



Leaching potential of nano-scale titanium dioxide in fresh municipal solid waste



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HIGHLIGHTS

- Leaching potential of nano-TiO₂ in real fresh MSW was investigated.
- Batch tests were conducted at different pH, ionic strength and Ti concentrations.
- For all experimental conditions, most of the added Ti was retained in the waste.
- All MSW components contributed to the retention of the nano-TiO₂.

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ABSTRACT

With the rapid development in nanotechnology in recent years, the number of commercially available products containing engineered nanomaterials (ENMs) has increased significantly. It is expected that large fractions of these ENMs will end up in landfills for final disposal. Despite the wide use of ENMs, little data is available on their fate within landfills. This study examined the leaching behavior of nanoscale titanium dioxide (nano-TiO₂), one of the mostly used ENMs, in fresh municipal solid wastes (MSWs). Batch reactors containing municipal waste samples were spiked with a range of nano-TiO₂ concentrations at different pH and ionic strength conditions. The Ti concentrations in leachate decreased rapidly and reached steady state after about 12–24 h. Results suggest that, for the environmental conditions considered, approximately 3–19% of the added nano-TiO₂ remained in leachate. Batch tests conducted with individual synthetically-prepared solid waste components also showed low leaching potential (5.2% for organic waste, 3.3% for glass, 1.7% for both textile and paper and 0.6% for metal), indicating that all components of MSW contributed to the retention of the nano-TiO₂ mass within the solid matrix.

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1. Introduction

Rapid development in nanotechnology within the last decade has led to tremendous increase in the number of commercially available products containing engineered nanomaterials (ENMs). Studies indicate that more than 1300 products (about one sixth of globally available commercial goods) contain ENMs (Bondarenko et al., 2013). Production estimates of major ENMs range from 270,000 to 320,000 metric tons per year (Garner and Keller, 2014). ENMs are used in a variety of consumer products including electronics, textiles, cosmetics, medicine, and food (Peralta-Videa et al., 2011).

The growth in production and use of ENMs will inevitably cause their release to the environment either by accidental spillages, intentional releases (i.e., for remediation applications), or disposing as end-of-life waste (Keller et al., 2013). The exponential growth in the use of ENMs in consumer products is a genuine public health and environmental concern. Numerous eco-toxicological studies have been conducted to investigate the public health effects of widely used nanomaterials (Neal, 2008; Baun et al., 2008; Kahru and Dubourguier, 2009). However, environmental effects of ENMs are still not well-understood.

This study focused on nano-TiO₂, an extensively used ENM in various consumer goods and daily-use products such as cosmetics, paints, dyes and varnishes, textiles, paper and plastics, food and drugs, sunscreens and paving stones (Shi et al., 2013; Boldrin et al., 2014). Nano-TiO₂ is a white, non-combustible, and poorly soluble

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powder. It is widely used as a white pigment because of its high stability, anticorrosive and photocatalytic properties (Hashimoto et al., 2005). Nano-TiO₂ is also used in catalytic reactions, such as semiconductor photocatalysis, in the treatment of water contaminated with hazardous compounds, and in nanocrystalline solar cells as a photoactive material (Yuan et al., 2010). Photocatalytic effect of nano-TiO₂ has also found use in other applications, especially for self-cleaning and anti-fogging purposes (Montazer and Seifollahzadeh, 2011). TiO₂ accounts for 70% of the total production volume of pigments worldwide (Weir et al., 2012). In 2005, the global production of nano-scale TiO₂ was about 2000 tons and by 2010, the production increased to approximately 5000 tons. It is estimated that the use of nano-TiO₂ in sunscreen lotions alone ranges between 143 and 715 tons, with about 10–20% (14–143 tons) being discarded into the waste stream annually (Boldrin et al., 2014). It is expected that the global production of nano-scale TiO₂ will continue to increase in the near future; thus likely leading to increase the release of TiO₂ to the environmental (Keller et al., 2013).

Given the widespread general use of landfills for waste disposal, it is reasonable to expect that landfills are the major end-of-life fate for nanomaterials (Asmatulu et al., 2012; Gottschalk and Nowack, 2011). It is estimated that as much as 50% of ENMs produced worldwide may end up in landfills (Keller et al., 2013; Reinhart et al., 2010). Currently, little is known about the leaching behavior of these materials during waste processing and their final disposal in landfills. The fate and transport of ENMs from solid waste to leachate will depend on the biochemical characteristics present in the landfill environment. Therefore, it is important to investigate the leaching properties of nanomaterials under various environmental conditions representative of landfill environment (Musee, 2011; Nowack et al., 2012). Studies on this topic are lacking in literature. Among the few studies available, only one recent work investigated the behavior of coated nano-TiO₂ in real landfill leachate indicating that the coated nano-TiO₂ did not affect ongoing biological processes (Bolyard et al., 2013).

In this study, the leaching behavior of nano-TiO₂ in fresh municipal solid waste was investigated. Laboratory-scale batch reactor system was set up to examine the leaching of nano-TiO₂ from municipal solid waste. Both real and synthetically-prepared municipal solid wastes were employed to evaluate the short term behavior of non-coated nano-TiO₂ within the waste-leachate matrix under different conditions, namely: pH, ionic strength (IS), and TiO₂ concentrations.

2. Materials and methods

2.1. Materials

Real MSW samples were used to investigate the leaching behavior of nano-TiO₂. The waste samples were obtained from a sanitary landfill located in Izmit, Turkey. The samples were homogeneously mixed, shredded and stored at 4 °C prior to use. The waste samples had a moisture content of 65%. The concentrations of selected metals in the waste are given in Table 1.

Nano-TiO₂ was obtained from Sigma–Aldrich. Nano-TiO₂ was in uncoated powder form with an average particle size of 21 nm as indicated in the manufacturer specifications. The particle size distribution of nano-TiO₂ was also quantified by environmental scanning electron microscopy (ESEM) analysis as shown in Fig. 1.

Table 1
Metal content of MSW.

Parameter	Concentration (mg kg ⁻¹)
Titanium (Ti)	120
Silver (Ag)	ND*
Silicon (Si)	945
Zinc (Zn)	60
Aluminum (Al)	558
Cadmium (Cd)	ND*
Cobalt (Co)	0.8
Chromium (Cr)	13
Copper (Cu)	8.1
Iron (Fe)	660
Manganese (Mn)	94.3
Molybdenum (Mo)	0.5
Nickel (Ni)	8.8
Lead (Pb)	7.5

ND*: None detected.



Fig. 1. ESEM image of nano-TiO₂ used in batch tests.

2.2. Experimental approach

One liter bottles containing 250 g MSW and 300 mL deionized water (DI) were used as reactors for the leaching experiments. Each reactor was spiked with known amounts of nano-TiO₂ suspensions. The selected nano-TiO₂ concentrations were 0 (control reactor, without nano-TiO₂ addition), 10, 25 and 100 mg L⁻¹, respectively. Nano-TiO₂ stock solutions were prepared according to previously reported procedure (Weir, 2012). The required amount of stock solution was diluted and added to the reactors in each test. The list of leaching tests is summarized in Table 2.

The batch tests were conducted at two different pH ranges: one acidic and the other basic. Moreover, the impact of high IS conditions on nano-TiO₂ were also investigated. These conditions were considered because the pH normally changes from acidic to basic during waste stabilization in landfills. Stabilization is also accompanied by an increase in IS which can have a significant influence on the release of components from the waste matrix into leachate. The pH of the medium was adjusted using 3 mol/L H₂SO₄ or 6 mol/L NaOH stock solutions, respectively. The pH adjustment was performed at the beginning of each batch test; The pH was monitored throughout the duration of the tests. NaCl stock solution was used to provide increased IS

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