Utilization of raw red mud as a source of iron activating the persulfate oxidation of paraben

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ABSTRACT

The degradation of emerging micro-contaminant propylparaben (PP) by persulfate oxidation was studied in this work. The activation of sodium persulfate (SPS) was done utilizing raw red mud (RM), a by-product of bauxite processing. RM with a specific surface area of $\sim 10\,m^2/g$ is rich in metal oxides, including Fe, Al, Ti, Si, Na and Cu, as this has been evidenced by X-ray diffraction (XRD) patterns, and scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS). Experiments were conducted at RM concentrations between 0.5 and 4 g/L, SPS concentrations of 1 and 2 g/L and PP concentrations between 0.4 and 6.4 mg/L at pH = 3 in ultrapure water. PP degradation, approached by a pseudo-first order rate expression, increased with increasing SPS and RM concentrations (for the latter up to 2 g/L) and decreasing PP concentration. Acidic conditions favor iron dissolution, whose extent depends on the operating conditions; leached iron contributes significantly to PP degradation. The reaction is retarded in environmental matrices, i.e. bottled water and secondary treated wastewater highlighting possible interactions amongst RM, PP, inherent water constituents and reactive species; the latter include sulfate and hydroxyl radicals as this has been evidenced by electron paramagnetic resonance (EPR) measurements. SPS activation by RM was also coupled with other activators, i.e. simulated solar irradiation, 20 kHz ultrasound or heating to 40 °C and 50 °C in an attempt to evaluate the level of synergy. Depending on the integrated processes and the operating conditions in each case, the effect was negative (i.e. −177% for solar light), near zero or positive (i.e. 48% for ultrasound at 8 W/L).

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1. Introduction

Red mud (RM) is the waste product generated during aluminium production through the Bayer process. RM, which is also referred to as bauxite residue, originates from the extraction of alumina from bauxite at alkaline conditions and elevated temperatures and pressures (Paramguru et al., 2005). RM is a mixture of compounds originally present in the parent mineral, as well as compounds formed or introduced during the Bayer cycle. It mainly consists of various oxides with Fe_2O_3, Al_2O_3, SiO_2, TiO_2, CaO and Na_2O being the dominant ones (Paramguru et al., 2005). Depending on the bauxite quality, 1–2.5 kg of RM are generated per kg of alu-

mina extracted; in this respect, the annual, global RM production is estimated at $9\ 10^{10}$ kg (Rai et al., 2017), while the global levels of RM at the beginning of the current decade were estimated at $3\ 10^{12}$ kg (Sousa et al., 2018). Greece is one of the top alumina-producing states in Europe (Paramguru et al., 2005), with an annual RM generation estimated at $7\ 10^8$ kg.

Lagooning and dry stacking have traditionally been the most widely employed methods for RM handling (Rai et al., 2017); in recent years though, there have been increasing concerns in relation to the environmental impacts of RM disposal. Waste valorization not only promotes the principle of circular economy but may also alleviate the environmental burden associated with alumina processing, and, indeed, numerous other industrial activities. In this perspective, RM has been employed as an additive in construction materials (Scribot et al., 2018), skeleton binder for sewage sludge conditioning (Zhang et al., 2014) and fertilizer (Paramguru et al., 2005). Since the composition of RM is rich in oxides of vari-

ous metals (mainly iron, aluminium, silicon and titanium), it can be utilized as an adsorbent and/or catalyst in several environmental applications. Previous studies have shown that RM is an efficient and inexpensive adsorbent for the removal of organics (Ali et al., 2012) and heavy metals (Ahmed and Ahmaruzzaman, 2016; Jacukowicz-Sobala et al., 2015) from waters/wastewaters, as well as CO_2 from gaseous streams (Chan et al., 2017).

The occurrence of iron in RM makes it a suitable candidate for Fenton and photo-Fenton reactions, where hydroxyl radicals are generated from the catalytic dissociation of hydrogen peroxide. Costa et al (2010) treated RM at 300–600 °C under H_2 flow and the resulting catalysts were tested for the decolorization of methylene blue and the reduction of hexavalent chromium in the presence of H_2O_2. Dias et al (2016) prepared a RM/C catalyst by means of chemical vapor deposition of ethanol and tested it for the photo-Fenton degradation of reactive black 5. Shao et al (2016) acidified (using HCl, HNO_3 or H_2SO_4) and then calcined (in the range 200–600 °C) RM and the resulting materials were tested for the dark Fenton oxidation of butyl xanthate. In further studies from the same group (Wei et al., 2017), acidification was done using a combination of H_2SO_4 and molasses wastewaters and the materials were tested for the degradation of orange II. Another research strategy involves mixing of red mud with clays (Hajjaji et al., 2016) or other waste materials such as polyethylene terephthalate (PET) (Sousa et al., 2018; Bento et al., 2016) to synthesize catalysts for the dark and photo-Fenton degradation of various organics. Besides Fenton and alike systems, neutralized RM was doped with cobalt and the resulting composite was tested as a photocatalyst for the degradation of methylene blue under solar radiation (Sahu and Patel, 2016); in other studies (Xu et al., 2016), RM was doped with cerium and tested for the catalytic ozonation of bezafibrate.

In recent years, the use of persulfate salts as a source of reactive sulfate radicals has gained considerable attention for various environmental applications including wastewater treatment, drinking water production, in situ chemical remediation of subsurface contaminated sites, sewage sludge dewatering and abatement of atmospheric pollution (Ike et al., 2018). The use of persulfate to generate sulfate radicals instead of hydrogen peroxide (i.e. as in classical Fenton reactions) to form hydroxyl radicals is an attractive option since the former may have equal or even greater redox potential, higher selectivity and longer half-life than the latter, depending on the specific reaction conditions (Wang and Wang, 2018).

Persulfate conversion to sulfate radicals requires the action of a suitable activator including transition metals, metal oxides and nanomaterials, high temperatures, base, or some kind of irradiation (e.g. light, ultrasound) (Xiao et al., 2018; Matzek and Carter, 2016). In the case of transition metals (Me), the overall reaction is as follows:

$$2S_2O_8^{2-} \xrightarrow{Me^{n+} \leftrightarrow Me^{n+1}} SO_4^{\bullet-} + SO_4^{2-} + S_2O_8^{\bullet-} \qquad (1)$$
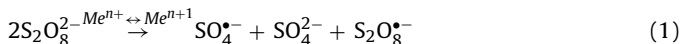
In addition to reaction (1), sulfate radicals can react with water to form hydroxyl radicals (Matzek and Carter, 2016):

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^+ \qquad (2)$$

In this respect and by analogy to the role of RM in Fenton reactions, its use as an activator of persulfate seems promising. However, relevant information in the literature is scarce since only two papers report the application of the RM/persulfate system for the degradation of trichloroethylene (Qian et al., 2016) and the antibiotic sulfadiazine (Feng et al., 2016).

In this work, raw RM (i.e. submitted to no treatment but drying) is employed as an activator of persulfate for the degradation of propylparaben (PP), a moderate endocrine disruptor (ED), in various aqueous matrices. EDs can be found in watercourses and

have the ability to mimic the functioning of endocrine systems of humans and animals, because of their structural resemblance to natural hormones (Vilela et al., 2018). To some extent, EDs may be removed in wastewater treatment plants through biodegradation and sorption processes; however, they can partially escape from conventional treatment processes, persist in the environment at unexpected levels, undergo bioaccumulation, and even react with other compounds to generate new unpredictable contaminants (Juliano and Magrini, 2017).

The effect of several parameters such as solution pH, RM, SPS and PP concentrations, leached iron, water quality, radical scavengers and the simultaneous application of other activators (i.e. heat, ultrasound and solar irradiation) on PP degradation kinetics is evaluated.

2. Materials and methods

2.1. Materials

Red mud was provided by Aluminium of Greece, the second largest bauxite producer in Europe, located in the region of Central Greece. RM was dried at 100 °C overnight and used without further conditioning or treatment.

Propylparaben ($C_{10}H_{12}O_3$, CAS no: 80-05-07), sodium persulfate ($Na_2S_2O_8$, CAS no: 7775-27-1), humic acid (HA, CAS no: 1415-93-6), methanol (CAS no: 67-56-1), sodium bicarbonate (CAS no: 144-55-8) and iron sulfate heptahydrate were provided by Sigma-Aldrich. *tert*-Butanol (CAS no: 75-65-0) was provided by Fluka. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO > 97%) was purchased from Cayman Chemical Company.

Most experiments were performed in ultrapure water (UPW) acidified at pH 3 with sulfuric acid. Some experiments were also carried out in other matrices, i.e. secondary treated wastewater taken from the University of Patras campus treatment plant (containing ∼8 mg/L organic carbon) and commercially available bottled water (mainly containing bicarbonate at ∼220 mg/L). Other matrix properties are given elsewhere (Metheniti et al., 2017).

2.2. Experimental procedures

A stock solution of PP was prepared in UPW (80.3 mg/L) and a measured volume was then added in the reaction solution to achieve the desirable PP concentration, which, in most cases, was 0.8 mg/L; this value is a trade-off between those recorded in environmental samples (i.e. up to the μg/L level (Montes-Grajales et al., 2017)) and the need to monitor the reaction progress within a reasonable timescale with the analytical protocols available in this work. The solution was also added the appropriate amount of RM (in the range 0.5–4 g/L) and SPS (1 or 2 g/L); these concentrations were selected after several preliminary trials at various PP:RM:SPS concentration ratios had been performed. Most of the experiments were conducted at initial solution pH = 3, which is typical of Fenton and Fenton-like reactions, allowing the partial dissolution of RM's iron oxides (see Section 3.2) to iron ions for the homogeneous SPS activation and PP degradation.

The reaction mixture was left to react for 180 min at ambient temperature (unless otherwise stated), during which time samples were periodically drawn, quenched with methanol, filtered and analyzed as described in Section 2.4. Experiments at 40 °C or 50 °C were performed using a temperature-controlled water bath. For process integration experiments (see Section 3.4), a solar simulator (Oriel, model LCS-100) equipped with a 100 W xenon, ozone-free lamp was used to provide irradiation at an incident intensity of 7.3 10^{-7} Einstein/(L.s), while a 20 kHz, horn-type sonicator (Branson Digital Sonifier 450 W) was used to provide ultrasound (US) irradi-