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Research paper

A novel study on the influence of cork waste residue on metakaolin-zeolite based geopolymers

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ABSTRACT

The effect of industrial waste from the cork industry on the strength and adsorption properties of zeolite-metakaolin based geopolymers has been studied. Cork residue 20% by weight was added to geopolymers that contained 0%, 25%, 50%, 75% replacement of metakaolin by zeolite in the structure. The SiO_2/Al_2O_3 and Na_2O/Al_2O_3 molar ratios were kept at 1 to reduce the environmental impact of sodium silicate and sodium hydroxide to the minimum. The compressive strength evolution after 1, 14 and 28 days in water and the heavy metals (Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}) adsorption of the geopolymers were determined. It was found that addition of zeolite and cork residue in minor amounts concurrently aided in increasing the compressive strength of geopolymers. The adsorption properties, however, were dominated by the presence of cork residue and metakaolin which resulted in increasing adsorption of all heavy metal cations with increasing metakaolin in the structure. The adsorption was well fitted by the Langmuir model with $R^2 > 0.98$ and the trend of adsorption was found to be $Pb^{2+} > Cd^{2+} > Cu^{2+}, Zn^{2+} > Cr^{3+}$. The significant improvement in compressive strength, as well as adsorption capacity observed with the addition of cork waste residue, connotes that it can be efficient as filler in geopolymers.

1. Introduction

Heavy metals (HM) have been increasing in the environment at alarming levels due to unconstrained industrial activities leading to untreated effluents being let into the ecosystems. In the recent years, it has become a critical cause of worry as it has given rise to several ecological disasters with high health risk like lead poisoning in Flint river in 2014 (Lovell, 2016), mining waste released by the Samarco dam burst in Brazil killing thousands of fish in 2015 (Phillips, 2016) and Galveston Bay which apparently has had an averaged 285 spills a year since 1998 resulting in death of thousands of birds (Tresaugue, 2014). Therefore, a considerable amount of research has been focussed on removing these toxic wastes from the environment by various methods such as biosorption, membrane adsorption, chemical precipitation, coagulation, and ion-exchange. Of these, adsorption has been a rather attractive technique for HM removal as it provides easy and efficient removal and the ability to use low cost natural or waste materials that are eco-friendly. HM adsorption has been observed on various natural clay minerals such as sepiolite (Bektaş et al., 2004), bentonites (Andrejkovičová et al., 2010; Eren and Afsin, 2008; Kaya and Ören, 2005), illite, kaolinite, beidellite and montmorillonite (Adebowale et al., 2005; Bhattacharyya and Gupta, 2008; Brigatti et al., 2005; Gupta and Bhattacharyya, 2005; Zhang and Hou, 2008) and also on other natural materials like algae marine (Jalali et al., 2002), egg shell (Mittal et al., 2016), corn chaff (Han et al., 2006), rice bran, luffa husk (Vashantha et al., 2016), cashew nut shell (Kumar, 2014) and cork powder (Pintor et al., 2012).

Cork oak tree is very abundant in several Mediterranean countries due to the high production of cork stopper for the wine industry. Portugal has a leading position in the cork industry due to the quality and quantity of cork stopper produced which amount to 50% of the total consumption by the world wine industry (Mota et al., 2006). This has resulted in an increase of residual cork by-product in industries known as cork powder. Therefore, alternative use of this low-cost biomass has been investigated in the last two decades. Chemically, cork is composed of five groups components: Suberin (a complex mixture of

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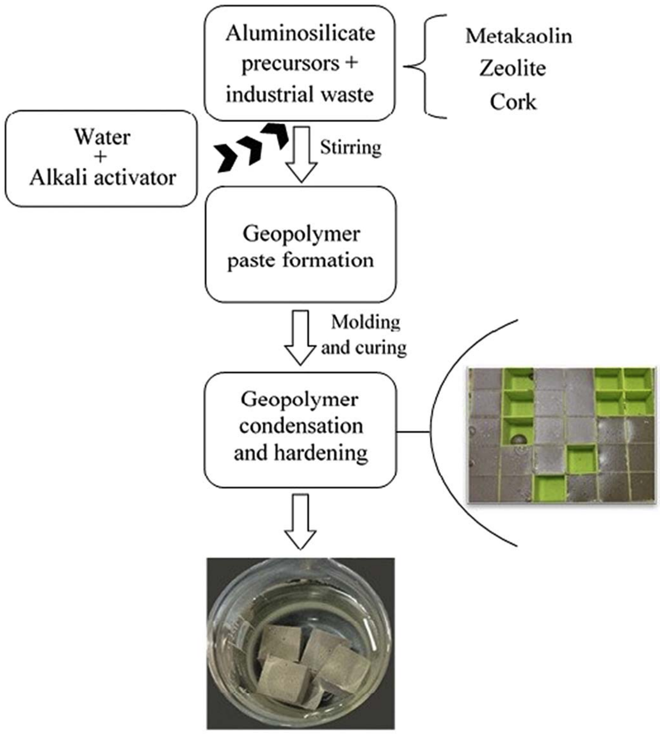

Fig. 1. Fabrication of geopolymers.

fatty acids and heavy organic alcohols (≈ 45% w/w), tannins (≈ 6% w/w), polysaccharides (≈ 12% w/w), lignin (polymer of partially aromatic structure and high molecular weight where monomer units are organic; ≈ 27% w/w), alkanes and long-chain alcohols. The mineral content, usually referred to as the cork ash, is low (≈ 5%). The most abundant element is calcium (0.038–0.625% w/w), followed by phosphorous, iron, magnesium and aluminium (Gil, 1997). Small amounts of silicon, potassium and other minerals have been observed depending on the origin of biomass as seen in the report by Ramos et al. (2014). Therefore, the burnt cork residue is expected to contain similar minerals. As cork residues have a very low commercial value, these waste materials have been primarily explored as bio-sorbents of HM and dyes from wastewaters, as thermal insulators and mechanical strength enhancers in cement and concretes (e.g. Branco et al., 2007; Chubar et al., 2004; Gil, 1997; Matos et al., 2015; Nunes et al., 2013; Psareva et al., 2005; Ramos et al., 2014; Tadeu et al., 2014).

Most of the natural and waste materials, however, are either not very effective on their own due to the low efficiency (Chubar et al., 2003; Mota et al., 2006) or require expensive pre-treatments (e.g. : Adebowale et al., 2005; Chubar et al., 2004; Eren and Afsin, 2008; Hadi and Yusof, 2010; Panesar and Shindman, 2012; Pintor et al., 2012) or there is a large variation in their composition according to the origin source as observed by Zeng and Wang (2016) and some also have been known to disintegrate during adsorption process (Uddin, 2017) and hence composites have been studied to improve their adsorption efficiencies and standardize these materials. On this subject, geopolymers have already been investigated for the adsorption of various HM and considered as an attractive replacement for Portland cement in the recent past. They are very interesting materials that can be formulated from a wide range of aluminosilicate minerals and industrial wastes (e.g. coal fly-ash, metallurgical sludge, rice husk ash, biomass fly-ash, blast furnace slag and baggasse fly-ash) reflected in previous research by Al-Zboon et al., 2011; Antunes et al., 2016; Assi et al., 2016; Duan et al., 2016; Gupta and Ali, 2004; Hadi and Ghafar, 2009; Hadi and Yusof, 2010; Novais et al., 2016; Sore et al., 2016; Sturm et al., 2016; Vashantha et al., 2016; Wang et al., 2007, as well as from natural materials as zeolites and natural pozzolans (Andrejkovičová et al., 2016; Cheng et al., 2012; El-Eswed et al., 2012; Haddad and Alshbuol, 2016; Nadoushan and Ramezanianpour, 2016; Javadian et al., 2015; Kara et al., 2017; Yousef et al., 2009) in order to reduce the cost of production, enhance properties and render them eco-friendly.

Ergo, cork waste composite geopolymers could potentially improve the HM adsorption efficiency. Both cork residue and clinoptilolite are cost-effective and environmentally friendly materials that are known to have excellent adsorption properties. Additionally, the effect of cork residue on the strength of the geopolymer matrix was also of significant interest. Thus, the aim of this work was to understand the impact of cork residue addition to geopolymers based on metakaolin and zeolite in the same ratios as previously researched by Andrejkovičová et al. (2016). Addition of cork residue could also be a way to obtain cost-effective and more environmentally friendly alternatives to the current existing materials in the market.

2. Materials and methods

2.1. Materials used for geopolymerization

Geopolymers were prepared according to Andrejkovičová et al. (2016) by using commercial metakaolin (1200S, AGS Mineraux, France, D_{50} = 1.1 μm, bulk density = 296 g·dm^{-3}), zeolite (ZeoBau micro 50, from Nižný Hrabovec, Zeocem, Slovakia, CEC = 83 meq/100 g,

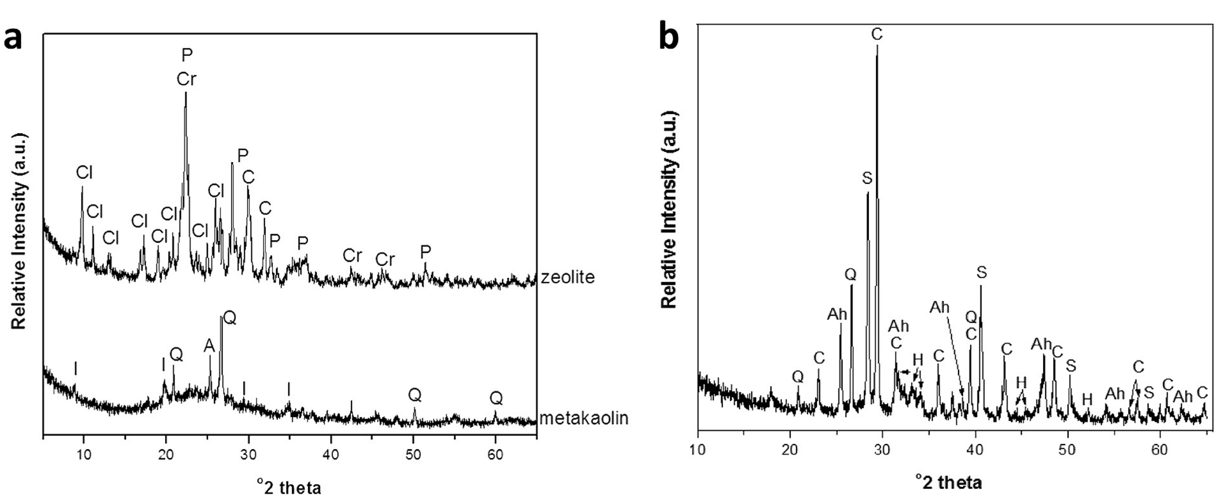

Fig. 2. X-ray diffraction patterns of (a) metakaolin, zeolite and (b) cork residue. (A-anatase, Ah-anhydrite, C-calcite, Cl-clinoptilolite, Cr-cristobalite, H-hydroxyapatite, I-illite, P-plagioclase, Q-quartz, S-sylvite).