Chemosphere 177 (2017) 65–76

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Remediation of organochlorine pesticides contaminated lake sediment using activated carbon and carbon nanotubes

Shan Hua [a], Ji-Lai Gong [a, *], Guang-Ming Zeng [a, **], Fu-Bing Yao [a], Min Guo [a], Xiao-Ming Ou [b]

[a] College of Environmental Science and Engineering, Key Laboratory of Environmental Biology and Pollution Control, Ministry of Education, Hunan University, Changsha 410082, PR China
[b] China National Engineering Research Center for Agrochemicals, Hunan Research Institute of Chemical Industry, Changsha 410014, PR China

HIGHLIGHTS

- AC and MWCNTs remediation effectiveness for HCH and DDTs are compared.
- AC was more effective than MWCNTs on treating DDTs and HCHs remaining in sediment.
- DDTs and HCH were not rereleased from the AC over 150 d.

ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form
14 February 2017
Accepted 25 February 2017
Available online 1 March 2017

Handling Editor: Chang-Ping Yu

Keywords:
Hexachlorocyolohexane
Dichlorodiphenyltrichloroethane
Sediment
Activated carbon
Multi-walled carbon nanotubes
Remediation

ABSTRACT

Organochlorine pesticides (OCPs) in sediment were a potential damage for humans and ecosystems. The aim of this work was to determine the effectiveness of carbon materials remedy hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethanes (DDTs) in sediment. Two different carbon materials including activated carbon (AC) and multi-walled carbon nanotubes (MWCNTs) were used in the present research. Sediment treated with 2 wt% AC and MWCNTs after 150 d contact showed 97%, and 75% reduction for HCH, and 93% and 59% decrease for DDTs in aqueous equilibrium concentration, respectively. Similarly, the reduction efficiencies of DDT and HCH uptake by semipermeable membrane devices (SPMDs) treated with AC (MWCNTs) were 97% (75%) and 92% (63%), respectively under the identical conditions. Furthermore, for 2 wt% AC (MWCNTs) system, a reduction of XAD beads uptake up to 87% (52%) and 73% (67%) was obtained in HCH and DDT flux to overlying water in quiescent system. Adding MWCNTs to contaminated sediment did not significantly decrease aqueous equilibrium concentration and DDTs and HCH availability in SPMDs compared to AC treatment. A series of results indicated that AC had significantly higher remediation efficiency towards HCH and DDTs in sediment than MWCNTs. Additionally, the removal efficiencies of two organic pollutants improved with increasing material doses and contact times. The greater effectiveness of AC was attributed to its greater specific surface area, which was favorable for binding contaminants. These results highlighted the potential for using AC as in-situ sorbent amendments for sediment remediation.

1. Introduction

Organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanne (HCH) are the most typical persistent organic pollutants (POPs), with high toxicity, persistence, half volatile and bioaccumulation characteristics, which may pose a potential adverse effect for human health and ecosystems (Cofield et al., 2007; Zeng et al., 2013a,b; Huang et al., 2008). High Concentrations of organochlorines pesticides contaminants in aquatic have resulted in health concerns, especially for children and pregnant women (Jiang et al., 2005; Mahmoud et al., 2016; Zeng et al., 2013a,b). In the 1970s, DDT has been explicitly disabled by all over the world, but enabled again by The World Health Organization (WHO) in 2002. China is the world's largest producers and consumers of OCPs between 1950s and 1980s

* Corresponding author.
** Corresponding author.
E-mail address: jilaigong@gmail.com (J.-L. Gong).

http://dx.doi.org/10.1016/j.chemosphere.2017.02.133

and the total production of HCH and DDTs was accounted for 33% and 20% of the total world production, respectively (Fu et al., 2003). As a kind of persistent and semi-volatile compounds, OCPs can migrate long distances as gases or aerosols in the air, and eventually fallen in low-temperature regions (Xu et al., 2013). In the aqueous environment, due to its high octanol-water partition coefficient (Kow) properties, OCPs are prone to adsorbing on particulate organic matter, ultimately makes the sediment become a potential contamination source. Because of sediment date were capable of providing the useful information of organic pollutants source, sediment have been widely applied to evaluate pollutants in water bodies (Nemr et al., 2016; Wang et al., 2013). A number of scholars believed that sediment resuspension might constitute a particular threat to associated biota throughout the food web. Moreover, organic pollutants could be released into overlying water from sediment and could be secondary contaminants for environments (Liu et al., 2008; Wang et al., 2013; Zhao et al., 2009). Hence, it is necessary to propose reasonable methods to manage these organic polluted sediments (Tang et al., 2008; Lin et al., 2016).

Dongting Lake, covering a very large surface water area of around 3000 km^2, is located in Hunan Province in the south of China. It is the second largest freshwater in China and a good source of drinking and surrounding industry. In 1970s, the usage of HCH and DDTs in this province was the second highest in China and the highest in 1980s (Li et al., 2001). Due to extensive applications of OCPs in history, Dongting Lake has received seriously contamination in its sediment (Qian et al., 2006).

If natural recovery is determined to be insufficient, in situ remediation using activated carbon (AC) is a appropriate remedial actions need to be considered. For the last few years, Europe and United States develop AC for in situ remediation and regarded it as a sediment amendment method (Ghosh et al., 2011). In situ remediation is a relatively low-cost and low-impact way to remediation of sediments polluted with organic contaminants (Yin and Zhu, 2016). Luthy et al. (Tomaszewski et al., 2007; Werner et al., 2005; Zimmerman et al., 2004) proposed that, by mixing AC into the biologically active supper layer of sediment, DDTs and PCBs would repartition and be sequestered in carbon, thus reduced DDTs and PCBs bioavailability and release to water. These experiments also showed that activated carbon amendment effectiveness was dependent on itself's physical adsorption capacity. However, the amended AC cannot be readily retrieved from the soil and sediment matrix, and may in some instances induce adverse ecological responses, such as Lumbriculus variegatus (Nybom et al., 2012). Carbon nanotubes (CNTs) as new adsorbents have been gained increasing attentions by many researchers. Long and Yang (Long and Yang, 2001) et al. first reported that CNTs were more efficient for the removal of dioxins than activated carbon. Due to their special properties such as electrical conductivity, hollow and layered structures, functional mechanical and thermal, CNTs have been proven to possess great potential as superior adsorbents for removing many kinds of contaminants (Zhang et al., 2007). At present, theoretical and experimental investigations on CNTs on their properties and application in multidisciplinary areas increase exponentially, such as Cd (II) (Fan T. et al., 2008; Feng Y. et al., 2010; Xu P. et al., 2012a; Xu J. et al., 2012b; Hu X.J. et al., 2011), 2,4-dichlorophenol (Xu et al., 2012a,b; Tang et al., 2008), cationic dyes (Gong et al., 2009), Humic acid (Shen et al., 2009), PAHs (Gotovac et al., 2007) and so on. Carbon nanotubes have been widely regarded as promising materials to sediment remediation due to its high adsorption and affinity for HOCs. Parks et al. (Parks et al., 2014) reported that the single-walled carbon nanotubes (SWCNTs) could effectively adsorb the PCBs and reduce the bioavailability of PCBs in field-contaminated sediment. Compared with biochar and AC, MWCNTs were the most effective material for reducing the risk of contaminates phytotoxicity in sediment since it has the smallest diameter and largest SSA (Jośko et al., 2013). CNTs are essentially different from activated carbon (AC) in the aspect that their structure at the atomic scale being far more well-defined and uniform (Matarredona et al., 2003; Ren et al., 2011). However, a major issue with CNTs is their aggregation in the natural environment, the aggregation of CNTs aqueous suspension limits the available sites for binding with pollutants. The surface modification to enhance the dispersion of the CNTs in solution can increase the removal capacity of CNTs in the preconcentration of pollutants (Ren et al., 2011). Work with activated carbon indicates size related ecotoxic effects on sediment dwelling organisms, and CNTs might be more toxic than activated carbon. Petersen et al. demonstrated that purified carbon nanotubes did not readily absorb into organism tissues, which didn't necessarily implied CNTs didn't have ecotoxic side-effects (Petersen et al., 2008).

This study is aimed to further investigate understanding of the impacts of mixing regime on the short-term effectiveness of activated carbon (AC) and multi-walled carbon nanotubes (MWCNTs) when they were amended to high-contaminated sediment. Changes in availability of DDTs and HCH were measured by aqueous equilibrium, semipermeable membrane devices (SPMDs) uptake as well as flux experiments.

2. Materials and methods

2.1. Materials

Organochlorine pesticides standard solution include α-HCH, β-HCH, γ-HCH, δ-HCH and *p,p′*-dichlorodiphenyldichloroethylene (*p,p′*-DDE), p, p′-dichlorodiphenyldichloroethane (p, p′-DDD), p,p,-DDT, o,p,-DDT, which were purchased from J&K Scientific Ltd of Beijing in China. Each pesticide in the stock standard was 10 mg and diluted to required concentration in experiments. All reagents used in this experiment were of analytical grade or higher.

MWCNTs were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Chengdu, China) and AC (10–24 mesh) was acquired from Aladdin chemistry Co., Ltd (Shanghai, China). The Brunauer –Emmett-Teller (BET) surface areas of the AC and MWCNTs were measured by N_2 gas sorption analysis at 77 K in a relative pressure range from 0 to 1 using a QUADRASORB SI surface area analyzer (Quantachrome, USA). The pore size distributions were estimated through Barrett- Joiner-Halenda (BJH) equation during desorption phases. The surface groups of the adsorbent were measured by Fourier transform infrared spectrum (FT-IR) using a Nicolet-5700 Spectrometer. The characteristics of AC and MWCNTs were listed in Table 1.

2.2. Sediment collection and spiked sediment preparation

The top 20 cm of the surface sediment samples were obtained from various locations of Dongting Lake in the north the Yangtze River, the largest river of China. The samples were named DT-1, DT-2, DT-3, DT-4, DT-5 and presented in Fig. 1. After collection,

Table 1
Physical characterization of the AC and MWCNTs.

Parameter	AC	MWCNTs
C% (wt)	55.0	88.3
O% (wt)	24.0	6.2
Other% (wt)	21.0	5.5
S_{BET} (m^2/g)	802.0	126.0
Total pore volume (cm^3/g)	0.342	0.922
Average pore diameter (nm)	2.86	2.81