Coal fly ash zeolites as adsorbents for effective removal of heavy metals and dyes from contaminated waters

Zgureva D.[1], Boycheva S.[2,*], Behunová D.[3], Václavíková M.[3]

Technical University of Sofia, [1]College of Energy and Electronics; [2]Department of Thermal and Nuclear Power Engineering, 8 Kl. Ohridsky Blvd., 1000 Sofia, Bulgaria;
[3]Institute of Geotechnics, Slovak Academy of Sciences,Watsonova 45, SK-043 53 Kosice, Slovak Republic

*corresponding author: e-mail: sboycheva@tu-sofia.bg

Abstract
In this study, fly ash zeolites (FAZ) of Na-X type were synthesized by alkaline atmospheric aging. FAZ with a specific surface value of 280 m^2/g was tested for removal of contaminants from waters in comparison to unconverted FA. The adsorption efficiency of FAZ toward methylene blue from water solutions is over 60 % for the studied concentration levels. The removal efficiency of FAZ toward Cd^{2+}-ions reaches 98 % and it is not affected by the pH from 3.0 to 7.0. The obtained results reveal that FAZ are suitable adsorbents in water remediation systems.
Keywords: Fly ash zeolites, Adsorption, Waste water remediation, Heavy metals, Dyes

1. Introduction

Recently, the purification of enormous amounts contaminated industrial, agricultural and municipal waters increases the demands of low-cost and technologically feasible techniques. The application of natural zeolites in wastewater treatment is known from many years. Zeolites are unique aluminosilicate minerals with excellent adsorption and ion-exchange ability. However, in order to conserve the natural resources by the reuse of wastes, synthetic zeolites that successfully replace their natural analogues in many applications are derived from aluminosilicate residues. An abundant resource of raw aluminosilicates is fly ash (FA) which is a by-product of energy production in coal-fired Thermal Power Plants. FA consists of fine solids obtained by thermal fractionation of non-combustible coal minerals. It is generated annually in enormous amounts worldwide due to the strong consumption of solid fuels in energy production. The utilization of coal ash residues is an important task to protect the environmental and to conserve natural resources (Ahmaruzzaman 2010). One perspective approach of FA utilization is its alkaline conversion into zeolites via different procedures (Querol et al. 2002). Fly ash zeolites (FAZ) are promising materials for adsorbents and ion-exchangers due to their extended specific surface and mixed micro-mesoporous structure that facilitates mass transport phenomena (Boycheva and Zgureva 2016). The purpose of this study is to evaluate the removal efficiency of FAZ toward water contaminants.

2. Experimental

The adsorption behavior of FAZ was tested toward methylene blue (MB) as a model dye. A stock solution of MB in concentration of 100 mg/l was prepared with deionized water and was subsequently diluted up to 10 mg/l for the adsorption tests. The adsorption isotherms were measured at 25 °C under magnetic stirring 100 rev^{-1} by batch tests immersing 0.2000 g FAZ into 50 ml flasks filled with MB solution. The optical transmission (T, %) was measured at λ_{max}=670 nm using optical glass cuvettes with 10.08 mm in length. The adsorption of MB on the raw FA was also studied for comparison. The Cd^{2+}-ions adsorption on FAZ was investigated in solutions of $Cd(NO_3)_2 4H_2O$. The tests were carried out by immersing 0.05 g of adsorbent in 25 ml of stock solutions at varying pH values. The final concentration of Cd^{2+}-ions was measured by Inductively Coupled Plasma Mass Spectrometer ICP-MS Agilent 7700 after 24 hours of continous magneting stirring of the adsorption slurry.

3. Results and Discussions

FAZ of Na-X type obtained by alkaline aging of lignite coal FA was investigated as an adsorbent of water contaminats. FAZ is characterized with a specific surface value of 280 m^2/g and a mixed micro-mesoporous stucture established by nirogen adsorption/desorption studies. The adsorption isotherms of MB onto FAZ and raw FA are presented in Fig. 1. MB was used as organic pollutant for our investigations because it is broadly applied as one of the most common dyes in textile industry and as a medication. Although it is not strongly toxic, the polluted waters can causes serous risk for the environment and human health. The adsorbed qantity q of MB in FAZ was calculated as follow:

$$q= ((C_{MB,\ initial} - C_{MB,\tau})\ V)/m_s,\ mgMB/g$$

Where: $C_{MB,\ initial}$ is the MB concentration in the stock solution, mg/l; $C_{MB,\tau}$ is the current concetration of MB in water for tested time, mg/l; V is the volume of the test solution, l; m_s is the weight of FAZ or FA used for the adsorption, g.

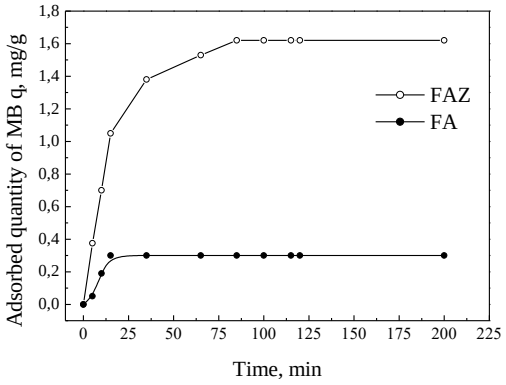

Figure 1. Adsorption isotherms of MB on FAZ and raw FA

The equilibrium adsoption potential of raw FA and FAZ to remove Cd^{2+}-ions from waters was investigated varying the concentrations and pH of the test solutions. Heavy metal uptake tests were performed with Cd^{2+}-ions because of the strong toxicity of candmium and its broad industrial applications, e.g.: in anticorrosion coatings, in stabilization of PVC products, as a pigment for coloration, for fabrication of Ni-Cd batteries, etc. The equilibrium adsorption capacities q_e of Cd^{2+}- ions on FAZ and raw FA were calculated according to the following equation:

$q_e = ((C_{Cd,initial} - C_{Cd,final}) V)/m_s$, $mgCd^{2+}/g$

Where: $C_{Cd,initial}$ is the concentration of Cd^{2+}-ions in the stock solution, mg/l; $C_{Cd,final}$ is the final concetration of Cd^{2+}-ions at the end of the adsorption test, mg/l. The values of q_e depending on pH of the test solutions are summarized in Table 1. The adsorption efficiency of FAZ and raw FA toward Cd^{2+}-ions uptake was calculated by the equation:

$R = ((C_{Cd,initial} - C_{Cd,final})/ C_{Cd,initial}) 100$, %

The dependences of the adsorption efficiency R versus the concentration of Cd^{2+}-ions and pH of the stock solutions are presented in Fig. 2 a,b, correspondingly.

Table 1. Adsorption of Cd^{2+}- ions at different pH.

Parameters	**FAZ**			**FA**		
pH	3	5	7	3	5	7
$C_{Cd,\ initial}$, ppm	100	100	100	100	100	100
$C_{Cd,final}$, ppm	1.2	0.99	1.1	85.0	81.0	60.5
q_e, mg/g	49.4	49.5	49.5	7.5	9.5	19.8

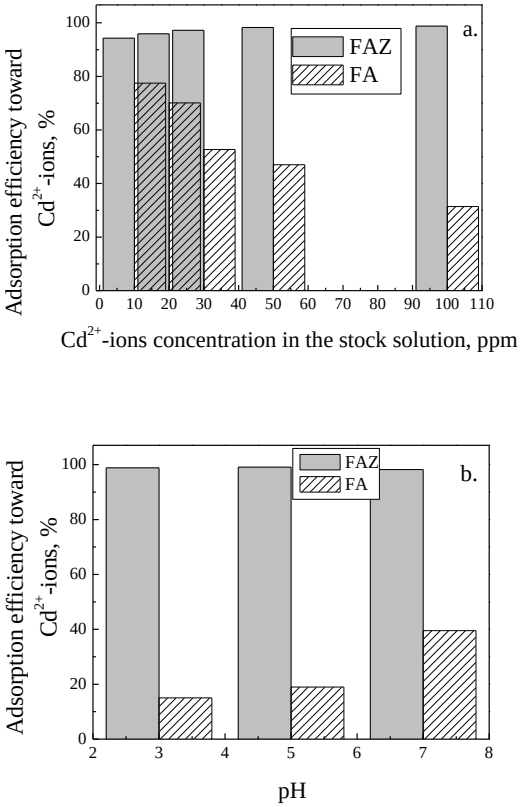

Figure 2. Adsorption efficiency of Cd^{2+}-ions on FAZ and raw FA at different concentrations of stock solution (a) and at varying pH-values (b)

4. Conclusions

FAZ of Na-X type obtained by atmospheric crystallization possesses high removal efficiency toward methylene blue and cadmium ions from waters. FAZ is suitable material for adsorbent in waste water remediation systems.

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