Original scientific article

EFFECT OF ALKALI MODIFICATION ON ADSORPTION EFFICIENCY OF FLY ASH

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Abstract

As coal combustion in thermal power plants generates huge amounts of waste such as bottom ash and fly ash, there is a need to find new applications for these materials. One of the ways of its reuse is chemical or thermal modification of the ash in order to obtain new materials, which can be further used as adsorbents of various pollutants from water. The subject of this research was the alkali modification and alkali activation of fly ash in purpose to increase the adsorption capacity towards heavy metal ions. The success of modification process and characterization of the obtained materials was monitored by Fourier transform infrared spectroscopy, X-ray fluorescence spectroscopy and scanning electron microscopy. The concentration of zinc and cadmium ions after adsorption was determinated by atomic absorption spectroscopy. The kinetics of the adsorption process on the most efficient adsorbent were examined and the experimental data were compared with pseudo-first and pseudo-second order models. The achieved results show a positive effect of alkaline modification of fly ash on adsorption efficiency of both metals, while alkaline activation gives an exceptionally effective adsorbent in the case of zinc.

Keywords: fly ash, environment, modification, heavy metal, waste reuse.

Introduction

Burning coal in thermal power plants produces huge amounts of ash. Fly ash (FA) is deposited in several large-scale landfills and has a negative impact on the environment and human health. Fly ash is considered a pollutant because it contains acidic, toxic and sometimes radioactive substances. Fly ash particles have a direct harmful effect on human health and the environment (Vilakazi et al., 2022). Due to size of fly ash particles, the wind easily blows them to greater distances from the thermal power plant and they can remain in the air for a long time, which increases the possibility of their inhalation. Fly ash landfills also cause degradation of agricultural land, which requires some control and monitoring. As a way to reduce the amount of waste, the possibility of using ash in construction as an additive to cement and concrete, and in road construction, has been observed (Krithika & Kumar, 2020). Application for soil stabilization and photocatalyst production were also investigated (Indiramma & Sudharani, 2018; Jala & Goyal, 2006). Likewise, great interest is focused on the development of efficient adsorbents for the removal of dyes and heavy metals from water (Hussain et al., 2022; Banerjee et al., 2003; Sahoo et al., 2013). The advantage of using fly ash is its availability and low cost. Through different modification processes, it is possible to improve the adsorption and selective characteristics of the obtained adsorbents (Zhuang et al., 2016; Kato et al., 2019; Pengthamkeerati et al., 2008). Modification can be mechanical, thermal and chemical. Mineral acids (nitric and hydrochloric), sodium and calcium hydroxide, alkaline silicate solution can be used as modification agents (Sočo et al., 2016; Wang et al., 2005; Gollakota et al., 2019).

Materials and Methods

Fly ash containing SiO_2 (58.40%), Al_2O_3 (21.80%), Fe_2O_3 (4.21%), CaO (2.83%) from power plant in Serbia was used. The material was sieved, then washed with deionized water and dried at temperature of 105 °C in oven (sample FA_0). Two different modification procedure of fly ash, based on literature with slight difference, were performed. In first, washed and dried fly ash was mixed with 2M NaOH in a cuvette (1:3) and put on a shaker (120 rpm) to mix for 7 days. After that, obtained material was washed with about 1.5 l of distilled water and dried in the oven for 24 hours at a temperature of 60 °C (sample labelled FA_1). During second modification, FA was mixed well with diatomaceous earth in a plastic mold and sodium silicate was added (2:1:2). For better mixing, a few drops of 16M NaOH were added. The sample was placed in the oven for 2 h at 105 °C to dry, and then left in a closed mold at room temperature to age for 15 (sample marked as FA_2), and 30 days (sample marked as FA_3).

The morphological characteristics of the surface of unmodified and modified materials were examined by scanning electron microscopy - SEM (SEM JEOL JSM-6610LV). The content of functional groups on the surface of the material was determined by Fourier transform infrared spectroscopy - FTIR (Nicolet iS10, Thermo Scientific). The efficiency of unmodified and modified fly ash to adsorb Cd and Zn ions from aqueous solution was tested in batch system at room temperature. Concentration of metal ions after adsorption were determined by atomic absorption spectroscopy. The adsorption efficiency (%E) of the prepared adsorbents in the removal of metal ions was calculated using the following equation (1):

$$\%\,E = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where C_e is the equilibrium and C_0 is the initial concentration of metal ions in solution (mg dm^{-3}).

The two kinetic models, the pseudo-first order model (equation (2)) and the pseudo-second order model (equation (3)) were used to calculate the adsorption rate:

$$q_t = q_e \cdot \left(1 - e^{-k_1 \cdot t}\right) \qquad (2)$$

$$q_t = q_e - \left(\frac{1}{q_e} - k_2 \cdot t\right)^{-1} \qquad (3)$$

where q_t is the amount of metal ions adsorbed at the time t (mg g^{-1}), q_e is the amount of metal ions adsorbed at equilibrium (mg g^{-1}), k_1 is the pseudo-first-order kinetic rate constant (min^{-1}), and k_2 is the pseudo-second-order kinetic rate constant (mg g^{-1} min^{-1}).

Results and discussion

The SEM micrographs of the unmodified and modified fly ash are shown in Fig. 1. Both treatments, alkali modification and alkali activation, changed the surface of starting material. With the addition of NaOH (Fig. 1b), the surface of the material becomes rougher and more porous in comparison to unmodified fly ash (Fig. 1a). Surface of alkali activated fly ash (Fig. 1c and 1d) contains cracks and a heterogeneous matrix containing unreacted fly ash particles.

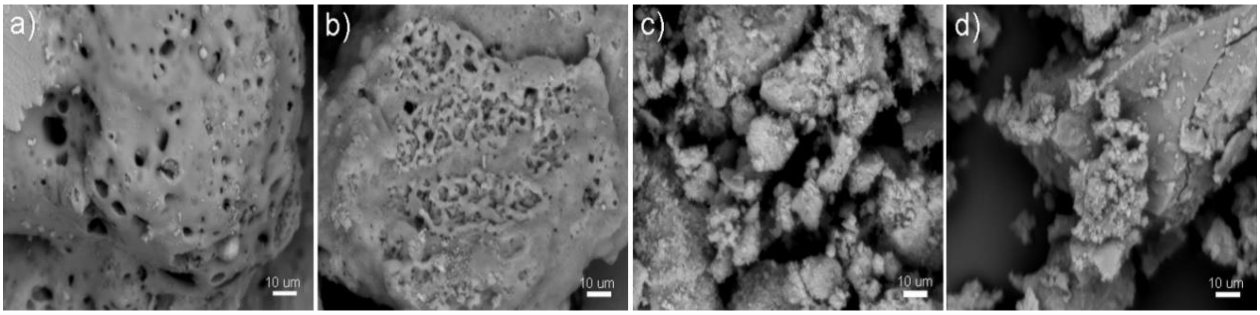

Figure 1. SEM micrographs of a) unmodified fly ash, b) FA_1, c) FA_2, and d) FA_3 samples

FTIR spectra of unmodified and modified materials before and after adsorption are shown in Fig. 2a. Sharp peaks at around 1000 and 780 cm^{-1}, can be ascribed to the stretching of asymmetric Si - O -Si and symmetric Si - O -Si bond, respectively. The small shifts to lower values in the range around 1000 cm^{-1} and absence of peak at 797 cm^{-1} in FA_2 and FA_3 spectra confirms formation of alkali activated materials. The band at 1450-1500 cm^{-1} originated from atmospheric carbonation of materials surface. After adsorption, changes in the intensity of bands around 1000 cm^{-1} are visible, indicating the interaction of these groups with metal ions.

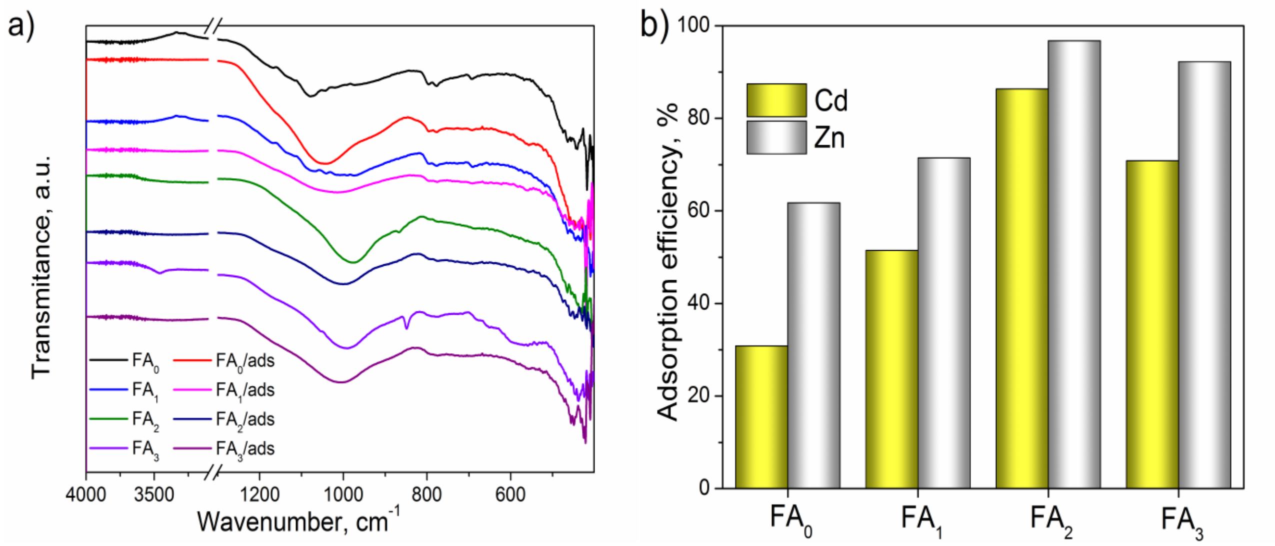

Figure 2. FTIR spectra (a) and adsorption efficiency (b) of unmodified and modified materials

The adsorption efficiency of the prepared adsorbents towards Zn and Cd ions is shown in Fig. 2b. An improvement in the efficiency of modified materials compared to the unmodified fly ash is evident. This increase is more pronounced in the case of zinc ions adsorption. Alkali-activated samples (FA_2 and FA_3) have proven to be the most effective in Zn and Cd adsorption. This is the consequence of introducing the polymeric Si-O-Al-O- bonds into the structure of materials during alkali activation, which increase the number of active sites for metal ion binding. These conclusions are consistent with the FTIR results.

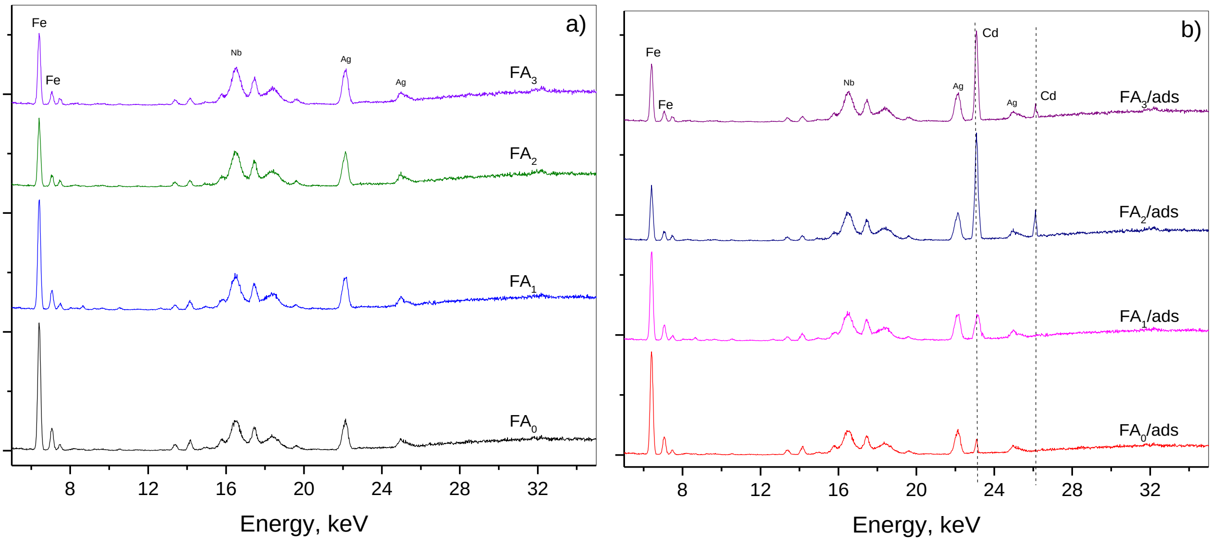

Figure 3. XRF spectra of adsorbents a) before and b) after adsorption of cadmium

Adsorption of cadmium, in the range of 5-50 keV can be confirmed by XRF spectrum. The peaks corresponding to the Kα1 and Kβ1 lines of cadmium, at values 23.17 and 26.09, respectively, confirm that cadmium ions are adsorbed on the surface of examined materials (Fig. 3b), since there is no confirmation of their presence on the samples surface before the adsorption (Fig. 3a). Also, the most intense peaks of cadmium are observed for adsorbent FA_2, which confirms the previously obtained results.

To evaluate the adsorption kinetic data and investigate the adsorption mechanism, the pseudo-first order and pseudo-second order equations were used. Graphical comparison of experimental data and applied models is shown in Fig. 4. Calculated kinetic constants and correlation coefficients for Zn and Cd adsorption are shown in Table 1.

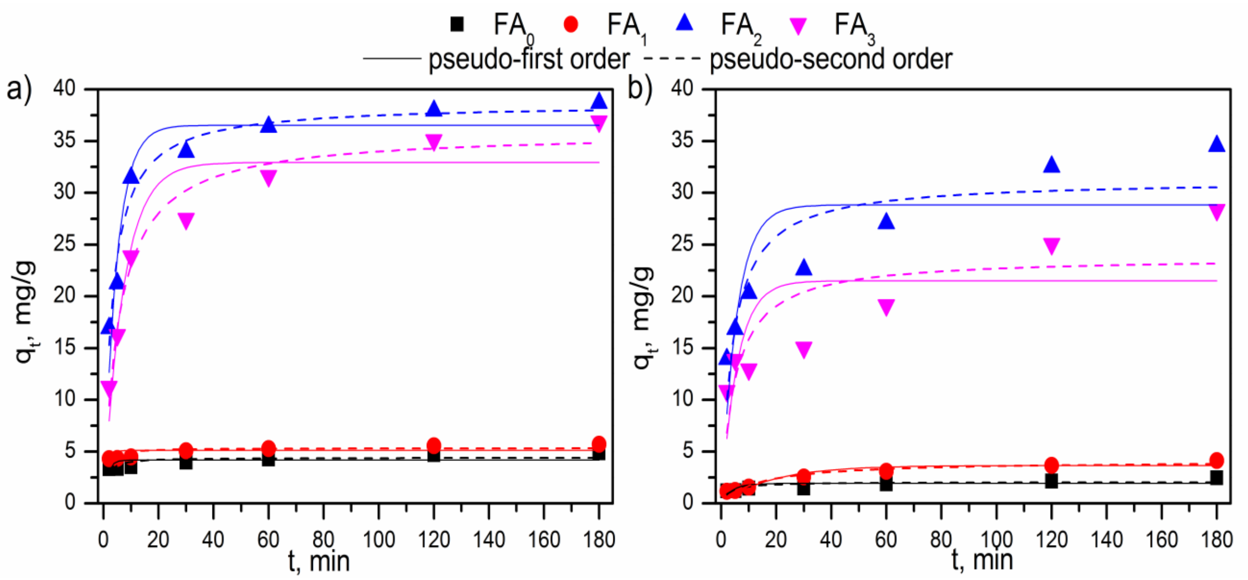

Figure 4. Kinetic adsorption models of metals a) Zn and b) Cd on unmodified fly ash (FA_0) and modified samples FA_1, FA_2, and FA_3

Based on the results of kinetic models, it can be seen that the process of metal adsorption on all investigated materials was relatively fast and that equilibrium was reached at about 30 min for both metals. The alkali activated materials showed higher adsorption capacity especially towards Zn ions

(Fig. 4a). The calculated value of the correlation coefficient (R^2) is used as a criterion for explaining the kinetics of the adsorption process. According to Table 1, it can be concluded that in the examined process there is a better agreement with the pseudo second-order model, and that chemisorption takes place.

Table 1. Kinetic parameters for Cd and Zn adsorption onto examined samples

	Sample	Pseudo-first order			Pseudo-second order			
		$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	$q_{e,exp}$
Cd	FA_0	1.917	0.27029	0.25466	2.062	0.18004	0.53397	2.465
	FA_1	3.643	0.05356	0.81858	4.093	0.01744	0.9047	4.117
	FA_2	28.82	0.17861	0.57461	31.25	0.00757	0.77737	34.53
	FA_3	21.50	0.17193	0.30742	23.80	0.00845	0.55253	28.33
Zn	FA_0	4.170	0.69652	0.12527	4.408	0.23180	0.5331	4.861
	FA_1	5.108	0.84559	0.13628	5.338	0.26688	0.57163	5.716
	FA_2	36.53	0.21267	0.89327	38.63	0.00847	0.95737	38.70
	FA_3	32.93	0.13842	0.8745	35.90	0.00497	0.95992	36.89

Conclusion

In this study, influence of alkali modification and alkali activation of fly ash on its ability to remove the polluting substances from aqueous solutions was analyzed. During the modification process, changes occurred both on the surface and in the structure of the material, which was confirmed by the applied instrumental methods. The adsorption efficiency increases after both type of modification of fly ash. By alkali activation of fly ash, more effective adsorbent towards heavy metal ions was obtained. Alkali-activated materials are more effective due to polymeric Si-O-Al-O- bonds introduced into the structure of materials thus increasing the number of active sites for metal ion binding.

The positive impact that applied alkali modification and alkali activation had on the adsorption characteristics of fly ash requires continued investigation of the possibility of using adsorbents obtained in this way for the removal of other inorganic and organic pollutants.

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