

Application of fly ash agglomerates in the sorption of arsenic

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The scope of this contribution was to investigate in detail an application of fly ash adsorbent for the removal of arsenite ions from a dilute solution. The experiments have been carried out using fly ash from black coal burning power plant „Siersza” and brown coal burning power plant „Turów” (Poland), which was wetted, then mixed and tumbled in the granulator with a small amount of cement to increase the mechanical strength of agglomerates. The measurements of arsenic adsorption from the aqueous solution were carried out in the flask (with shaking), as well as in the column (with circulation), in order to compare two different methods of contacting waste with adsorbent. The adsorption isotherms of arsenic were determined for granulated material, using the Freundlich model. Kinetics studies indicated that the sorption follows a pseudo-first-order (PFO) model (Lagergren) and the Elovich-type model.

Keywords: fly ash, adsorbents, arsenic.

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INTRODUCTION

Arsenic is an unwanted hazardous waste generated during the processing of variety of ores, including those of copper, gold, nickel, lead and zinc¹. High toxicity of arsenic and its salts requires an efficient method of adsorption and binding to prevent leaching into the environment. Arsenite is known to be much more toxic than As(V), more soluble, and mobile under acidic conditions; hence, its separation is of great interest. As(III) ions are chemically known to present rather peculiar speciation in aqueous solution, as mainly they remain protonated, as arsenious acid (H_3AsO_3), at pH values lower than 9; in the alkaline region the form H_2AsO_3^- starts to appear, and in the acidic the form H_4AsO_3^+ is found too, at lower concentration². Many efforts have been made to remove arsenic from water and waste water using various adsorbents³.

Cement and hydrated lime and other pozzolanic materials, e.g. fly ash, have been widely and successfully applied for such purpose^{4,5}. Our interest has been focused on fly ash, a common by-product of coal incineration. More than 150 millions tons of fly ash are produced annually worldwide from the combustion of coal in power plants. However, the rate of production is greater than the consumption^{6,7}. The relatively small percentage of the material finds an application as the ingredient of cement and other construction products; a small amount is used as a binder for the formation of agglomerates from mine tailings to prevent acid mine drainage from mine tailings⁸. It immobilized the reactive components, which remained resistant to weathering and leaching. More than a half of waste material is collected in dumps or ponds⁹. One possible solution of the problem is conversion of fly ash into zeolite by means of recrystallization^{10,11,12,13,14,15}. Fly ashes are complex mixtures with unique, polycomponent, heterogeneous and variable composition, containing intimately associated and finely dispersed solid, liquid and gaseous components. The phase and mineral composition of fly ash normally includes an inorganic

component (90 – 99%), an organic component (1 – 9%), and a fluid component (less than 0.5%)¹⁶. Fly ash consists mainly of silica and alumina particles, and is a strongly alkaline material of pH 10 – 13 when added to water, hence, one can expect that metal ions can be removed from aqueous solutions by precipitation or electrostatic adsorption. Industrial wastewater can contain a substantial amount of heavy metal ions which may mutually enhance adsorption, act relatively independently or interfere with each other¹⁷. Arsenic can be chemically fixed into cementation environment of the solidified/stabilized matrices by three important immobilization mechanisms¹⁸. Several researchers have shown that As-immobilization is mainly controlled by the formation of Ca-As precipitates¹⁹. The recent study suggested that calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$ is a probable host for As in fly ash. Chuanyong and co-workers²⁰ reported a significant reduction of arsenic mobility with cement because of the formation of the sparingly soluble calcium arsenate. They also confirmed the conversion of the adsorbed arsenic to calcium arsenate precipitate. Oxidation prior to immobilization with cement has been suggested to lower the leaching of As²¹. Arsenic was also successfully removed from samples of industrial wastewater using fly ash^{22,3}.

Adsorption of arsenic on fly ash was found to conform to the Freundlich's isotherm¹⁷ and the efficiency of adsorption was comparable to the activated carbon. Some authors reported a better fit with the Freundlich's isotherm than the Langmuir one for arsenic adsorption onto the activated carbon²³ or ferric hydroxide². Aguilar-Corrillo and co-workers⁵ applied the Langmuir isotherms for the sorption of As, Cd and Tl onto fly ash.

Determination of the kinetics parameters and explanation of the mechanism in heterogeneous systems is often a complex procedure, as surface effects can be superimposed on chemical effects. 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 the experimental results of the adsorption of heavy metals². The rate con-

stants for the adsorption of metal ions (zinc, lead, cadmium and copper) on fly ash were determined using the pseudo-first-order model of Lagergren¹⁷. The pseudo-second-order equation has been used for the description of arsenic, cadmium and tall adsorption kinetic onto fly ash, followed by the parabolic diffusion equation⁵.

The purpose of this study was to investigate the possibility of the utilization of coal fly ash as a low-cost and effective adsorbent for arsenic removal.

MATERIALS AND METHODS

The fly ashes of different origin were used to prepare a sorbent: the one from „Elektrownia Turów” power-plant (Poland) – brown coal (lignite) burned in the pulverized coal boiler (WB – unit No. 9) and another from burning of black coal in „Elektrownia Siersza” power-plant (Poland) – fluidal coal boiler (unit No. 1) – WK. The fly ash from brown coal (Turów) contains more clay minerals (aluminosilicates), while the one from black coal is silica-rich. The chemical analysis indicated that SiO₂ (20 – 50%), Al₂O₃ (about 30%), CaO (up to 30%) and Fe₂O₃ (about 5 – 6%) are the main components of the WB and WK fly ash^{11, 14, 24}. The X-ray diffraction analysis showed the presence of the following minerals: anhydrite, calcite, quartz and mullite. The contents of particular components in the fly ash samples differed from each other due to combustion conditions and the nature of fuel, i.e. WB sample contains more unburned coal and much more calcium (because of the lime method used for flue gas desulphurisation). The particle size analysis showed the mean diameter (*d* 0.5) of about 36.7 μm and 28.3 μm for WB and WK, respectively. Particle analysis was undertaken using the Mastersizer 2000 laser diffractometer (Malvern), equipped with the HydroMu dispersion unit (Malvern). The surface area was measured by the BET method for helium/nitrogen mixture using FlowSorbII (Micromeritics) and found to be 3.8 and 4.8 m²/g for WB and WK, respectively. After granulation with 15 wt% of portland cement in the presence of water, the surface area of agglomerates increased to 4.5 (WB) and 9.4 (WK) m²/g. One can explain it by the pozzolanic reaction occurred during the hardening of agglomerates²⁵.

Granulation experiments

The tumble agglomeration experiments have been conducted in the laboratory granulator. The agglomeration process was performed in the 6-liter and 185 mm-diameter plastic container placed horizontally and driven by motor with the 60 r.p.m. speed. Water (80 – 90 ml) was used as the binder liquid. In each experiment, 170 g of fly ash samples and 30 g of Portland blastfurnace cement (which contains up to 70% ground granulated blast furnace slag with the rest Portland clinker and a little gypsum) were taken. The agglomeration was provided for 1 hour. After this time, the green agglomerates were formed. Wet product was cured in a curing chamber at room temperature for 1 week under cover to achieve the hydration of cementitious components^{26, 27, 28}.

Arsenic adsorption isotherms determination

The removal of arsenic by sorbents from the solution was determined as follows. Sorbent (5 g) was added to 20

ml of acidic As (III) stock solution (1 – 1000 ppm solution), and the resulting suspension was shaken at room temperature for 24 h. After this time 0.5 ml aliquot was taken and analysed spectrophotometrically (UV-Vis Helios Gamma (ThermoFisher) spectrophotometer) by means of the molybdenum blue method followed according to the standard procedure.

Batch adsorption of arsenic

40 g of the fly ash agglomerates with 200 ml of arsenic solution (100 ppm of As (III)) in the glass Erlenmeyer flask was kept in the laboratory shaker, and shaken with the speed of 60 c.p.m. for 3 days. During the first day, 0.5 ml aliquot was taken every 2h. After 2 days – twice a day.

Continuous-flow adsorption of arsenic

40 g of adsorbent with 200 ml of arsenic solution were placed in the glass column. The diameter of the column was 45 mm, and the height – 250 mm. The ceramic sinter was at the bottom of the column. The circulation of arsenic solution through the bed was performed using the peristaltic pump with the 5 ml per minute efficiency. The experiment was conducted for 3 days.

Removal of arsenic from adsorbent

After 1 week of adsorption experiments, the adsorbent was separated on sieve and washed twice with distilled water, then mixed with 200 ml of distilled water. The leaching of As(III) was analysed after 1 day and 1 week. Arsenic content was below the detection limit of the method, i.e. 1 ppm.

RESULTS

Two samples of fly ash (WB and WK) have been agglomerated in a drum-granulator. Granulation of fine fly ash increases its workability compared to a highly dispersed material^{25, 29}. The Portland furnaceblast cement was used as a stabilizer to increase the mechanical strength and sorption capacity of aggregates. Fly ash from black coal required more water and longer time to agglomerate. Hycnar²⁵ explains it by higher hydrophobicity and lower wettability of WK compared to WB; this also explains better mechanical strength of agglomerates formed from the latter. Granulation of WK requires addition of cement or ground slag. Hycnar's observations have been confirmed in our studies – the addition of cement decreased water consumption and made the agglomeration easier. The different fly ash-cement-water proportions have been examined. Finally, the mixture of 85% fly ash and 15% of cement has been selected for adsorption of arsenic. The average size of agglomerates was 12.28 and 8.53 mm, for WK and WB samples, respectively (Table 1). The pictures of agglomerates from WB and WK samples are presented in Figures 1 and 2. After curing in the humid environment for 1 week, the granules were further seasoned for 3 weeks and then subjected to adsorption experiments.

Table 1. The size of agglomerates

Sample	d0.1 (mm)	d0.5 ± σ* (mm)	d0.9 (mm)
WK	9.32	12.28 ± 2.38	14.98
WB	6.68	8.53 ± 1.85	11.04

* Standard deviation



Figure 1. The picture of the agglomerates obtained from the WK fly ash

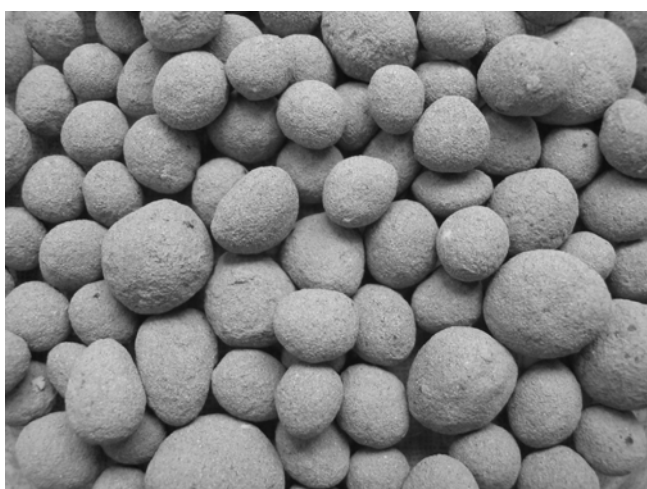


Figure 2. The picture of the agglomerates obtained from the WB fly ash

Various kinds of adsorption isotherms, especially the Langmuir and Freundlich were tested to fit the experimental data of arsenic adsorption on solid materials^{2, 5, 23, 30}. In this study, the equilibrium adsorption data of As(III) for fly ash agglomerates did not obey the Langmuir equation, perhaps due to the heterogeneity of the sorbent surface^{2, 17}. Another explanation is related to the high content of arsenic in fly ash. Koniecznyński and co-workers^{31, 32} determined the amount of As in fly ash to be as high as 1200 ppm; such high amount may strongly affect the shape of the adsorption isotherm. The best fit has been achieved using the Freundlich isotherm given by the equation:

$$q_e = K_F c_e^{1/n}$$

where q_e is the amount of metal ions adsorbed at equilibrium [mg/g_{solid}], c_e is the concentration of metal ions in solution at equilibrium [ppm], and K_F [mg/g] and n are constants related to adsorption capacity and adsorption intensity. Figure 3 shows the Freundlich isotherm plots for WK and WB agglomerates at native pH (about 11 for WK and 12 for WB). Since our research has been carried out at a low concentration of arsenic, thus, we cannot estimate the behaviour of the isotherm, i.e. the presence of the second region¹⁷. Also the solid/liquid ratio was high and there is no saturation limit as well as no Henry law limit³³. For WB both slope and intercept are higher compared to WK (Table 2 and Figure 3).

Table 2. The Freundlich constants

Sample	pH	1/n (-)	K_F (mg/g)
WK	11.0	0.59	0.13
WB	12.3	2.16	0.47

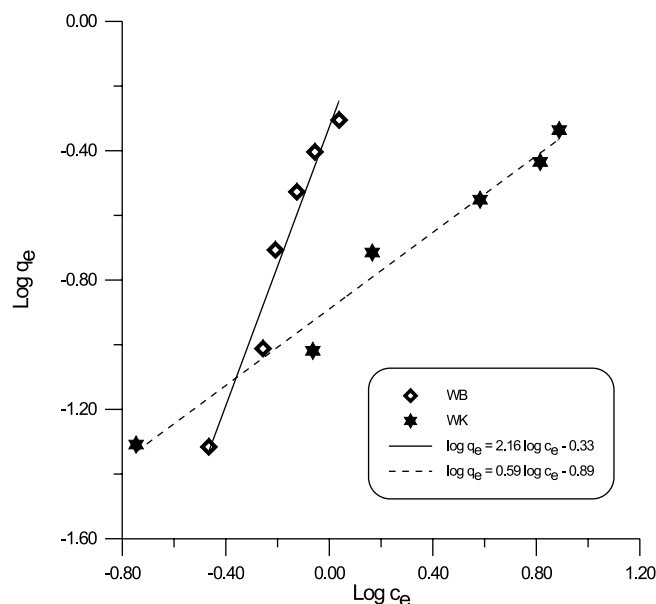


Figure 3. The Freundlich isotherm plot for the sorption of arsenic on WK and WB samples

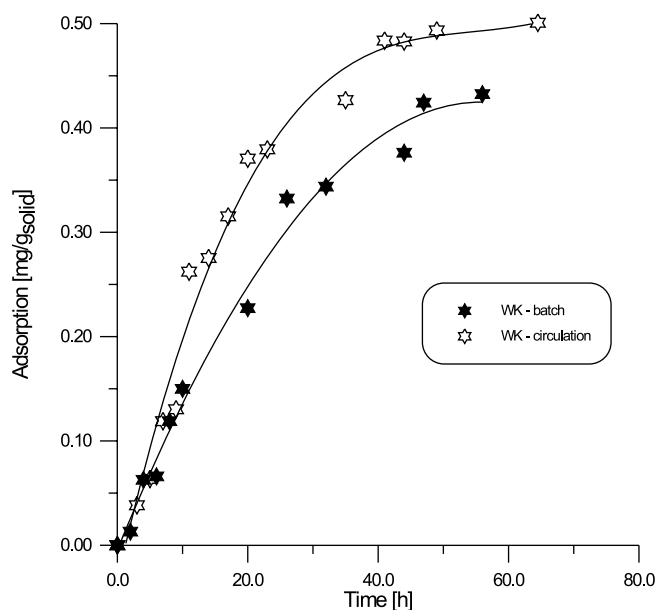


Figure 4. Sorption kinetics of arsenic onto the fly ash agglomerates (WK)

A first look into the sorption kinetic of arsenic on WK fly ash, presented in Figure 4, revealed the time necessary for its removal. Equilibrium concentration and almost a complete removal of arsenic has been achieved after 48 hours in the process conducted at circulation conditions. Probably, in batch condition more time was required to equilibrate the system.

In order to investigate the mechanisms of sorption and the potential rate controlling step, such as mass transport and chemical reaction processes, kinetic models have been used to test the 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, (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 surface³⁰. In case of surface adsorption, a variation in the rate should be proportional to the first power of concentration. The most widely used for the sorption of heavy metals from a liquid solution is the Lagergren pseudo-first order equation^{4, 17}:

$$\ln(q_e - q) = \ln(q_e) - K_{ad} \cdot t$$

where q_e and q are the amounts of solute adsorbed at equilibrium and at any time, t , respectively. The value of K_{ad} (Table 3) calculated from that equation showed the better removal of arsenic in column, and WB fly ash agglomerates are slightly more effective adsorbent than WK.

Table 3. Kinetics study calculations for the Lagergren model

Sample	K_{ad} (1/min)	R^2
WK batch	0.00068	0.9419
WK circulation	0.00131	0.9782
WB batch	0.00137	0.9796
WB circulation	0.00148	0.9962

Unfortunately, the Lagergren equation is of the same form as the equation of Boyd, which represents a film diffusion model, so differentiating between film diffusion control and the pseudo-first-order reaction control will be difficult. In the sorption studies of the intensively agitated samples, film diffusion is usually the only rate-controlling step for the first few minutes³⁰.

A satisfactory fit with the experimental data was achieved by the application of the Elovich kinetic equation^{30, 34}:

$$q = q_0 + \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln(t)$$

The parameter α is the initial sorption rate, the parameter β is related to the extent of surface coverage and activation energy of chemisorption, and $q=q_0$ at $t=0$. The parameters calculated from the Elovich equation are given in Table 4.

Table 4. Kinetics study calculations for the Elovich-type model

Sample	α (mg/g·min)	β (g/mg)	R^2
WK batch	0.00083	7.28	0.9559
WK circulation	0.00016	7.58	0.9361
WB batch	0.00158	7.42	0.9778
WB circulation	0.00127	6.77	0.9668

Figure 5 illustrates the comparison of the experimental data and the theoretical outcomes based on the Lagergren and Elovich models.

If the rate-limiting step is an interparticle diffusion, a plot of solute sorbed against square root of contact time should yield a straight line passing through the origin. This possibility has been tested. As it results from Figure 6, the relationship between the amount of As(III) adsorbed on fly ash and the square root of time do not give the straight line. It suggests that the pore diffusion is not the rate controlling step^{4, 34}.

CONCLUSIONS

The sorption of arsenic (As(III)) from the dilute solution has been examined onto the fly ash agglomerates under batch and column conditions. From the experimen-

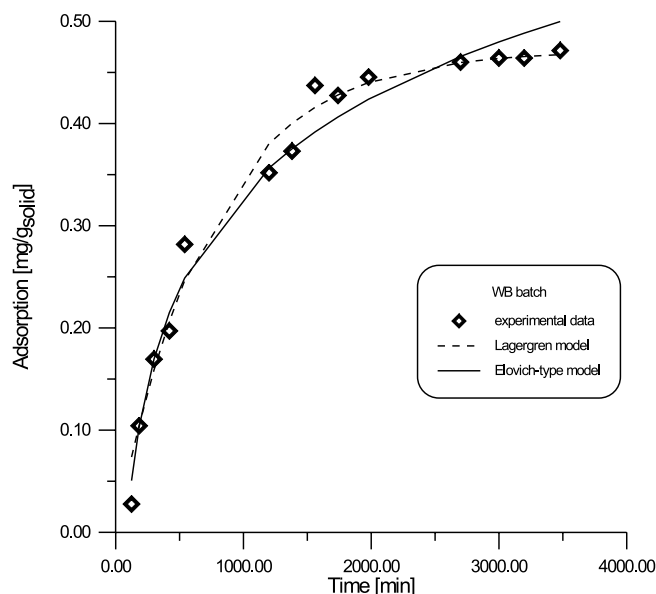


Figure 5. Sorption kinetics of arsenic onto WB. Comparison of the experimental data with the theoretical prediction

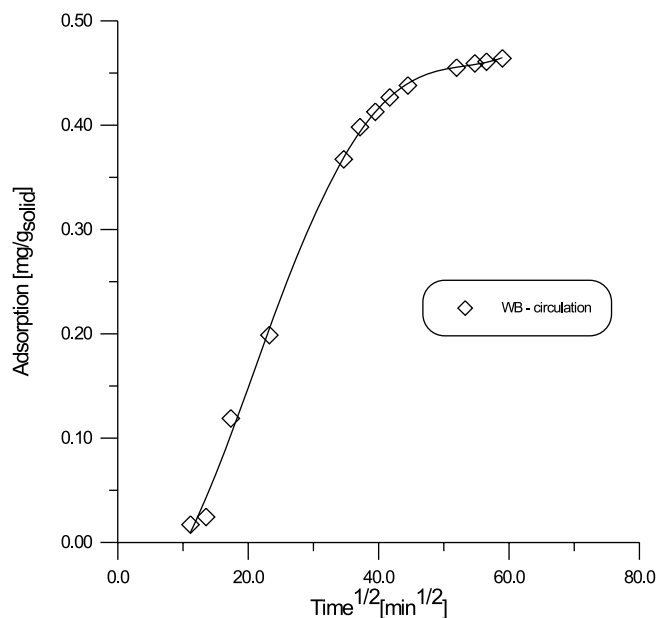


Figure 6. Plot of the amount of As(III) adsorbed vs. square root of time on WB agglomerates in circulation condition

tal results and the theoretical predictions the following conclusions can be drawn:

1. Fly-ash can be efficiently granulated into spherical agglomerates with some addition of furnaceblast cement, which increases the mechanical strength of granules and enhances the agglomeration process.

2. The granulated materials can be easily handled and stored, including packing in adsorption columns.

3. The experimental data can be fit by the Freundlich isotherm, at least at the low concentration of arsenic used in a current study. We cannot draw a conclusion about a higher concentration of As(III) ions, particularly the presence of the second region of a different slope as shown by Cho and co-workers¹⁷.

4. Our studies confirm that even the small amounts of arsenic can be removed from wastewater, lowering its concentration below 1 ppm. Unfortunately, the analytical

method used didn't allow us to test if it is acceptable for drinking water, i.e. below 0.05 ppm.

5. The kinetic data were fitted using both the Elovich and Lagergren models. Both gave approximately the same quality of the fit, with the correlation coefficient close to 0.95. The latter one is in the same form as the Boyd film diffusion model. Unfortunately, current results are insufficient to judge whether it is the process pseudo-first order reaction controlled or diffusion controlled.

6. The WB samples are more effective sorbents than the WK ones. It can be explained by the higher porosity of the former, as shown in Figures 1 and 2.

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