OUTLOOKS IN EARTH AND PLANETARY MATERIALS

Highlighting the capability of zeolites for agro-chemicals contaminants removal from aqueous matrix: Evidence of 2-ethyl-6-methylaniline adsorption on ZSM-12

ELISA RODEGHERO1, LUISA PASTI2,*†, GIUSEPPE NUNZIANTE1, TATIANA CHENET2, LARA GIGLI3, JASPER R. PLAISIER3, and ANNALISA MARTUCCI4,*

1Department of Physics and Earth Sciences, University of Ferrara, via Saragat 1, I-44100 Ferrara, Italy
2Department of Chemistry and Pharmaceutical Sciences, University of Ferrara, I-44100 Ferrara, Italy
3Elefra-Sincrotrone Trieste, I-34149, Basovizza Trieste, Italy
4Department of Physics and Earth Sciences, University of Ferrara, via Saragat 1, I-44100 Ferrara, Italy; Orcid 0000-0002-6467-881X

ABSTRACT

Chloroacetanilides and their degradation products are frequently detected in surface and subsurface water due to their relatively high water solubility and their high potential to leach and migrate through the soil and contaminate groundwater.

In this study, we explored for the first time the capability of ZSM-12 zeolite for 2-ethyl-6-methylaniline \[\text{[C}_2\text{H}_5\text{C}_6\text{H}_3(\text{CH}_3)\text{NH}_2, labeled EMA}\] removal from water by combining chromatographic, thermogravimetric, and synchrotron X-ray powder diffractometric techniques. Rietveld refinement revealed the incorporation of about 4 EMA molecules per unit cell, in very good agreement with the weight loss given by TG analyses and with the saturation capacity determined by the adsorption isotherms.

The formation of supramolecular complexes mediated by co-adsorbed water and their strong interaction to framework O atoms confers stability to the pollutants in the zeolite cages. This prevents adsorbed molecules from desorbing as well as the entering of other competitive molecules. The rapid kinetics combined with the good adsorption capacity makes ZSM-12 a promising material to control and minimize water pollution from acetanilide compounds as well as other agro-chemicals contaminants.

Keywords: 2-ethyl-6-methylaniline adsorption, water pollution, ZSM-12, chromatography, thermogravimetry, synchrotron X-ray powder diffraction; Microporous Materials: Crystal-chemistry, properties, and utilizations

INTRODUCTION

The degradation of water resources is an increasing problem worldwide, and many efforts have been made to control point source pollution from homes and industry. However, water pollution from agriculture is becoming a major concern due to the widespread use of agro-chemicals in modern agriculture. Indeed, many of these substances have (Otero et al. 2013, 2014) harmful effects on aquatic organisms, insects, and mammals, and they persist in the aquatic systems for many years after their application (Shukla et al. 2006). In Europe, pesticides are considered hazardous substances as specified in current directives regarding water (Levitan 2000). The World Health Organization reported that ~3 000 000 cases of pesticide poisoning and 220 000 deaths occur in developing countries (World Health Organization 2010).

Drinking water quality standard should not exceed \(1 \times 10^6\) \(\mu\text{g/L}\) for an individual pesticide concentration and \(5 \times 10^6\) \(\mu\text{g/L}\) for the total pesticide concentration (Commission Directive 98/83/EC 1998). Due to the diffuse nature of contamination from agro-chemicals and the mobility of these compounds in the environment, their presence is difficult to control.

The pesticides are transferred from soil to water through various pathways (e.g., surface runoff, subsurface, and groundwater flows) either in solution or adsorbed onto particles. (Boithias et al. 2011). Among the agro-chemicals mentioned above, Metolachlor \([\text{C}_3\text{H}_7\text{ClNO}_2]\), 2-chloro-N-(2-ethyl-6-methylphenyl)-N-\((\text{-2-methoxy-1-methylethyl})\text{acetamide, labeled MTC}\) and its metabolites are frequently detected in surface and subsurface water (from \(1 \times 10^6\) \(\mu\text{g/L}\) to more than \(1 \times 10^9\) \(\mu\text{g/L}\)) (Traub-Eberhard et al. 1995; Gaynor et al. 1995) due to its relatively high water solubility (530 mg/L) that facilitates leaching, migrating through the soil, and contaminating groundwater (Nennemann et al. 2001). Moreover, chloroacetanilide degradation products such as 2-ethyl-6-methylaniline \([\text{C}_2\text{H}_5\text{C}_6\text{H}_3(\text{CH}_3)\text{NH}_2, labeled EMA}\) are more or equally toxic compared to their parent pesticide compound (Fava et al. 2000, 2001; Kimmel et al. 1986; Osano et al. 2002a, 2002b) and are promutagens in the Ames test (Kimmel et al. 1986). The rate and the extent of chloroacetanilide degradation strongly depend on environmental conditions such as temperature (Osano et al. 2003), moisture content (Gerstl et al. 1998), concentration of hydroxyl radicals (OH) (Webster et al. 1998), and microbial activity (Bollag et al. 1986; Liu et al. 1995; Stamper and Tuovinen 1998). Therefore, it is mandatory to develop mitigation measures able to prevent diffusion of pollutants into environment to reduce their impact (Zhang and Zhang 2011). Many treatment strategies have been proposed for the removal of these pollutants, including biological, chemical,