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Assessment on the performance of nano-carbon black as an alternative material for extraction of carbendazim, tebuthiuron, hexazinone, diuron and ametryn

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ABSTRACT

The aim of this study is to evaluate the adsorptive performance of nano-carbon black for removing pesticides from aqueous media. The characterization of material was accomplished by SEM, FT-IR, TGA as well as by surface area measurements. Pesticide adsorption occurs in a wide pH range (2–7). The nano-carbon black presented a high surface area (306.9 $m^2 g^{-1}$) and the maximum adsorption capacities were found to be 74.4, 63.1, 59.7, 89.5 and 105.2 mg g^{-1} for carbendazim, tebuthiuron, hexazinone, diuron and ametryn, respectively, obtained from dual site Langmuir-Freundlich isotherm model. From kinetic data, the equilibrium times were found to be 30 min for diuron, 80 min for ametryn and 45 min for the other pesticides, while experimental data were well adjusted to pseudo-second-order models, thus suggesting that the adsorption of pesticides takes place in binding sites with different energies. From thermodynamic adsorption parameters, it was observed for all pesticides negative values of ΔG and ΔH, thus suggesting that the adsorption process is spontaneous and of exothermic nature. Multiresidue adsorption was not affected by the presence of 1.0 mg L^{-1} humic acid. When compared to other carbonaceous adsorbent materials, nano-carbon black has as the main advantages the low equilibrium time, low cost and satisfactory adsorption capacity.

1. Introduction

In the past decade, Brazil has been one of the four countries that most produce and consume pesticides in the world and the first one in Latin America. Approximately 80% of Brazilian smallholders use pesticides in order to enhance crop yield and to combat agricultural pests and diseases [1,2]. In addition, Brazil is the largest sugarcane producer and the second larger citrus producer in the world over the past decade [3] and these crops are concentrated mainly in the São Paulo state region [4]. Many herbicides are used in weed control and other plagues in crops. In sugarcane, tebuthiuron (TBT), hexazinone (HEX), diuron (DIU) and ametryn (AME) are widely used, being essential to prevent reductions in crop productivity [5,6]. Carbendazim (CAR) is a fungicide used in the control of the post bloom fruit drop, caused by a fungus called *Colletotrichum Acutatum* in citrus plantation [7].

Tebuthiuron (N-t5-(1,1-dimethylethyl) -1,3, 4-thiadazol-2-yll -*N, N*-dimethylurea) and diuron (*N'*-(3,4-dichlorophenyl)-N, *N*-dimethylurea) are member of the substituted urea class of herbicides [8]. Tebuthiuron is highly soluble in water (2.5 g L^{-1}) and had a low absorption coefficient ($\log K_{ow} = 1.79$) [9]. These characteristics give it the potential to leach through soils and contaminate shallow groundwater aquifers. Diuron solubility in water is 42 mg L^{-1} and it is generally persistent in water, soil and groundwaters [10]. In addition, diuron is classified by EPA as a likely human carcinogen [11]. Hexazinone (3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-(1H,3H)-dione) and ametryn ((2-ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine) are herbicides of triazine family [12,13]. They are considered one of the most important classes of chemical pollutants due to their toxicity and high resistance. Also, they are known to induce oxidative stress, cellular and DNA damage and cell death [14]. Carbendazim (methylbenzimidazol-2-ylcarbamate) is a benzimidazole fungicide with a benzimidazolic ring in its structure, which is difficult to break, therefore, its degradation is slow and consequently it can persist for a long

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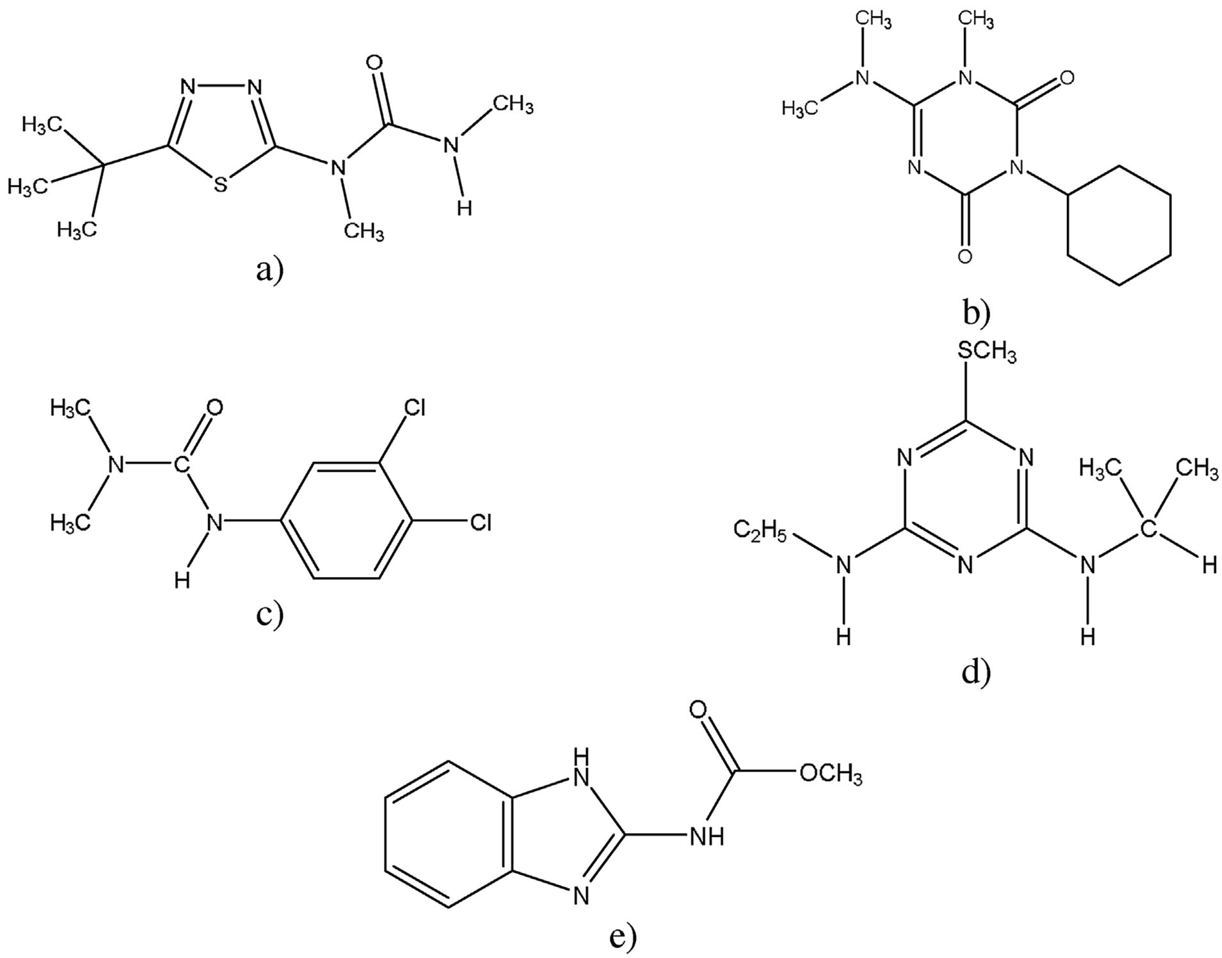

Fig. 1. Chemical structure of pesticides used in this work. a) Tebuthiuron b) Hexazinone c) Diuron d) Ametryn e) Carbendazim.

time in the environment [15].Structures of the pesticides are shown on Fig. 1.

Despite of their persistence in the environment and toxicity, some institutions such as the World Health Organization (WHO) and European Commission (EC) do not include the maximum recommended limit of these pesticides in their guidelines [16]. Brazilian Ministry of Health (BMH) includes only diuron and carbendazim, recommending a maximum limit in drinking water of 90.0 and 120.0 μgL^{-1}, respectively [17].

One of the most well-known methods used in the removal of hazardous compounds from polluted waters is the adsorption [18]. The most commonly adsorbent used commercially is activated carbon, which has a high cost production [19]. Many materials have been studied for adsorption of pesticides from aqueous media, such as activated carbon fibers [18], clay minerals [19–21], carbon nanotubes [22], black carbon [23] and polymeric materials [24–26]. However, these materials generally require a previous treatment, such as a clean-up procedure or surface modification, which makes the method more expensive and time-consuming. In addition, some of these materials also provide a low mass transfer or a low adsorption capacity. Therefore, the interest in studying alternative low-cost materials as adsorbents for pesticides has been increasingly investigated.

Nano-carbon black (NCB) is a nano-carbonaceous material manufactured by subjecting heavy residual oil feedstock to extremely high temperatures in a carefully controlled combustion process. It may be produced by means of different processes, which strongly influence the properties of the final product, such as purity, structure, particle size and porosity. Oil-furnace process, based on partial combustion of residual aromatic oils, accounts for over 95% of total world production of NCB and provides the best product reproducibility in comparison to other processes [27].

Nano-carbon black differs from others carbonaceous materials such as black carbon, soot, bone black and activated carbon (or charcoal), mainly regarding their composition and manufacturing process [28]. Furthermore, NCB is usually macro and mesoporous and generally shows a less developed porous texture than other carbonaceous materials [29]. One should note that nano-carbon blacks possess very low cost for acquisition regarding other carbonaceous materials (around 1 euro per 1 kg) [30].

Nano-carbon black contains more than 97% of elemental carbon, with oxygen and hydrogen as other major constituents, consisting in nearly spherical particles with different degrees of aggregation. The main binding points for adsorption of molecules onto nano-carbon black, which also influence its physicochemical properties, are carbon-oxygen structures. These functional groups are believed to be attached to the edges of graphitic layers and are mainly carboxylic acid, phenolic, quinonic and lactone groups [31].

Nano-carbon blacks are widely used in rubber applications, which consume approximately 90% of NCB production and pigments, corresponding to 9% of total use [32]. Only the 1% remaining is used as an essential ingredient in hundreds of other different applications [33]. Therefore, even being very interesting taking into account the low cost and high surface area, the use of nano-carbon blacks as adsorbents has been still very incipient, whose applications have been focused on only some molecules,