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Value-added utilization of maize cobs waste as an environmental friendly solution for the innovative treatment of carbofuran

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ABSTRACT

A new route for the conversion of maize cobs waste, a natural low-cost lignocellulosic biomass abundantly available from the food processing industries into an eco-friendly biosorbent (CC) via chemical treatment has been presented. The effectiveness for the adsorptive removal of a highly hazardous carbamate derivative pesticide, carbofuran from the aqueous solution was attempted. The operational parameters including the effects of modification agents and chemical impregnation ratio on the adsorption capability were investigated. The porosity, functionality and surface chemistry of CC were featured by means of low temperature nitrogen adsorption, elemental analysis, scanning electron microscopy, Fourier transform infrared spectroscopy, evaluation of surface acidity/basicity and zeta potential measurement. The effects of adsorbent dosage, initial concentration, contact time and solution pH on the adsorption performance were evaluated in a batch mode study. Equilibrium data were simulated by non-linear fittings using the Freundlich, Langmuir, and Temkin isotherm models. Kinetic modeling was fitted to the pseudo-first-order and pseudo-second-order equations. Langmuir isotherm model provided a better correlation to the experimental data, with a maximum monolayer adsorption capacity of 149.15 mg/g, while the adsorption kinetic was best fitted to the pseudo-second-order kinetic model. The results illustrated the potential of maize cobs waste derived biosorbent for the on-site remediation of pesticide contaminated wastewater.

1. Introduction

To date, the abusive use and indiscriminate release of parental pesticides and their metabolites has prevailed to be a detrimental ecological concern, due to the great tendency to exist indefinitely, streaming, and pseudo-persistent properties over the food chain (Ferreira et al., 2015). In the last two decades, these anthropogenic products have raised scientific and public concerns regarding their low biodegradability and detrimental implications on the biological equilibrium of natural media and human health (Lladó et al., 2015). It is well established that these emerging pollutants, notably in the form of herbicides, insecticides, fungicides, algaecides, antimicrobials, avicides, miticides, molluscicides, nematicides, rodenticides, bactericides, defoliants, piscicides and virucides, constitute the important pathway of a wide array of toxic substances released into the environmental matrices (Sahithya et al., 2016). The continuous presence of these constituents, even at sub-therapeutic concentrations, indicates an external exposure to the public health, flora, fauna, and represents a sharp threat to the natural ecosystems (Ammari et al., 2015).

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On a worldwide basis, intoxications attributed to pesticides have been estimated to be as high as 3 million cases of acute and severe poisoning annually, with 220,000 of reported deaths/year (Yadav et al., 2015). Among all, carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl-N-methyl carbamate), a broad spectrum systemic acaricide, insecticide and nematicide included in the general group of the carbamate derivative pesticides, is widely used against a wide range of soil dwelling and foliar feeding insects, including corn root-worm, wireworms, boll weevils, mosquitoes, alfalfa weevil, stem borers, aphids, and white grubs (Agrawal and Sharma, 2010). Carbofuran is characterized by its high solubility and mobility, with the half-life of approximately 30-117 days. According to the United States Environmental Protection Agency (USEPA), the maximum acceptable carbofuran concentration in the potable drinking water is recorded at 0.09 mg/L, while the maximum concentration admitted by the World Health Organization (WHO) is 3 μg/L (Gupta et al., 2006).

Prolonged exposure to carbofuran is vulnerable to a broad variety of reproductive failure and developmental toxicity presage as neurotoxicity, teratogenicity, mutagenicity and carcinogenicity. Additionally, scientific evidence has documented that carbofuran could induce the disruption of estrous cycle in female hemiovariectomized albino mice, significant decrease in ovarian weight with the concomitant decrease of compensatory ovarian hypertrophy, reduction in epididymal sperm count; and exert neurotoxic effect by impairing mitochondrial functions leading to the oxidative stress. Due to its effect on the reproductive system, carbofuran has been listed as one of the endocrine disrupting chemicals (Gbadegesin et al., 2014). This highlights the necessity of priority attention to identify a dedicated pretreatment method of the leaching run-off from agricultural or deposited carbofuran.

Comparatively, adsorption is a competitive treatment process for the removal of a broad range of organic and inorganic pollutants, mainly ascribed to the ease of operation, simplicity of design, low sensitivity to the variation of temperature or toxic substances, and high adsorption capability (Abbas and Trari, 2015). Despite its prolific use in adsorption processes, the biggest barrier of its application by the industries is the high cost of adsorbents and difficulties associated with regeneration (Anirudhan and Ramachandran, 2015). Structurally, agricultural by-products, which composed of lignin, hemi-cellulose and cellulose as the major polymeric constituents, contain a variety of polarities to bind molecules via physical attractive forces, ion exchange and physiochemical interactions. Maize corncob, a highly voluminous, costless agricultural waste of corn milling process, is characterized with the bulk density of 0.32 g/cm^3, and different functionalities, alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers, making it an abundant source of potential scavenger of water pollutants. Additionally, dissection of maize fruit illustrated that the dry weight of grain represents only 38% of the entire fruit (Šæiban et al., 2008).

In the formal practice, some quantity of these residues is used as boiler fuel, where major portion is discarded by open burning. Although maize corncob has been reputed to be a valuable source of glucose, xylose, furfural, ethanol via catalytic hydrolysis, the reaction is accompanied by the co-generation of polysaccharide, arabinose, galactose, and mannose, which are difficult to be isolated from the biomass hydrolyzates to influence the downstream process (Ding et al., 2013). For this purpose, the present work was undertaken towards upgrading of the available maize corncob biomass from the food processing plants into a low-cost, active biosorbent by chemical modifications for the innovative treatment of a carbamate derivative pesticide, carbofuran. The significant influences of modification agents and chemical impregnation ratio on the adsorption capacity were investigated systematically. Structural, functional and surface chemistry of the prepared adsorbent was evaluated. Moreover, the adsorption equilibrium, isotherms, kinetics and thermodynamics were elucidated.

2. Materials and methods

2.1. *Adsorbate*

Carbofuran, a carbamate derivative pesticide difficult to be degraded in natural environment was selected as the model adsorbate in this work. The standard stock solution was prepared by dissolving accurately weighted carbofuran in double distilled water to the concentration of 300 mg/L. Working solutions of desired concentrations were prepared by successive dilution.

2.2. *Preparation of functionalized biosorbent*

Corn cob (CC), a by-product collected from the food manufacturing industries was selected as the raw precursor in this study. The collected sample was washed exhaustively with deionized water to remove adhering impurities from the surface. The raw precursors were manually chosen, cleaned, air-dried, crushed and screened to the desired mesh size of 125 to 250 μm. The modification process was performed by mixing 100 g of dried precursor with different modification agents at room temperature and 200 rpm for 24 h, with the chemical impregnation ratio defined as:

$$\mathrm{IR} = \frac{w_{\mathrm{AG}}}{w_{\mathrm{CC}}} \quad (1)$$

where w_{AG} and w_{CC} is the dry weight of modification agent (g) and CC (g). The modified biosorbents were rinsed and washed repeatedly with hot and cool distilled water until the filtrate reached to the neutral pH. All modification agents [phosphoric acid (85%), sulphuric acid (95%), nitric acid (70%), sodium hydroxide (99%), and sodium carbonate (99.995%)] used throughout the study were analytical-grade chemicals.

2.3. *Batch adsorption studies*

The batch adsorption experiments were conducted in a series of 250 mL Erlenmeyer flasks containing 200 mL of carbofuran solutions and prefixed amount of biosorbent. The flasks were capped and agitated in an isothermal water bath shaker at 30 °C with an agitation speed of 120 rpm until the equilibrium was reached. The influence of biosorbent dosage on the adsorptive uptake of carbofuran was performed by varying the CC dosage from 0.05 to 0.80 g, while keeping the other parameters constant. The effect of pH was examined by regulating the pH from 2 to 12, with an CC dosage of 0.30 g/200 mL and adsorption temperature of 30 °C. The pH was measured using a pH meter.

The carbofuran concentrations in the supernatant were withdrawn at predetermined period and determined using a double beam UV–Vis spectrophotometer (UV-1601 Shimadzu, Japan) at 273 nm. All samples were filtered prior to analysis to minimize interference of the CC fines with the analysis. Each experiment was duplicated under identical conditions.