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Recycling of spent adsorbents for oxyanions and heavy metal ions in the production of ceramics

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ABSTRACT

Spent adsorbents for oxyanion forming elements and heavy metals are classified as hazardous materials and they are typically treated by stabilization/solidification before landfilling. The use of lime or cement for stabilization/solidification entails a high environmental impact and landfilling costs are high. This paper shows that mixing spent adsorbents in the raw material for the production of ceramic materials is a valuable alternative to stabilize oxyanion forming elements and heavy metals. The produced ceramics can be used as construction material, avoiding the high economic and environmental impact of stabilization/solidification followed by landfilling. To study the stabilization of oxyanion forming elements and heavy metals during the production process, two series of experiments were performed. In the first series of experiments, the main pollutant, Mo was adsorbed onto iron-based adsorbents, which were then mixed with industrial sludge (3 w/w%) and heated at 1100 °C for 30 min. Mo was chosen, as this element is easily adsorbed onto iron-based adsorbents and it is the element that is the most difficult to stabilize (i.e. the highest temperatures need to be reached before the concentrations in the leachate are reduced). Leaching concentration from the 97/3 sludge/adsorbent mixture before heating ranged between 85 and 154 mg/kg; after the heating process they were reduced to 0.42–1.48 mg/kg. Mo was actually stabilized, as the total Mo concentration after addition was not affected by the heat treatment. In the second series of experiments, the sludge was spiked with other heavy metals and oxyanion forming elements (Cr, Ni, Cu, Zn, As, Cd and Pb) in concentrations 5 times higher than the initial concentrations; after heat treatment the leachate concentrations were below the regulatory limit values. The incorporation of spent adsorbents in ceramic materials is a valuable and sustainable alternative to the existing treatment methods, saving raw materials in the ceramics production process and avoiding the use of stabilizing agents. Besides, spent adsorbents added to the raw material for ceramic products, may improve their aesthetic and structural properties.

1. Introduction

Oxyanion forming heavy metals like As, Cr, Mo, Sb, Se, V and W are nowadays high on the environmental agenda due to their toxicity and high mobility (Cornelis et al., 2008). Their removal from wastewater before discharge was already studied extensively in literature. Several techniques exist to remove oxyanion forming elements (and other heavy metals) from wastewater: (a) (co)precipitation, (b) adsorption, (c) ion exchange and (d) membrane techniques (nanofiltration, reverse osmosis and electrodialysis). All these techniques finally result in clean water and some sort of hazardous solid waste that contains the element removed: a sludge in (a), a column packing in (b) and (c), and a concentrate from which the water can be evaporated to give a sludge for (d) (Holm and Wilson, 2006; Mohan and Pittman, 2007).

Adsorption is a simple and cheap technique, capable of removing different oxyanions simultaneously. Examples of adsorbents that can be used to remove oxyanions are activated carbon, manganese/aluminum/titanium oxides, and iron oxides and hydroxides. Activated carbon is a relatively expensive adsorbent, which can readily adsorb organic compounds like PCBs and PAHs, pesticides, dyes and aromatic solvents. Inorganic components do not bind well to activated carbon, and to obtain good removal capacities e.g. for metals and oxyanions, the surface of activated carbon should be pretreated or coated, by impregnating the surface with e.g. iron oxides (Vaughan and Reed, 2005; Chen et al., 2007), or

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by modifying the surface e.g. by cationic surfactants (Choi et al., 2009). Iron oxides and hydroxides can however be produced at low-cost and are widely used for the adsorption of oxyanions, as they have a high affinity for oxyanions; their adsorption efficiency is highest at low pH (Adegoke et al., 2013; Hua et al., 2012; Gallegos-Garcia et al., 2012). To achieve a high capacity, use can be made of iron oxide nanoparticles with a high specific surface. Such nanoparticles cannot be used as such in an adsorption column, the most widely used continuous adsorption setup in wastewater treatment, because of high pressure requirements. For column applications, nanosized materials must be coated on a larger sized carrier materials. Therefore adsorbents for oxyanions, consisting of magnetite supported by a zeolite or perlite matrix were developed (Verbinnen et al., 2012, 2013b, 2015; Vaclavikova et al., 2010).

One of the main questions that arises when discussing adsorption is whether or not the adsorbent can be regenerated after usage. For the adsorption of oxyanion forming elements and heavy metals on adsorbents, the regeneration of the spent adsorbent is not straightforward in most cases. Due to the strong interactions (i.e. inner-sphere complex formation) of most other oxyanion forming heavy metals with adsorbents, techniques to regenerate the adsorbent are limited and/or expensive (Verbinnen et al., 2012). For some elements, eluting with alkaline solutions can be sufficient to remove the adsorbate from the adsorbent and to reuse the adsorbent after regeneration (Bujnakova et al., 2013). This again leads to a contaminated waste stream. When regeneration is economically not feasible, the adsorbent needs to be discharged after a single use, and this is often considered the main drawback of adsorption.

The main disposal strategies for spent adsorbents are either incineration or landfilling (Mohan and Pittman, 2007). Incineration is mainly used for carbonaceous adsorbents, so landfilling is the preferred option for most adsorbents (i.e. iron-based compounds) for oxyanions. The toxic characteristics of many oxyanion forming elements require solidification/stabilization of the adsorbent before landfilling. Cement and lime were proven to be effective to stabilize/solidify spent (iron-based) adsorbents, but at least 25% of lime and/or cement has to be added to bring leaching below the regulatory limit values (Kundu and Gupta, 2008). Although being low-cost materials, the environmental impact of both lime and cement is high due to the release of carbon dioxide in the production process. After stabilization/solidification, the spent adsorbents need to be landfilled, entailing extra costs, i.e. landfilling taxes.

In this paper, an alternative strategy to dispose spent inorganic adsorbents is proposed. By blending adsorbents with the raw materials for ceramics, primary resources for the ceramic production can be saved, and the costs and the environmental impact of landfilling the adsorbent can be avoided. Examples of such ceramic products can be (but are not limited to) bricks, floor and roof tiles as well as lightweight and dense aggregates. Contaminated sludge and sediments have often been used to produce ceramics (Alonso-Santurde et al., 2008; Gonzalez-Corrochano et al., 2012). From earlier research on recycling of sludge from soil cleaning for the production of ceramics (Verbinnen et al., 2014), it appeared that upon heating inorganic sludge, the leaching concentrations of the toxic elements Ni, Cu, Zn, As, Cd and Pb could be reduced (Table 1). This was also reported for other waste streams that were used to produce ceramics (Chang et al., 2007; Xu et al., 2008; Quijorna et al., 2012), and is related to removal of organic acids responsible for the formation of mobile organo-metallic complexes, and/or a change in pH, and/or incorporation of the heavy metals in stable phases from which they do not leach easily (Xu et al., 2008).

Contrarily, the leaching of the oxyanion forming elements Cr and Mo increases upon heating (Table 1). This was also observed by other researchers producing ceramics from different types of waste: Waelz slag (Quijorna et al., 2012), aggregate sludge and fly ash (Gonzalez-Corrochano et al., 2012), and sewage sludge (Xu et al., 2008). At temperatures below 700 °C, Cr(III)- and Mo(IV)-compounds are oxidized and leach as their mobile (and for Cr most toxic) hexavalent oxidation state. At temperatures above 700 °C, the mobile Cr compounds are incorporated into low-melting silicates, and the leaching concentrations are reduced (Fig. 1). For Mo compounds, temperatures above 1000 °C are needed to incorporate them into silicates.

It is evidenced from the literature cited above that some hazardous waste streams can be stabilized by producing ceramics. Nevertheless, attempts to incorporate other heavily polluted waste streams, like spent adsorbents, in the raw material for ceramics production, in view of stabilizing the oxyanions and heavy metals present in the waste, are scarce to non-existent in literature. These materials are normally landfilled.

The aim of this paper is to explore the possibility of adding spent adsorbents to contaminated sludge and produce ceramic materials in order to stabilize the oxyanion forming elements and heavy metals. More specifically, it is investigated whether spent zeolite or perlite-supported iron-based adsorbents saturated with oxyanions can be mixed with industrial sludge (see Section 2.2) and subsequently fired at high temperature to obtain aggregates in which the oxyanions are stabilized. In a first series of tests, Mo was loaded onto iron-based adsorbents, mixed with the raw material for ceramics (the industrial sludge), and subsequently fired at 1100 °C to produce ceramics, from which the leaching concentrations were measured. Mo was chosen, as this element is easily adsorbed onto iron-based adsorbents (Verbinnen et al., 2012) and it is the element that is the most difficult to stabilize (i.e. the highest temperatures need to be reached before the concentrations in the leachate are reduced). To study the stabilization after heating of other oxyanion forming elements and cation forming heavy metals (Cr, Ni, Cu, Zn, As, Cd and Pb), the industrial sludge was spiked with these elements, ceramics were produced and the leachate concentrations were measured.

2. Materials and methods

2.1. Adsorption experiments

Adsorption experiments were performed with zeolite- and perlite-supported magnetite, prepared as described by Verbinnen

Table 1
Leachate concentrations of Cr, Ni, Cu, Zn, As, Mo, Cd and Pb from contaminated sludge heated at 400, 600 and 800 °C for 4 h, d.l. = detection limit (0.01 mg/kg), $n = 2$.

Temperature (°C)	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Mo (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
Not heated[a]	0.13 ± 0.00	1.31 ± 0.02	4.43 ± 0.08	3.78 ± 0.05	0.21 ± 0.00	2.02 ± 0.02	0.02 ± 0.00	<d.l.
400	0.94 ± 0.06	0.19 ± 0.00	0.35 ± 0.03	0.17 ± 0.03	0.43 ± 0.05	3.36 ± 0.11	0.02 ± 0.00	<d.l.
600	19.62 ± 1.24	0.04 ± 0.00	0.02 ± 0.00	0.56 ± 0.53	0.04 ± 0.01	5.94 ± 0.31	0.01 ± 0.00	<d.l.
800	4.44 ± 0.96	0.04 ± 0.00	<d.l.	0.04 ± 0.06	0.12 ± 0.05	5.67 ± 0.06	0.02 ± 0.00	<d.l.

[a] As reported by Verbinnen et al. (2014).

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