

Methods of slag (CFBC-S) characterization and Cu(II) adsorption

In the research, slag (CFBC-S) particles with a diameter less than 0.212 mm were used. Firstly, physico-chemical properties of the materials were analyzed using several methods, including:

1) Determination of granulation was performed by a sieve method in accordance with the standard PN-C-97555-01:1988P. In order to separate individual ash fractions, they were screened through four sieves with mesh diameters of 0.212 to 1.0 mm over 1 hour. Fractions retained on individual sieves were weighed and the procedure was performed in triplicate. The main composition was percentage content of particles of a certain diameter (grain fraction, X [%]) was calculated according to the equation (1).

$$X = \frac{m_1 \times 100\%}{m_2} \quad (1)$$

where: m_1 [g] is mass of sifted material and m_2 [g] - initial mass of a sample.

2) The elemental composition and mapping of fly ash samples was examined with a scanning electron microscope (SEM) Hitachi S-3700N with an attached a Noran SIX energy dispersive X-ray spectrometer (EDS) microanalyser (ultra-dry silicon drift type with resolution (FWHM) 129 eV, accelerating voltage: 20.0 kV).

3) X-ray diffraction measurements were made using Bruker AXS D8 Advance (Germany). In configuration the diffractometer is equipped with Johansson monochromator ($\lambda_{\text{Cu K}\alpha 1} = 1,5406 \text{ \AA}$) and silicon strip detector LynxEye. The minimum measurement angle is $0,6^\circ 2\theta$ deg. The XRD powder diffraction method needs delivered sample to be carefully powdered. A standard measuring dish has container for powder with diameter ca. 25 mm and ca. 1.5 mm depth. Before measurement sample powder needs to be mildly pressed.

4) The specific surface area and the average pore diameter were determined with the Brunauer, Emmett and Teller (BET) method using Autosorb iQ Station 2 (Quantachrome Instruments, USA).

5) The pore volume was determined by Barret, Joyner and Halenda (BJH) method using Autosorb iQ Station 2 (Quantachrome Instruments, USA).

6) The morphology of the fly ash samples was examined with a scanning electron microscope (SEM) EVO-40 (Carl Zeiss, Germany).

7) The surface structure of fly ash was examined in infrared spectroscopy using a Fourier transform attenuated total reflection (FT-IR ATR) Spectrum 100 (Perkin-Elmer, Waltham, USA).

8) Determination of the efficiency of Cu(II) ions removal process on slag CFBC-S was carried out in batch experiments. CuCl_2 (1 g/L standard solution for AAS, Sigma-Aldrich (Germany)) was used in the research. The adsorbent (0.25 - 25 g/L) and the solution (20 mL) containing metal ions were placed in a 50 mL conical flask and shaken at 200 rpm for 1 hour until equilibrium was reached. Initial pH of the stock solutions was adjusted with 0.1 M HCl and NaOH. Then, adsorption solutions were centrifuged for 15 minutes (4000 rpm) for phase separation. The

concentration of metal ions was analyzed using atomic absorption spectrophotometry (F-AAS, wavelength $\lambda = 324.8$ nm for copper, SpectrAA 800 (Varian, Palo Alto, USA)). Measurements were carried out in triplicate at room temperature (23 ± 1 °C) under normal pressure and the results are presented as mean values. Adsorption efficiency R [%] and adsorption capacity q_e [mg/g] were calculated according to equations 3 and 4, respectively:

$$R = \left[\frac{C_0 - C_e}{C_0} \right] \times 100\% \quad (2)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

where: C_0 and C_e are initial and equilibrium Cu(II) ion concentrations [mg/L], respectively; V - volume of solution [L] and m - mass of slag [g].

The following conditions were applied in the experimental procedure:

- A) effect of initial pH: initial pH range of 1.8 – 5.6, initial concentration of Cu(II) ions 100 mg/L, adsorbent dosage 1 - 5 g/L, contact time 60 min, $T = 23$ °C, agitation speed 200 rpm,
- B) effect of CFBC-S dosage: initial pH 1.9, initial concentration of Cu(II) ions 100 mg/L, contact time 60 min, $T = 23$ °C, agitation speed 200 rpm,
- C) effect of initial concentration of Cu(II) ions: initial concentration of Cu(II) (2.5 - 100 mg/L), slag dosage 2 - 5 g/L, initial pH 1.9, contact time 60 min, agitation speed 200 rpm, $T = 23$ °C,
- D) effect of contact time: initial concentration of Cu(II) ions 100 mg/L, initial pH 1.9, slag dosage 1 - 5 g/L, $T = 23$ °C, agitation speed 200 rpm.

Kinetic and isothermal studies were performed using pseudo-first-order and pseudo-second-order, Langmuir and Freundlich models based on the equations 5 - 7, respectively:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

where: q_t is the amount of Cu(II) ions adsorbed [mg/g] at any time t [min.]; q_e - the maximum amount of Cu(II) ions adsorbed per mass of the biosorbent [mg/g] at equilibrium; k_1 - the rate constant of pseudo-first-order adsorption [1/min.]; k_2 - the rate constant of pseudo-second-order adsorption [g/(mg·min.)]; q_{max} - the maximum adsorption capacity [mg/g]; K_L - the Langmuir constant; C_e - the equilibrium concentration after the adsorption process [mg/L]; K_F - the Freundlich constant and $1/n$ - the intensity of adsorption.