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Removal of a potentially hazardous chemical, tetrakis (hydroxymethyl) phosphonium chloride from water using biochar as a medium of adsorption

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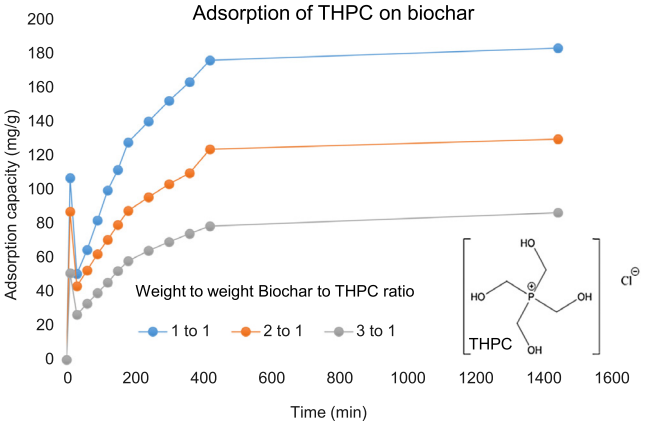
HIGHLIGHTS

- Elimination of an emerging contaminant, THPC through adsorption using biochar.
- Activation of biochar using chemical treatment.
- Favourable THPC adsorption at low temperature and low biochar dosage.
- Enquiry of adsorption/desorption mechanism through kinetic and isotherm studies.

GRAPHICAL ABSTRACT



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ABSTRACT

The research investigates the efficiency of biochar to eliminate an emerging contaminant, flame retarding chemical, a.k.a. Tetrakis (Hydroxymethyl) Phosphonium Chloride (THPC) from water. The THPC, which is a water-soluble, organophosphorus salt, is mainly used by textile industries as a flame retardant and crease resistant for cotton and cellulose fabrics. Our research explores the possible removal process of THPC from water while using biochar as a mode of adsorption. Commercial biochar was used to investigate the adsorption efficiency of THPC. Spectroscopic and surface characterization data were provided for the commercial biochar. Study showed the presence of several organic functional groups on biochar which have potential to contribute to an efficient adsorption process. Batch adsorption studies were conducted varying several parameters like biochar dosages, contact time of the substrate to biochar, agitation time, and temperature during the experiment. It was found that benign experimental conditions such as lower biochar dosage, lower temperature and lower agitation time maximized the adsorption capacity. Furthermore,

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biochar was chemically treated with various activation agents and the removal efficiency was compared between activated and non-activated biochar. It was found that chemical activation on biochar indeed improved the THPC removal efficiency. Results also indicates that the adsorption mechanism of THPC on to biochar surface followed both Langmuir and Freundlich isotherms. Finally, it was observed that the adsorption process was fitted best with pseudo-second-order kinetic model which might indicate a possible chemisorption mechanism for the adsorption of THPC on biochar surface.

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1. Introduction

Water is a limited resource and today, the environmental importance of water is considered as a major necessity everywhere in the world. Today irrespective of developed or less developed countries, water resources are facing threats from the global increase in human population, agricultural expansion and chemical use. Besides, the usages in energy development, continuous pollution from industries, mining, agriculture, urban and residential activities, water is under extreme stress (Bundschuh et al., 2012; Szalinska et al., 2013).

There is a growing concern over a new class of compounds, known as CECs. The term "chemical contaminants of emerging concern" (CEC) refers to chemicals with unknown ecological effects and with no associated regulatory standards (Narragansett Bay Estuary Program, 2017). They include pharmaceuticals, personal care products, pesticides, herbicides, endocrine disrupting compounds, plasticizers and flame retardants (Erickson et al., 2014). Flame retardant chemicals are certain kind of CECs which are commercialized for the purpose of inhibiting flames in textile and polymeric products. It is estimated that more than 175 flame retardant chemicals are in the market and the industry is worth over $600 million per year in U.S., and nearly $2 billion worldwide, according to the European Flame Retardants Association (Flame Retardant Report USA, 2017). There has also been an increase in the development and use of new flame retardant chemicals due to the prohibition of use of halogenated flame retardant chemicals. This is because they have been found to be persistent and highly toxic in the environment (Cristale et al., 2013; van der Veen and de Boer, 2012). Organophosphorus flame retardants are among the new flame retardant chemicals, and are commonly used as additives in many materials such as foams, hydraulic fluids, anti-foam agents, plasticizers, coatings for electronics, and fabrics. Organophosphorus flame retardants are less toxic and less persistent than the halogenated flame retardants (Covaci et al., 2011; van der Veen and de Boer, 2012; Zhang et al., 2016).

Unfortunately the health effects of these organophosphorus chemicals are not widely explored, although halogenated flame retardant chemicals have been screened for bioaccumulation, environmental persistence and health effects (Strempel et al., 2012). Most flame retardant chemicals come from polymers and textile industries since they rely heavily on water usage for dyeing and finishing processes using such chemicals (Moore and Ausley, 2004; Derden and Huybrechts, 2013). One such chemical is Tetrakis (hydroxymethyl) Phosphonium Chloride (THPC), a water soluble organophosphorus salt with a chemical formula $[P(CH_2OH)_4]Cl$ as shown in Scheme 1.

THPC is formed by treating phosphine with formaldehyde in the presence of hydrogen chloride (NRC , 2000; WHO , 2000; Svara et al., 2008) and is used as an ingredient in flame retardant chemicals. It has been used by textile industries mainly for cotton and cellulose fabric as a flame retardant and crease resistant material (Reeves and Guthrie, 1956; IARC , 1990; THPC-MSDS , 2011). However, from industrial discharges trace amounts of THPC can be leached into surface and ground water which can lead to potential environmental hazard as was observed in massive fish kill in Ogeechee River in Georgia 2011 (Georgia Conservancy, 2011; Nguyen, 2015). Although the findings were not conclusive but THPC was among the list of suspected chemicals detected near the discharge pipes of the textile company who reportedly discharged chemicals to water without a permit (Georgia Conservancy, 2011). THPC has been known to cause various health conditions in many laboratory vertebrate animals particularly mammals (WHO , 2011; NTP , 1987; Shi et al., 2016; Nguyen, 2015). However, there was no report in the literature on wastewater treatment strategy concerning THPC and here in, our research group delves in to the possible removal technique of THPC from water.

Numerous methods such as chemical precipitation, coagulation, reverse osmosis, ion exchange, membrane filtration and adsorption have been routinely used for elimination of hazardous chemicals from water (Georg-Steinhauser, 2008; Onundi et al., 2010; Adeyemo et al., 2014). One of the popular and economical method is adsorption which is considered as a simple, easy to operate, fairly inexpensive, and efficient method for the removal of hazardous chemicals mainly organics from the environment even at low concentrations (Gonza´lez et al., 2011; Amuda and Edewor, 2013; Kampalanonwat and Supaphol, 2014). Among the various adsorbents biochar has gained much importance lately. Biochar is defined as a black carbon rich and porous material obtained from the pyrolysis of biomass, typically between 300 to 700 °C under oxygen-deprived conditions (Cao et al., 2009; Lehmann and Joseph, 2009; Shackley et al., 2012). It is known to be used in agricultural remediation as a soil amendment and recently interest has been directed towards its application in environmental remediation. Biochar and its production from different biomass make it an inexpensive alternative to activated carbon (Lwin et al., 2008; Amuda and Edewor, 2013). In addition, biochar is known to possess large surface area, and different pore sizes lead to high sorption capacity. It also has various functional groups and Brunauer–Emmett–Teller

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