WATER RESEARCH 70 (2015) 64–73

Available online at www.sciencedirect.com

ScienceDirect

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

Filtration of triazine herbicides by polymer-clay sorbents: Coupling an experimental mechanistic approach with empirical modeling

Ido Gardi, Shlomo Nir, Yael G. Mishael*

Dept. Soil and Water Sci., The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot 76100, Israel

A R T I C L E I N F O

Article history:
Received 21 September 2014
Received in revised form
17 November 2014
Accepted 18 November 2014
Available online 29 November 2014

Keywords:
Triazine herbicides
Simazine
Polymer-clay composites
Competitive adsorption
Filtration
Modeling

A B S T R A C T

Triazine herbicides detected in surface and groundwater pose environmental and health risks. Removal of triazine herbicides (simazine, atrazine and terbuthylazine) by polymer-clay composites was studied and modeled. Their binding by a poly 4-vinyl pyridine co styrene-montmorillonite (HPVP–CoS–MMT) composite was especially high due to specific interactions between the herbicides and polymer, mainly hydrogen bonds and π-π stacking. The binding kinetics to the composite was in the order of simazine > atrazine > terbuthylazine, which was in accord with their equilibrium Langmuir binding coefficients; 44,000, 17,500 and 16,500 M^{-1}, respectively, which correlated with herbicide accessibility to form specific interaction with the polymer. Simazine binding kinetics to the composite was significantly faster than to granulated activated carbon (GAC), reaching 93% vs 38% of the maximal adsorption within 10 min, respectively. Herbicide filtration by composite columns was adequately fitted by a model which considers convection and employs Langmuir formalism for kinetics of adsorption/desorption. Filtration of simazine (10 $\mu g\ L^{-1}$) by composite columns (40 cm long, which included 26 g composite mixed with sand 1:40 (weight ratio)), was well predicted by the model with nearly 120 L purified, i.e., effluent concentrations were below regulation limit (3 $\mu g\ L^{-1}$). Effluent concentrations from GAC columns exceeded the limit after filtering 5 L. Experimental results and model predictions suggest that while GAC has a high capacity for simazine binding, the composite has higher affinity towards the herbicide and its adsorption is faster, which yields more efficient filtration by composite columns.

1. Introduction

Pesticides provide substantial agronomic and economic benefits. However, pesticide migration may cause soil, surface and ground-water contamination (Werf, 1996). For example, tens of thousands of tons of triazine herbicides are being manufactured and applied to fields all over the world, and are frequently detected in high concentrations in surface and groundwater (Pionke and Glotfelty, 1989; Pucarević et al., 2002). Due to its stability, high concentrations of atrazine have been detected in groundwater under fields years after it

---

* *Corresponding author*. Tel.: +972 8 948 9171; fax: +972 8 948 9856.
E-mail address: yael.mishael@mail.huji.ac.il (Y.G. Mishael).

http://dx.doi.org/10.1016/j.watres.2014.11.032
0043-1354/© 2014 Elsevier Ltd. All rights reserved.

was banned by the EU (Armstrong et al., 1967; Fava et al., 2010). Triazines are categorized as potential carcinogenic (Gammon et al., 2005; Kettles et al., 1997) and their regulation limits in drinking water are 3 ppb and 0.1 ppb in the US and EU, respectively (EPA, 2003; Sass and Colangelo, 2003).

Triazine herbicide removal from water by oxidation or coagulation was found to be ineffective (Jiang and Adams, 2006) and photo catalytic degradation using TiO_2 did not achieve mineralization (Pelizzetti et al., 1990). The isolation of bacteria (*Pseudomonas* sp. *strain ADP*) that utilize atrazine as a nitrogen source and can efficiently degrade atrazine was reported (Mandelbaum, 1995). This report prompted a large number of studies which demonstrated the biodegradation of triazine compounds found in water (Feakin et al., 1995; Katz and Dosoretz, 2000). However, biodegradation is not the most suitable technology, and the EPA recommendation for treating triazine contaminated drinking water is by filtration with granular activated carbon (GAC) (EPA, 2012).

The development of sorbents which may remove organic pollutants from water, more efficiently than GAC, has been addressed and sorbents such as organo-clays, in which the hydrophilic clay surface is modified by organic cations to form a more organophilic surface, have been suggested (Beall, 2003; Mortland et al., 1986; Ruiz-Hitzky and Serratosa, 1998). More recently, polymer-clay composites have drawn attention as attractive sorbents (Alexandre and Dubois, 2000; Yue et al., 2007). The first study to acknowledge the sorptive properties of polymer-clay composites was published by Churchman (2002), which suggested that the polymer can form specific interactions with the pollutant, therefore enhance its binding. Indeed, specific interactions between a pollutant (imazapyr, picric acid and MTBE) and the adsorbed polymer have shown to enhance pollutant removal (Ganigar et al., 2010; Radian and Mishael, 2008; Zadaka-Amir et al., 2012).

Concerning atrazine, we have reported (Zadaka et al., 2009) its efficient removal by an acidified poly-4-vinylpyridine co styrene-montmorillonite composite (PVP–CoS–MMT). Filtration tests demonstrated enhanced removal of atrazine by composite columns in comparison to its removal by GAC columns. Atrazine removal by the composite columns was extremely efficient from an acidic solution (pH~4), but was dramatically compromised at a higher pH, which was attributed to polymer desorption at a neutral pH. However, further investigation of filtration by these composite columns showed that the removal of pyrene was high at a wide range of pH (Radian and Mishael, 2012). These studies demonstrated the high potential of the PVP–CoS–MMT composite to bind aromatic pollutants, but indicated that the mechanism of pollutant binding to the composite is complex, pollutant specific and not fully understood.

In addition to shedding light on the binding mechanism of atrazine to the composite, we aimed to elucidate the mechanism of simultaneous binding of pairs of triazine herbicides. Only a few studies have looked at simultaneous binding of pollutants to natural sorbents (Matsui et al., 2003) or to engineered ones, such as GAC (Xing and Pignatello, 1997; Xing et al., 1996), organo-clays (Lee and Tiwari, 2012; Rytwo et al., 2002) and micelle clay composites (Nir et al., 2012). Several studies have reported the promising potential of new sorbents by batch experiments (Zhu et al., 2010) and in some cases also by filtration tests (Li et al., 2002). However, when extrapolating results obtained from laboratory filters to the pilot scale filters, it is essential to be able to yield reliable estimates for filter capacities under a variety of pollutant concentrations, flow rates, column size etc. For this purpose a semi-empirical model for the kinetics of filtration, (Nir et al., 2012) which could yield predictions, was developed and employed.

In the current study we explore experimentally and by modeling the removal of three triazine herbicides (simazine, atrazine and terbuthylazine) by PVP–CoS–MMT composites and GAC, attempting to shed light on the binding mechanism and study the complex simultaneous removal of the herbicides. We aim to model the removal of simazine by filtration with composite columns, at a wide range of concentrations. Furthermore, the removal of simazine by the composite columns will be compared to the removal by GAC filters.

2. Materials and methods

2.1. Materials

Na-montmorillonite clay (SWy-2) (MMT) was purchased from Source Clays Repository of The Clay Mineral (Columbia MO). S-triazine herbicides: simazine (6-chloro-2N,4N-diethyl-1,3,5-triazine-2,4diamine), atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5triazine-2,4-diamine), terbuthylazine (N2-tret-buthyl-6-chloro-4N-ethyl-1,3,5-triazine-2,4-diamine) were obtained from Makhteshim-Agan Industries Ltd. Their physical–chemical properties ("PPDB: Pesticide Properties DataBase," 2007) are shown in Table 1. Poly-4-vinylpyridine-co-styrene (PVP–CoS) with average ratio of 9:1 PVP to PS, was purchased from Sigma–Aldrich. Granular activated carbon, Hydraffin 30N was purchased from Benchmark Ltd.

2.2. Analytical methods

Polymer concentration in water was determined by spectrophotometer measurements (Thermo–UV–Vis) (see details below). Herbicide concentrations were measured by an Aglient 1200 series HPLC instrument equipped with a G1315D UV–vis Diode Array Detector ($\lambda = 222$ nm) with a Lichrospher® RP-18 (25 cm) column; the mobile phase was acetonitrile and water 70:30 v/v, flow rate of 1 mL min^{-1} (LOD 0.05 mg L^{-1}, LOQ 0.1 mg L^{-1}). Herbicide concentrations lower than 0.1 mg L^{-1} were determined by LC-MS using EPA standard method number 525.2 (LOQ 0.1 μg L^{-1}).

2.3. Experimental methods

2.3.1. Batch experiments

2.3.1.1 Preliminary tests showed that the binding of atrazine (10 mg L^{-1}) was positively correlated with PVP–CoS loading on the clay (0–0.25 g polymer per g clay) at a composite concentration of 0.834 g L^{-1}. The binding of the herbicides by the bare clay was relatively low. A polymer loading higher than 0.2 g polymer per g clay showed only minor improvement in herbicide binding; therefore this loading was selected. A similar optimal loading was reported for atrazine binding, by Zadaka et al. (2009).