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SORPTION PROPERTIES OF FLY ASH FROM BROWN COAL BURNING TOWARDS ARSENIC REMOVAL

WŁAŚCIWOŚCI SORPCYJNE POPIOŁÓW Z WĘGLA BRUNATNEGO POD KĄTEM USUWANIA ARSENU

Abstract

In the present work, the sorptive capacity of fly ash from the combustion of brown coal in relation to arsenic(III) removal from the standard solution as well as the potential application of fly ash in actual wastewater purification have been evaluated.

Keywords: fly ash, arsenic removal, adsorption

Streszczenie

W tym artykule zbadano pojemność sorpcyjną popiołów lotnych powstających podczas spalania węgla brunatnego w stosunku do arsenu(III) usuwanego z roztworu standardowego oraz zbadano możliwość zastosowania popiołów w oczyszczaniu ścieku rzeczywistego.

Słowa kluczowe: popiół lotny, usuwanie arsenu, adsorpcja

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1. Introduction

The problem of the disposal of coal combustion by-products, as well as effluent containing large amounts of heavy metals, can be solved comprehensively [1]. Arsenic, highly toxic for the human being, appears in ground waters as a result of geothermal processes, as well as the industrial activity of the man [2]. Many attempts have been made to remove arsenic from water and wastewater using various adsorbents [3, 4]. From the literature reports [5, 6] and earlier works of the authors [7–9] a conclusion can be drawn that fine fly ash has sorptive properties in regard to heavy metals. The chemical constitution of fly ash depends on many factors, among others, the kind of fuel and the method of combustion [10]. Fly ash consists mainly of silica and aluminosilicates, but due to the desulphurization process, it also contains calcite, anhydrite, and calcium oxide [11]. For this reason, the water suspensions of fly ash reach a highly alkaline pH, favourable for the removal and immobilization of pollutants, especially arsenic.

Arsenic can be chemically fixed into cementation environment of the solidified/stabilized matrices by three important immobilization mechanisms: sorption onto C-S-H phase (calcium silicate hydrate), replacing SO_4^{2-} ions of ettringite, and reaction with cement components to form calcium-arsenic compounds [12]. The effectiveness of both As (III) and (V) immobilization in lime-treated slurries increases with an increasing Ca/As molar ratio [13]. Vandecasteele and co-workers [14] verified that the formation of $Ca_3(AsO_4)_2$ and $CaHAsO_3$ precipitates in the presence of $Ca(OH)_2$ controls the immobilization of arsenic in fly ash.

Adsorption of arsenic on fly ash was found to conform to Freundlich's isotherm [15, 9], and the efficiency of adsorption was comparable to that of activated carbon. Aguilar-Corrillo and co-workers [16] applied the Langmuir isotherms for the sorption of As, Cd and Tl onto fly ash. Some authors reported a better fit with Freundlich's isotherm than the Langmuir one for the arsenic adsorption onto the activated carbon [17], reused sanding waste [18] or ferric hydroxide [19].

The determination of kinetics parameters and the explanation of mechanism in heterogeneous systems is often a complex procedure. Kinetic models including the pseudo--first-order model of Lagergren (PFO) and the pseudo-second-order (PSO) model of Ritchie have been tested very often for the simulation of experimental results of the adsorption of heavy metals [19]. The rate constants for adsorption of metal ions (zinc, lead, cadmium and copper) on fly ash were determined using the pseudo-first-order model of Lagergren [14]. The pseudo-second-order equation has been used in the case of arsenic, cadmium and thallium adsorption kinetics onto fly ash, followed by the parabolic diffusion equation [15]. The adsorption of arsenic onto fly ash is usually the kinetic control process, whereas the equilibrium is achieved over three hours, diffusion control is also considered [20].

In the present work, the sorptive capacity of fly ash from the combustion of brown coal in regard to arsenic (III) removal from the standard solution as well as the possibility of sewage water purification have been evaluated.

2. Materials and methods

Fly ash from the Turów Power Plant (Poland), from brown coal (lignite) burned in circular fluidal boiler (unit No. 4), was used as a mineral adsorbent in these investigations. The X-ray diffraction analysis of the mineral sample showed the presence of the following minerals:

anhydrite (desulphurization product), calcite (unreacted sorbent for desulphurization), quartz, haematite, illite, and calcium oxide [9]. The particle size analysis was carried out by using a Mastersizer 2000 laser diffractometer (Malvern), equipped with a HydroMu dispersion unit (Malvern), and showed the volume median diameter (d50) of about 28 μm, while d10 and d90 were about 4 and 113 μm, respectively. The density of fly ash measured with the use of a pycnometer was determined to be 2.70 g/cm^3. The specific surface area of fly ash powder was measured by the BET method for helium/nitrogen mixture using FlowSorbII (Micromeritics) and turned out to be 6.5 m^2/g.

The acidic As(III) stock solution of the concentration of about 1 g/dm^3 was prepared as follows: 1.32 g of As$_2$O$_3$ was dissolved in 20 ml of 2M NaOH, then acidified using 2M HCl and diluted with deionised water to 1 dm^3. The arsenic concentration in the solution was determined spectrophotometrically (UV-Vis Helios Gamma, ThermoFisher) by means of the molybdenum blue method, according to the standard procedure.

The wastewater sample was collected from the "Górka" reservoir which is located in the post-mining excavation in the southern part of the Trzebinia town. This brownish liquid is a filtrate from a dump of cement and tailings from the production of high-alumina materials. The extremely high pH value (12.9), high mineralization and the presence of some trace elements as well as heavy metals, whose concentrations are several times higher than the natural geochemical background and vary with the pond depth, characterise the wastewater [21].

Firstly, the sorption capacity of fly ash was determined. For this purpose, the particular weighted amounts of fly ash were mixed with the As(III) stock solution, and the resulting suspensions were shaken in a laboratory planar shaker at 60 cpm for 24 h. After this time, the concentration of arsenic in the filtrate was determined. The concentration of adsorbent from 5 to 250 g/dm^3 was examined. The adsorption isotherms were evaluated for four weighted amounts of fly ash (10, 15, 20 and 25 g/dm3), and the As(III) concentration from 10 to 1000 ppm. After 24 h of shaking, the arsenic concentration was determined. The kinetic experiments were carried out for seven weighted amounts of fly ash (20–250 g/dm^3), and the concentration of arsenic was sampled for eight hours starting at the 3rd minute. All experiments were conducted at room temperature of 25°C and the natural pH of 11–12.5, i.e. imposed by fly ash.

In order to determine the possibility of using fly ash to wastewater purification, a given amount of fly ash (25–50 g/dm^3) was mixed with the "Górka" filtrate, and shaken for 24 h. Starting at the 30th minute, a small amount of supernatant was taken, and the spectrum in the range of 325–800 nm was measured using the spectrophotometer.

3. Results

The fly ash sorption capacity experiments show the possibility of complete arsenic(III) removal from the standard solution with the concentration of adsorbent about 35 g/dm^3. The maximum static uptake in this system was achieved for 0.02 g/ml adsorbent-to-arsenic ratio (20 g/dm^3), and was 36.7 mg As/g of the adsorbent. The previous research by the authors [9] pointed out that the maximum uptake for brown coal fly ash was 33 mg As/g (for 40 g/dm^3 of the adsorbent). In that case, the mineral sample was collected from another Turów Power Plant boiler (unit No. 6) and had a smaller surface area. Thus the results are coherent and these values are comparable to the literature data of the maximum uptake for As(III) adsorption

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onto various adsorbents [4], such as soot (29.9 mg/g) [22] and fungal biomass (51.9 mg/g) [3], as well as commercial product ArsenXnp resin (38 mg/g). The maximum adsorption of As(V) onto fly ash reported by Diamadopoulos [23] and Wang [5] were 30 mg/g and 0.8 mg/g, respectively.
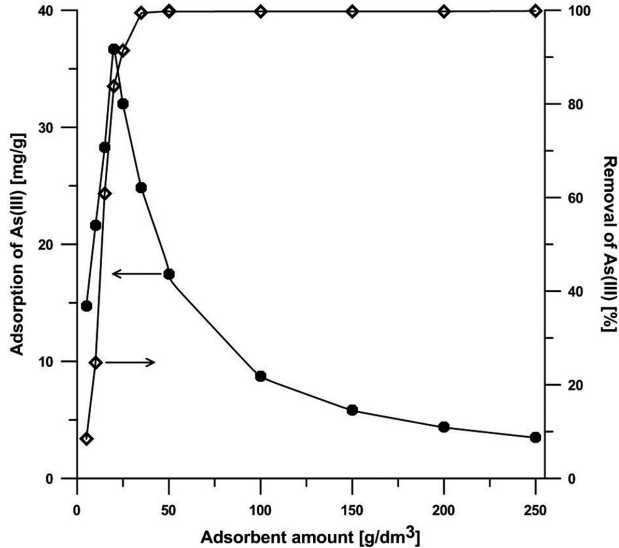

Fig. 1. Sorption capacity of fly ash and arsenic(III) removal from standard solution

Rys. 1. Pojemność sorpcyjna popiołów i usunięcie arsenu(III) z roztworu standardowego

In this study, the best fit of experimental data of the arsenic adsorption onto fly ash has been obtained using the Langmuir isotherm given by the equation
where ceq is the concentration of metal ions in solution at equilibrium [mg/dm³] and qeq is the amount of metal ions adsorbed at equilibrium (mg/g of adsorbent). QL and KL stand for monolayer maximum capacity [mg/g] and binding energy of the system [dm³/mg], respectively. Accordance with the Langmuirian adsorption model suggests that adsorption sites have equal

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{K_L \cdot Q_L} + \frac{c_{eq}}{Q_L}$$

activity but contradicts the heterogeneity of the fly ash surface. The isotherms parameters in Tab. 1. show that the maximum adsorption is attained with 20 g/dm³ of adsorbent while the amount of 10 g/dm³ is too small so there is a deviation from the model and the correlation coefficient R2 is low. These results are in line with adsorption capacity outcomes (Fig. 1).

In order to investigate the mechanisms of sorption and potential rate-controlling steps, such as mass transport and chemical reaction processes, kinetic models were used to fit experimental data. The sorption process can be described by four consecutive steps: (i) transport in the bulk of the solution, (ii) diffusion across the film surrounding the sorbent particles,

Table 1

Langmuir isotherm parameters of As(III) adsorption

	K_L [dm³/mg]	Q_L [mg/g]	R^2
10 g/dm³	0.018	25.05	0.9175
15 g/dm³	0.012	25.14	0.9935
20 g/dm³	0.015	36.65	0.9956
25 g/dm³	0.312	32.14	0.9957

(iii) particle diffusion in the liquid contained in the pores and in the sorbate along the pores walls, (iv) sorption and desorption within the particle and on the external surface [20]. In this work, kinetic studies indicated that the sorption of arsenic onto fly ash agglomerates follows a pseudo-second-order (PSO) chemisorption model. The linear form of this model is as follows

$$\frac{t}{q_t} = \frac{1}{k_m \cdot q_m^2} + \frac{1}{q_m}$$

where:

k_m – the adsorption rate constant [g/mg×min],
q_m – the amount of adsorbate at equilibrium [mg/g$_{solid}$],
q_t – the amount of adsorbate at any time,
$k_m \cdot q_m^2 = h$ denotes the initial adsorption rate in mg/g·min.

The plots of t/q_t versus t showed very good linearity in all cases of adsorbent amount in relation to arsenic concentration in the solution. The calculated values of the model parameters are shown in Table 2. The parameter q_m is the amount of arsenic at equilibrium estimated from the model, while q_{eq} value was obtained from the experiment, and the data are corresponding. The values of correlation coefficient, R^2, confirm that the kinetics of arsenic adsorption onto fly ash agglomerates follows this model. The equilibrium adsorption capacity, q_m, decreases when the concentration of adsorbent increases, in the investigated range of adsorbent load. As expected, both h and k parameters rise when the amount of adsorbent rise. This can be explained by the fact that more adsorption sites are available

Table 2

Kinetic study calculations for PSO model of As(III) adsorption

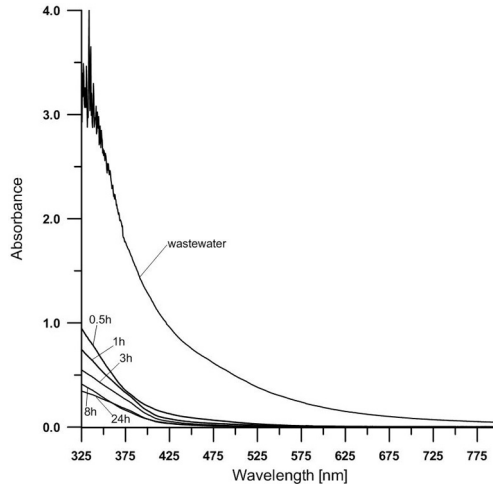|	h [mg/g·min]	k_m [g/mg·min]	q_m [mg/g]	q_{eq} [mg/g]	R^2
20 g/dm³	0.445	3.03×10⁻⁴	38.35	36.65	0.9982
35 g/dm³	3.026	4.71×10⁻³	25.35	24.86	0.9993
50 g/dm³	7.270	2.29×10⁻²	17.83	17.50	0.9994
100 g/dm³	13.84	1.79×10⁻¹	8.79	8.75	0.9999
150 g/dm³	37.58	1.15	5.83	5.83	1.0000
200 g/dm³	39.38	1.96	4.38	4.37	1.0000
250 g/dm³	41.55	3.39	3.50	3.50	1.0000

Fig. 2. Change of wastewater spectrum during adsorption on fly ash (50 g/dm^3)

Rys. 2. Zmiana widma ścieku w czasie adsorpcji na popiele lotnym (50 g/dm^3)

In Figure 2 the spectrum of wastewater from the "Górka" reservoir and the change of spectrum in time after the adsorption on fly ash have been demonstrated. One can see the significant decrease in colour intensity, so the purification of wastewater is undeniable. Fig. 3 presents the effect of adsorbent amount on wastewater spectrum change. In the investigated range of adsorbent weighted amounts (25–50 g/dm^3) the spectrum modification is not substantial, so the load of adsorbent weakly affects the purification process.
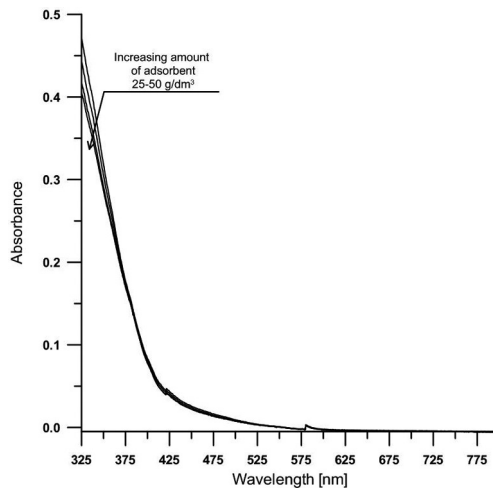

Fig. 3. Effect of fly ash amount on wastewater spectrum

Rys. 3. Wpływ ilości popiołu lotnego na zmianę widma ścieku

4. Conclusions

The obtained results indicate the considerable adsorption capacity of fly ash in relation to As(III). The complete removal of arsenic is feasible using 35 g of adsorbent per one litre of the standard As(III) solution. The best fit of adsorption experimental data has been obtained using the Langmuir equation. Investigations of the sorptive capacity proved that the sorbent took up to 37 milligrams of arsenic per gram, which is comparable to commercial ion-selective resins uptakes. The model of chemisorption with the reaction of the pseudo-second-order (PSO) has been applied to fit the kinetic experimental data. The purification of wastewater using fly ash is also possible; the change of the UV/Vis spectra within the range of 325–800 nm is significant. The results analysis provided the evidence that fly ash from brown coal burning can be used as a cheap adsorbent for arsenic removal from water, especially for arsenic-rich leaches generated during the regeneration of ion-selective resins, such as ArsenX and Lewatit FO36. Additionally, the pre-treatment of heavy metal ions-bearing wastewater can be carried out using fly ash, so the contamination concentration is minimized.

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