
	n	2.265	1.866	1.884
	R	0.988	0.981	0.992

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