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Enantio-selective molecular dynamics of (±)-*o,p*-DDT uptake and degradation in water-sediment system

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ABSTRACT

Enantio-selective molecular dynamics of (±)-*o,p*-DDT uptake and degradation in water-sediment system is described. Both uptake and degradation processes of (-)-*o,p*-DDT were slightly higher than (+)-*o,p*-DDT enantiomer. The optimized parameters for uptake were 7.0 μg L^{-1} concentration of *o,p*-DDT, 60 min contact time, 5.0 pH, 6.0 g L^{-1} amount of reverine sediment and 25 °C temperature. The maximum degradation of both (-)- and (+)-*o,p*-DDT was obtained with 16 days, 0.4 μg L^{-1} concentration of *o,p*-DDT, pH 7 and 35 °C temperature. Both uptake and degraded process followed first order rate reaction. Thermodynamic parameters indicated exothermic nature of uptake and degradation processes. Both uptake and degradation were slightly higher for (-)-enantiomer in comparison to (+)-enantiomer of *o,p*-DDT. It was concluded that both uptake and degradation processes are responsible for the removal of *o,p*-DDT from nature but uptake plays a crucial role. The percentage degradations of (-)- and (+)-*o,p*-DDT were 30.1 and 29.5, respectively. This study may be useful to manage *o,p*-DDT contamination of our earth's ecosystem.

1. Introduction

It is well identified that one of the antipodes of the chiral pesticides may be more toxic (Ali and Aboul-Enein, 2004; Ali et al., 2005). Approximately 25% pesticides exist in the form of racemates and, consequently, to establish the exact enantio-selective toxicity of these pesticides, the uptake and degradation are essential in the environment (Ali et al., 2003). Among various pesticides 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane (*o,p*-DDT) is very important to control several insects in agriculture, forestry and horticulture. Besides, it is being used to control several diseases such as malaria, typhus etc. globally. Unfortunately, *o,p*-DDT is very toxic as reported by WHO and other workers (World Health Organization, 2005; Rogan and Chen, 2005; Eskenazi et al., 2009). It is also endocrine disturbing pesticide (Ali and Aboul-Enein, 2002; Vos et al., 2000). It is observed that (-)-*o,p*-DDT is a additional vigorous estrogen mimic than its (+)-counter part. It has also been observed that *o,p*-DDT is persistent pesticide and found in water and sediment, and soil for several years (Kupfer, 1975; Ali and Jain, 1998; Meister, 1992; Matsumura, 1985; Jorgensen et al., 1991). The disappearance of *o,p*-DDT is controlled by uptake and degradation of this pesticide in earth's eco-system. The environment is chiral in nature (Aboul-Enein and Ali, 2003) and the uptake and degradation of the enantiomers of *o,p*-DDT may be stereo-selective in the water and sediment system. There is no publication on the enantio-selective fate of *o,p*-DDT. No paper also describes the enantio-selective uptake and degradation. In view of these facts, the enantio-selective molecular dynamics of *o,p*-DDT uptake and degradation in water-sediment system is described. The various parameters controlled were concentration of the antipodes of *o,p*-DDT, pH, time period, amount of sediment in water and temperature.

2. Experimental

2.1. Chemicals and reagents

(±)-op-DDT and optically active pure *o,p*-DDT were supplied by Chemical Service, West Chester (USA). The solutions of these pesticides (0.01 mg mL^{-1}) were prepared in natural water of the Ganga river. LiChrosolve acetonitrile and 2-PrOH were obtained from Merck, India. Ascorbic acid of AR grade was also supplied by Merck, India. The chromatographic conditions used are described somewhere else (Ali and Aboul-Enein, 2002). The column used was Chiralpak AD-R with

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water-acetonitrile (50:50) mobile phase, 220 nm UV detection and 1.0 mL min^{-1} flow rate. The reverine sediment and water samples were collected from the Ganga river at Rishikesh, Uttrakhand, India.

2.2. Molecular uptake of o,p-DDT

Supra-molecular dynamics *o,p*-DDT uptake was carried out by spiking the dissimilar concentrations of racemic and optically pure *o,p*-DDT separately to 100 mL riverine water samples (1.0–10.0 μg L^{-1}); which were prior filtered. The spiked water samples were shaken for different time intervals. The different pH and amount of riverine sediments were applied. These samples were studied at 20, 25 and 30 °C temperatures. The sediment samples were separated by centrifugation and the residual concentrations of the antipodes of *o,p*-DDT were analyzed by the standard method (Ali and Aboul-Enein, 2002).

2.3. Dynamics and kinetics

To decide the dynamics of *o,p*-DDT uptake the effects of diverse parameters viz. concentration of racemic *o,p*-DDT, touch time, pH, temp., and amount of river sediment were studies. The dynamics of the stereomers in sediment and water system was carried out using 1.0–10.0 μg L^{-1} concentrations, 10–80 min contact times, 2–8 pH, 20, 25 and 30 °C temperatures, and 1–10 g L^{-1} amount of riverine sediment. The experiment procedure was utilized as discussed elsewhere (Ali et al., 2016a). The thermodynamics and kinetics of *o,p*-DDT in natural conditions were also described by various equations and models (Ali et al., 2016b, 2016c, 2015). The amounts of the enantiomers of *o,p*-DDT in samples of water and sediment were monitored by the procedure described earlier (Ali and Aboul-Enein, 2002).

2.4. Enanio-selective degradation of o,p-DDT in different systems

The enantio-selective degradation of *o,p*-DDT was carried out with the plant extract of kudzu (*Pueraria thunbergiana*). The plant (10 g) extract was carried out by grinding in the Ganga water (100 mL) and filtered through membrane with 0.45 μm. The extract was kept at 4 °C till further use. The degradation was carried out in water, sediment and water-sediment systems. The degradation was carried out with racemic mixture of *o,p*-DDT. The plant extract (40 mL) and *o,p*-DDT (1.0–5.0 mL of 1.0 mg L^{-1} concentration; 0.1–0.5 μg L^{-1}) were mixed with 45–49 mL of the Gnaga river water. 100 μL of 1 mM Ascorbic acid was also added in to this solution. This solution was kept in sun light for 1–20 days. In case of sediment system, the sediment was mixed with 20 mL plant extract and 1.0 mL of 1.0 mg L^{-1} concentration following air dried. Similarly, this system was kept in sun light for 1–20 days. Water-sediment system was same as water system except that having varied amounts of reverine sediment.

3. Results and discussion

To understand the fate of the stereomers of *o,p*-DDT in our ecosystem the active equilibrium studies were done on river sediment. This work involved the uptake of *o,p*-DDT enantiomers on river sediment, dynamic equilibrium between river water and sediment, kinetics and degradation with plant extract (Fig. 1).

3.1. Equilibrium dynamics of uptake

The equilibrium uptake of *o,p*-DDT was carried at different concentrations (1.0–10.0 μg L^{-1}), contact time (10–80 min), pH (2.0–8.0), dose (1.0–10.0 g L^{-1}) and temperature of 20, 25 and 30 °C. The effects of these parameters are plotted in Figs. 2–6. It was noted that the maximum uptake of (-)-*o,p*-DDT was 85% while it was 83% for (+)-*o,p*-DDT enantiomers. The optimized conditions were 7.0 μg L^{-1} concentration (Fig. 2), contact time 60 min (Fig. 3), pH 5.0 (Figs. 4), 6.g

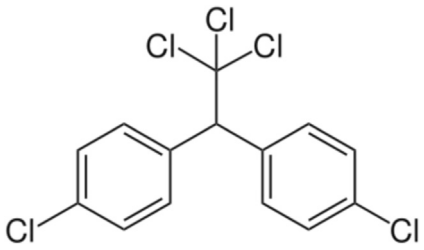

Fig. 1. Chemical structures of *o,p*-DDT.

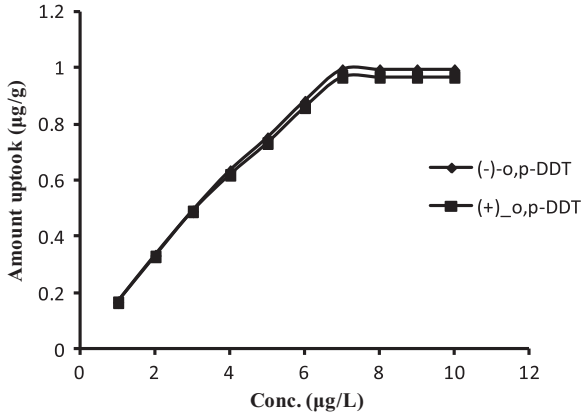

Fig. 2. Effect of concentrations on uptake of (-)- and (+)-*o,p*-DDT.

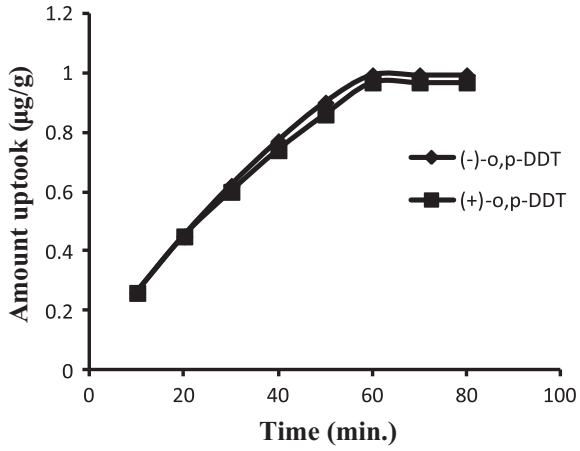

Fig. 3. Effect of contact time on uptake of (-)- and (+)-*o,p*-DDT.

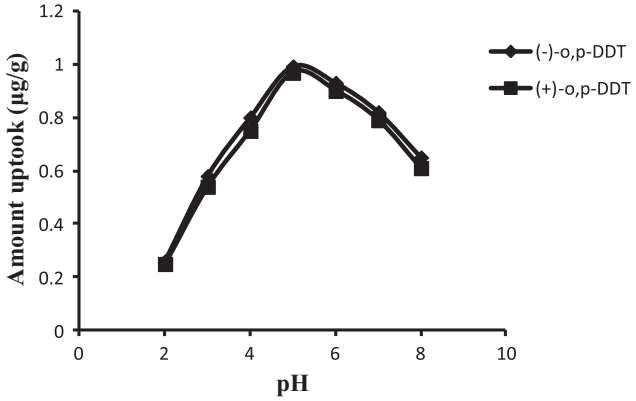

Fig. 4. Effect of pH on uptake of (-)- and (+)-*o,p*-DDT.