International Journal of Mineral Processing 169 (2017) 111–118

Contents lists available at ScienceDirect

International Journal of Mineral Processing

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

New ways to use the red mud waste as raw material for inorganic-organic hybrid hydrogels

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ARTICLE INFO

Article history:
Received 6 February 2017
Received in revised form 19 October 2017
Accepted 9 November 2017
Available online 15 November 2017

Keywords:
Red Mud
Kaolin
Sodium silicate
Acrylic hydrogels
Hybrid materials
Wastes recovery

ABSTRACT

The present paper was aimed at developing innovative hybrid composites by using cheap filler, like red mud (RM). The study importance refers to RM recycling, a recent trend in environmental science. Besides its causticity, large amounts of RM are produced yearly, calling for recovery measurements. Herein, poly (acrylic acid)- based inorganic-organic hybrid hydrogels (PAA hydrogels) incorporating RM were synthesized.
Furthermore, the possibility of involving inorganic additives (kaolin and/or sodium silicate) together with RM was investigated. Incorporation of all three inorganic compounds (RM + Kaol + Sil) in hydrogels was also evaluated, novel hybrids being prepared. The obtained hybrids were characterized by different techniques (DR UV-VIS; DRIFT; TGA/DTG; SEM) and in terms of swelling behavior. DRIFT and DR UV-VIS confirmed the occurrence of characteristic bands of raw materials. Final properties (water uptake, thermal stability, porosity) can be controlled by modifying preparation conditions. Hydrogels yielded, by calcinations, iron- rich ceramic foams, able to promote water removal of sulfide ions from wastewaters.

1. Introduction

Red Mud (RM), a solid brick red slimy waste residue resulting from caustic digestion of bauxite ores in the process of alumina (Al_2O_3) production, occurs as alkaline slurry (pH = 10–13) containing various oxides (Al_2O_3, Fe_2O_3, Na_2O, SiO_2, CaO and TiO_2). Large amounts of RM are generated worldwide yearly, its disposal becoming a major problem [Wang et al., 2008; Ribeiro et al., 2012; Ramprasath et al., 2014; Biswas and Satapathy, 2009; Jena and Satapathy, 2012; Banjare et al., 2014; Zhang et al., 2014; Lv et al., 2013; Balomenos et al., 2011; Smiljanic et al., 2011]. Currently, Al is produced using a two-stage process: (I) high metallurgical grade Al_2O_3 is obtained from bauxite (Bayer, 1888) and then (II) Al_2O_3 is reduced to Al (Hall-Heroult). Despite of its high alkalinity (it bears various hydroxides and, also, due to NaOH treatment), RM is classified by EC as a non-hazardous. However, RM causes a significant environment impact (it forms small powder particles by drying, it bears various chemical and mineralogical species, it occurs in large amounts), recovery of useful compounds from RM gaining significant importance. Bayer himself suggested iron recovery in 1892. Considering both the high content in iron oxides as well as the presence of TiO_2 in RM, this solid could be utilized for obtaining oxidation catalysts. One of the most important properties of a catalyst is the dispersion of active sites on its surface. The higher the dispersion degree, the catalytic activity is higher. Since RM exhibits a low surface, it would be expected to show also a low dispersion of active sites. A modality to increase the dispersion degree could be the incorporation of the RM in a polymeric matrix. Using this approach, red mud ceramic foams with hierarchical porous organization of active phase can be obtained following the calcinations of the polymeric hydrogel [Ramprasath et al., 2014; Balomenos et al., 2013; Smiljanic et al., 2011].

Hydrogels represent three-dimensional hydrophilic polymer networks, either chemically or physically crosslinked, able to absorb plenty water, without dissolution [Ray et al., 2009; Zaharia et al., 2015a; Zaharia et al., 2015b].

One important pollution source consists of dissolved sulfides rising from various industry branches such as: oil processing; fossil fuel gasification; dyes and pigments; kraft paper; tanneries; viscose rayon processing; sewer networks, as a result of anaerobic sulfate reduction processes. These sulfides are further released in wastewaters and are

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https://doi.org/10.1016/j.minpro.2017.11.005
0301-7516/

very toxic for living beings, especially at concentrations in water exceeding 0.2 mg/L. In addition, they can also affect biological processes occurring in wastewater treatment plants (Ahmad et al., 2009; Firer et al., 2008; Nielsen et al., 2005; Zhang et al., 2008). The addition of iron salts (chloride, sulfate, nitrate in ferric or ferrous forms) proved to be a successful approach for abatement of sulfide-associated issues. These above mentioned iron forms act in a different manner. Ferrous salts remove sulfide by precipitation as ferrous sulfide (FeS). Ferric salts remove sulfide by oxidizing it chemically to elemental sulfur; ferric ion is, subsequently reduced to Fe (II), FeS being finally produced (Zhang et al., 2008). The main drawback of this treatment process is the release of FeS in treated water. To surpass this inconvenient, sulfide may be converted to elementary sulfur using oxygen from air as an oxidant and red mud-derived ceramic foams as catalyst. These foams, because of their high iron content, are expected to have potential for water remediation. To provide a final use of the obtained hydrogels, preliminary results (proving ceramic foams functionality as catalysts for the processes of sulfide ions removal from wastewaters) are given. In this respect, results referring to the oxidation of sulfide oxidation in wastewater are presented.

The present paper was aimed at obtaining inorganic-organic hybrid composites by RM incorporation in polyacrylic acid-based hydrogels. Furthermore, the possibility of using other inorganic additives (kaolin and/or sodium silicate) besides RM was examined, followed by the investigation of the properties of the new materials. Even though lot of works are published on hydrogels, only few dealt with inorganic compounds incorporation in hydrogels, most of them being dedicated to incorporation of organic compounds (like drugs or bioactive compounds) based on their resemblance to soft tissues (high moisture) [Dragan et al., 2012; Zaharia et al., 2015; Lungu et al., 2012; Sandu et al., 2013]. Despite that RM polymer composites were previously obtained [Yang et al., 2016; Jankovic et al., 2013; Kinnarinen et al., 2015; Kirwan et al., 2013], the use of hydrogels for their synthesis is not widely reported. Therefore, the present paper provides new information in this field. To the best of our knowledge, this kind of hybrid materials having such complex composition (rendered using both inorganic and organic phases, and, moreover, the inorganic phase consisting not only of one but also of either two or three components) has not been reported before. Samples prepared under different conditions were characterized by different physico- chemical modern techniques (DR UV-VIS/ DRIFT, TGA/DTG and SEM), estimating the importance of each component in the hybrid materials. Moreover, water uptake tests were carried out.

The obtained samples are further calcined at elevated temperature to yield ceramic foams with a significant content in iron (provided by RM), that could be used as oxidation catalysts. Therefore, our study provides new information both in waste recovery and in giving a new route for obtaining advanced composite materials with useful properties.

2. Experimental

2.1. Materials

The monomer involved in hydrogels preparation, acrylic acid (noted hereafter AA; Merck- Darmstadt, Germany) was distilled for inhibitor removal. Redox initiation system, potassium persulfate (KPS) - sodium pyrosulfite (MS), pro-analysis, from "Reactivul" (Bucharest, Romania) and the crosslinking agent, *N*, *N′*-methylene bisacrylamide (MBA, more than 99% purity, Merck) were used as received. RM slurry (Alumol Plant Tulcea, Romania) was dried and neutralized with CO_2 up to a pH of 7. It must not be used an alkaline RM, because this would lead to changes in the overall pH, which are detrimental for redox initiation system, leading to issues in the global process. Two batches of RM (RM 1 and RM 2, coming from two different locations of Alumol red mud discharge pond) were used to estimate the effect of inorganic phase on the final properties of the prepared hybrids. The chemical composition of RM samples (determined by chemical analyses and inductively coupled plasma atomic emission spectroscopy) is given in Table 1.

Table 1
Chemical composition as oxides in the investigated RM samples (wt%/wt).

Component	RM1	RM2
Fe_2O_3	36.6	41.1
FeO	2.3	1.6
Al_2O_3	17.5	17.5
SiO_2	7.1	7.3
CO_2	4.0	5.7
Na_2O	2.5	3.6
MgO	0.5	0.0
CaO	10.2	7.5
TiO_2	13.1	5.2
H_2O	6.1	9.5
PC(1000 °C)[a]	10.1	15.1

[a] *Loss on calcination at 1000 °C.*

Sodium silicate (Sil), (RASIN SRL- Bucharest, technical purity, 50 wt%/wt. aqueous solution, was used as received. Kaolin (Kaol, Sigma Aldrich) was used without further purification. The dispersant, involved in AA homogenization with the inorganic phase (neat RM, RM + Kaol, RM + Sil, RM + Kaol + Sil) is ammonium polyacrylate (noted $PAANH_4$).

2.2. Samples' preparation

2.2.1. $PAANH_4$ preparation

The dispersant was prepared by submitting a 20 wt% aqueous AA solution to polymerization under N_2 atmosphere (to remove O_2) at 45 °C for 1 h, using a redox initiation system (KPS = MS = 0.5 wt%, with respect to AA amount). After the polymerization ended, the pH was adjusted to 8 (with NH_3 25 wt%), getting a solution used for dispersing inorganic powders, before samples preparation.

2.2.2. Hybrid hydrogels preparation

Samples of hybrid hydrogels were prepared as follows: (I) inorganic phase was dispersed in the aqueous medium until a uniform distribution. To this end, RM either by itself or together with other additive (Kaol; Sil; Kaol + Sil) was mixed with $PAANH_4$ and water for 50 min, under magnetic stirring; (II) solutions of crosslinking agent (MBA) and of initiators (KPS and MS, respectively) were prepared by dissolution in water and mixed with the RM dispersion and (III) AA is added. AA has to be added the last, as the components of RM proved to be able to promote polymerization before crosslinking occurrence, making the control of the polymerization challenging. Eight samples were prepared (Table 2).

2.3. Physico-chemical characterization

2.3.1. Structural characterization

X-Ray Diffraction (XRD) patterns were recorded on a Bruker D8 Advance Diffractometer equipped with a DIFFRAC^{plus} XRD Commender

Table 2
Samples' preparation conditions.

Sample	RM sample	Organic/inorganic ratio wt/wt	RM/Sil/Kaol/organic wt/wt/wt/wt
1			1.5/0/0/1
2			0.9/0.6/0/1
3	RM1	1.5/1	0.9/0/0.6/1
4			0.9/0.3/0.3/1
5			1.6/0/0/1
6			1/0.6/0/1
7	RM2	1.6/1	1/0/0.6/1
8			1/0.3/0.3/1