Environmental Technology & Innovation 8 (2017) 172–181

Contents lists available at ScienceDirect

Environmental Technology & Innovation

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

Adsorption equilibrium and mechanisms of tris(2-chloroethyl)phosphate (TCEP) on zeolite-β under environmentally relevant and competitive conditions with methyl tert-butyl ether (MTBE)

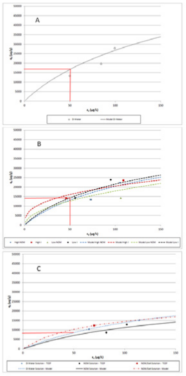
Scott A. Grieco [a,b,*], Bandaru V. Ramarao [b], Jürgen Schulte [c], David Kiemle [d]

[a] O'Brien & Gere Engineers, Inc., 333 West Washington Street, Syracuse, NY 13201, USA
[b] State University of New York College of Environmental Science and Forestry Department of Bioprocess Engineering, Syracuse, New York, 13210, USA
[c] State University of New York at Binghamton, Chemistry Department, 4400 Vestal Parkway East, Vestal, NY 13850, USA
[d] State University of New York College of Environmental Science and Forestry, Analytical & Technical Services, Syracuse, New York 13210, USA

HIGHLIGHTS

- Adsorption of TCEP onto Zeolite β in matrices of environmental relevance.
- Quantified TCEP adsorption in presence of MTBE.
- TCEP adsorption capacity (q_{max}) was reduced by 70% in samples containing MTBE.
- NMR data support hydrophobic surface interaction as primary adsorption mechanism.

GRAPHICAL ABSTRACT



Adsorption equilibrium results at lower c_e values for TCEP on 300:1 Zeolite β at pH=4.8 SU. Various solutions: A - DI water; B – NOM/salt background solutions; C - TCEP in presence of MTBE in NOM/salt background solutions.

Adsorption of TCEP in the presence of simulated environmental solution background [B] is comparable to DI [A]. Adsorption capacity of TCEP is reduced in presence of MTBE [C] indicating competition for adsorption sites.

ARTICLE INFO

Article history:
Received 18 July 2016
Received in revised form 31 January 2017
Accepted 1 March 2017
Available online 14 July 2017

Keywords:

ABSTRACT

Tris-2-chloroethyl phosphate (TCEP), an emerging contaminant of concern, is largely recalcitrant to removal due to its relatively high water solubility and non-degradability. Adsorption from wastewater is an option for separation, with a suitable adsorbent. In this study, equilibrium adsorption of TCEP onto zeolite–β (300:1 Si: Al ratio) is reported for simulated environmental waters with commonly occurring competing adsorbates. The equilibrium adsorption capacity of the adsorbent to TCEP in pure water which is about 103

---

* Corresponding author at: O'Brien & Gere Engineers, Inc., 333 West Washington Street, Syracuse, NY 13201, USA.
E-mail address: Scott.grieco@obg.com (S.A. Grieco).

http://dx.doi.org/10.1016/j.eti.2017.03.006

Emerging contaminant
Tris(2-chloroethyl)phosphate
Zeolite
Competitive adsorption
MTBE
Nuclear magnetic resonance

mg/g is reduced by approximately 30% in the presence of natural organic material (NOM) and several common salts. The data show that increasing NOM and salt concentrations do not have a proportionately increased effect. The equilibrium adsorption capacity of TCEP was reduced, by up to 70% under competitive conditions with methyl t-butyl ether (MTBE), another common contaminant in industrial wastewaters. Solid state NMR analyses of the zeolite subsequent to TCEP adsorption provide insight to the preferred zeolite adsorption sites. The NMR data for both Si and C appear to indicate that a hydrophobic surface interaction between the organic carbon and zeolite silica surfaces is the most likely adsorption mechanism.

1. Introduction

One particular Emerging Contaminant (EC) in industrial wastewaters and also in municipal water supplies that is of growing interest is tris-2-chloroethyl phosphate (TCEP). It is an organo phosphate ester that finds wide use as a flame retardant. TCEP is of special interest, because of the combination of potential toxicity to both aquatic organisms and humans, prevalence in the environment, and difficulty of removal through conventional wastewater treatment operations (Commission European Union Risk Assessment Report, 2009; Eurpoean Chemical Agency, 2009). Existing research shows that TCEP is one of the more recalcitrant compounds to remove with available wastewater technologies (Snyder et al., 2007). Activated sludge processes studied in Europe achieved up to 20% removal of TCEP (Reemtsma et al., 2006; Meyer and Bester, 2004). Oxidation processes that include chlorination, ozonation, and ultraviolet (UV) radiation and UV/hydrogen peroxide each achieved less than 40% removal of TCEP (Snyder et al., 2007; Reemtsma et al., 2008; Benotti et al., 2008). Moreover, there are limited studies available to support removal of TCEP using adsorption (Snyder et al., 2007; Westerhoff et al., 2005).

Zeolites are a class of porous materials that comprise inorganic oxide atoms covalently linked into a crystalline framework (Kuznicki et al., 2001). One specific family of zeolites comprises an alumino-silicate framework. Zeolites comprising pure silica are hydrophobic, whereas zeolites containing an increasing percentage of aluminum exhibit decreasing hydrophobicity (Krohn and Tsapatsis, 2005). Results of zeolite adsorption and separation of polar organic molecules can be found in the literature; however, prior to these efforts minimal information has been published related to zeolite adsorption application in the environmental field (Krohn and Tsapatsis, 2005, 2006; Li, 2007; Munsch et al., 1979; Wang et al., 2006).

In our previous work, Zeolite β was used to adsorb TCEP solutions in deionized water (Grieco and Ramarao, 2013; Grieco, 2014). Two materials were tested: one with low (25:1) and one with high (300:1) silica: alumina ratio. Testing was conducted at pH values of 4.8, 7, and 10 S.U. Both zeolites showed the best removal ($>$99%) of TCEP from solution at an acidic initial solution pH (4.8 S.U.). Adsorption equilibrium data were well described by Langmuir isotherms, and the maximum adsorption capacities of 77 mg/g and 103 mg/g were obtained for the 25:1 and 300:1 zeolites respectively. For this study, the more siliceous 300:1 material was selected given that it had the larger adsorption capacity.

This study provides further data on adsorption equilibrium of the TCEP-zeolite system in simulated environmental water matrices containing salts, natural organic matter (NOM), and a competing environment contaminant, methyl t-butyl ether (MTBE). MTBE was selected as a competitive adsorbate for these experiments since it has similar hydrophilicity (Log K_{ow} of 0.94) and water solubility (of 51 g/L) and that it is also a contaminant of current concern. MTBE is the most common oxygenated fuel additive used to enhance the combustion efficiency of gasoline (Hung et al., 2005). Studies have shown MTBE to be detected at low levels in drinking water, groundwater, and surface water samples (Landmeyer et al., 1998; Squillace et al., 1996; Reuter et al., 1998). MTBE adsorption to zeolites has been reported to be effective by other studies (Hung et al., 2005; Li et al., 2003; Knappe et al., 2007).

Solid state nuclear magnetic resonance (NMR) analyses were conducted for the Zeolite without and with the TCEP adsorbed. These analyses were used to evaluate TCEP-zeolyte interactions and postulate potential adsorption mechanisms.

2. Materials and methods

2.1. Materials

Zeolite β in powdered form was obtained from Zeolyst International (Pennsylvania, USA). The sample was received in H^+ form and was thermally conditioned to dry and the remaining organic template was eliminated by ramping up to a temperature of 180 C in a muffle furnace over a period of four hours, maintaining this temperature for two hours, and then allowing it to cool naturally under ambient conditions in a desiccator for 30 min.

TCEP was obtained from TCI Americas, received in liquid form ($>$99% purity). A 1 g/L stock solution of TCEP was made using neat TCEP and deionized (DI) water. Reagent grade 0.1M hydrochloric acid (HCl), 0.1N sulfuric acid (H_2SO_4), 0.1N sodium hydroxide (NaOH), methanol, and acetone were used as described in the following sections. HPLC-grade MTBE ($>$99.0%) was obtained from Avantor Performance Materials (JT Baker brand). Commercial humic acid (HA) sodium salt (2,000–500,000 Da) from Sigma Aldrich was selected as a reference dissolved organic carbon (DOC) to simulate NOM (Sentana et al., 2009;