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The removal of Zn^{2+}, Pb^{2+}, and As(V) ions by lime activated fly ash and valorization of the exhausted adsorbent

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ABSTRACT

This study focuses on the use of raw fly ash (FA) and modified fly ash – activated by lime (MFA), as effective and low-cost adsorbents for the removal of heavy metals (Zn^{2+}, Pb^{2+} and As(V)), followed by the revalorization of the exhausted adsorbent. The granulometric, elemental analysis, point of zero charge (pH_{PZC}), radiochemical and structural characterization were conducted using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and gamma spectrometry techniques. The optimal conditions and key factors influencing the adsorption process were assessed using the response surface method (RSM). The adsorption capacity of the MFA adsorbent for Zn^{2+}, Pb^{2+} and As(V) removal, calculated by the Langmuir model, was found to be 33.13, 26.06, and 29.71 mg g^{-1}, respectively. The kinetic and thermodynamic parameters indicated that the adsorption process is spontaneous and endothermic. Due to their low desorption potential of the exhausted adsorbents, their effective reuse was established to be feasible. For this reason, the valorization of this material as an additive in construction materials was thereafter studied, where testing its toxicity leaching (TCLP) as well as the mechanical properties of construction material containing exhausted MFA confirmed its safe use. Hence, this study points to a possible "two-in-one" reuse of coal ash, initially as an adsorbent and later as an additive in a construction material.

1. Introduction

Coal thermal power plants (TPP) actively generate numerous solid combustion by-products, including fly ash and bottom ash (Meawad et al., 2010). Although coal ash is a valuable resource, <30% of the total ash produced in the world is currently reused, being one of the most common industrial wastes produced worldwide (Jayaranjan et al., 2014). This TPP by-product has already been used in a variety of civil engineering applications, such as a substitute for sand and gravel in structures, and as a binding component in certain types of cement, mostly concrete and masonry (Sua-Iam and Makul, 2015). Furthermore, it has become a subject of increasing interest in environmental engineering as a low-cost and effective adsorbent for the removal of organic pollutants and heavy metals from wastewaters (Simate et al., 2016).

Heavy metals are widely spread throughout the environment (Tchounwou et al., 2012), leading to ecological and public health problems due to their toxicity, persistence, high solubility, and mobility. Their removal from various environmental components, including wastewater treatment, has been highly explored over the last few years (Adamczuk and Kołodyńska, 2015; Bilal et al., 2013). One particularly interesting study has been the ecofriendly approach of "using waste to treat the waste" by adsorption, based on the usage of widely available and low-cost materials recovered from TPPs for the removal of hazardous pollutants from aquatic media, instead of using expensive adsorbents (*e.g.* activated carbon and/or ion exchange resins). Due to its advantages, such as easy performance and maintenance, low operational costs and high efficiency (Fu and Wang, 2011; Visa, 2012), combined with potential waste reuse, adsorption is a competitive and promising solution for the removal of disparate pollutants from aquatic bodies (Visa et al., 2012). Coal ash has a significant potential in wastewater treatment due to the chemical properties of its major components

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(alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, glassy phase), as well as its physical properties, namely its porosity, particle size distribution, and specific surface area (Meawad et al., 2010; Pehlivan et al., 2006; Visa, 2012). The addition of fly and bottom ash, in a combination with lime and sodium hydroxide, to wastewater could increase its potential use as neutralization agent (Gratchev et al., 2013).

This study examined exploiting the potential of a "two-in-one"-reuse of TPP fly ash, first as an adsorbent for heavy metals and then as a construction material additive. The removal of heavy metals Zn^{2+} and Pb^{2+}, and As(V) from wastewater using raw fly ash (FA) and modified fly ash (MFA – FA activated by lime, leading to enhanced absorption properties and low desorption capabilities) were both studied. The reuse of the exhausted adsorbent was obtained through formulating a construction material according to the reaction of pozzolanic MFA particles and $Ca(OH)_2$, which is a cementitious calcium-silicate hydrate (Yao et al., 2015). The optimal conditions for removal of the target pollutants as well as the most influential factors to the adsorption were assessed by using the response surface methodology (RSM), a powerful statistical tool for design and analysis of experiments aimed at the optimization of complex chemical and physical processes (Aniceto et al., 2016; Shojaeimehr et al., 2014). While this statistical methodology has already been used for the optimization of the synthesis of adsorbents (Bajić et al., 2016; Budimirović et al., 2017; Taleb et al., 2016a) and the optimization process of adsorption (Chung et al., 2016; Murugesan et al., 2014; Xiyili et al., 2017), to the authors knowledge, a comparison of the results obtained by the prediction model in the RSM has yet to have been conducted outside of this paper.

The specific objectives of this study have been: (i) improvement of the adsorption performance of MFA, (ii) evaluation of the equilibrium, kinetic and thermodynamic aspects of the process as well as estimating the limiting step to the process, and (iii) investigation of the possible reuse of the exhausted adsorbent in the production of construction materials.

2. Materials and methods

All information on physico-chemical analyses, characterization methods of adsorbents, chemicals and reagents, adsorption experiments, kinetic, isotherm and thermodynamic models, optimization of the procedure, statistical criteria, and mechanical properties is provided in the *Supplementary material*.

2.1. Material activation

The FA used in this study was obtained as a waste product from a TPP (Morava, Serbia). According to the American Society for Testing and Materials (ASTM) standards, fly ash is classified according to the content of its silica, aluminum, and iron oxides (SiO_2 + Al_2O_3 + Fe_2O_3) (Adamczuk and Kołodyńska, 2015; Yao et al., 2015). The fly ash used here receives the classification of type F (Terzić et al., 2013; Terzić et al., 2015); (SiO_2 + Al_2O_3 + Fe_2O_3 oxides higher than 70% and CaO <10%). The raw FA substrate was used in all experimentals procedure carried out in this study. The chemical activation of FA by lime addition was performed to improve adsorption capabilities of the MFA and the mechanical properties of the construction materials containing the exhausted MFA. Simple method of dry blending of FA (10 g) and 5% of lime was applied to obtain MFA sample.

The adsorption capacity of the material is largely determined by the chemical nature of the surface (the adsorbent type and the grain size), characteristics of the target adsorbate, and the liquid phase (the presence of other cations, pH, initial metal concentration, and ionic strength) (Malamis and Katsou, 2013; Visa, 2012). Therefore, an extensive physico-chemical, mechanical, structural and morphological analysis was further performed on the FA and MFA samples.

2.2. Leaching test of adsorbent as a construction material

A leaching test was performed to provide the potential release of the chemical constituents in the MFA/As(V) and to confirm the eco-safety of such a material. The experimental procedure was performed according to the Toxicity Characteristic Leaching Procedure (TCLP) (Tiwari et al., 2015) and the EN12457-2003 Standard (Tiwari et al., 2015), using acetic acid (sample 1) and deionized water (sample 2) as an extraction fluid, respectively (Ivsic-Bajceta et al., 2013).

2.3. Semi-industrial material application

2.3.1. Adsorption experiments of as removal by MFA

The adsorption procedure for As(V) removal, was performed at the MFA adsorbent dosage of 1 kg. The adsorbents before and after the adsorption process (herein called MFA and MFA/As(V)), were used as additives for the production of construction materials. Preparation of the mortar, which includes MFA and MFA/As(V), was performed according to standard procedure (Terzić et al., 2013). The mechanical and leaching properties of both construction materials filled with MFA and MFA/As(V) yielded CM-MFA and CM-MFA/As(V) materials which were further subjected to the leaching test and the mechanical properties measurement.

3. Results and discussion

3.1. Optimization of fly ash-lime content in the MFA adsorbent

Optimizing the adsorbent preparation in producing effective adsorbents for the pollutant selected to be removed was based on the selection of the most influential factors, thereby determining the effectiveness of the adsorption process (lime content, temperature and pH). The range of variable changes was defined with respect to the highest adsorption capacity; thusly, the optimization goals were defined in relation to the adsorption efficiency (capacity/reusability) and adsorption kinetic.

Clear relationship between the quantities of the added lime *versus* the pH_i was observed (Table 1). Low influences of temperature on adsorption capacity were found, while oppositely large influence of lime content was observed (Fig. 1). The pH_i of the system water/FA was 9.78. The addition of lime ranged from 2 to 7%, whose pH_i value was changed as presented in Table 1.

The obtained results of the modeling were validated by means of analyzing the variants in the ANOVA test, and results of optimization are presented in Fig. 1.

With respect to As(V), the maximum of adsorption capacities were obtained at 5% lime addition whose FA pH_i was 11.1 (the obtained q_e ranged from 26 to 29 mg g^{-1}). Regarding the availability of the 10% CaO present in the FA, it was found that approximately 28% of the lime generated by the dissolution of the FA synergistically participated in processes of the pollutant removal. The higher loading of lime contributed to the slight increase of the adsorption capacity which is not beneficial from the point of maximum exploitation/content of fly ash as an adsorbent. By applying the simple methodology of FA/lime dry mixing at an appropriate ratio (95/5 wt%, respectively), the material achieved an optimal adsorption performance. At the initial point of the addition of the FA/lime blend into the water (degassed) the pH_i was 9.78, where an insignificant variation of the pH was observed