

Mine wastewater treatment by highly calcareous and siliceous fly ash: a comparative study

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KEYWORDS: fly ash, mine wastewater, heavy metals, acid drainage.

ABSTRACT

As the power generation sector in Greece is heavily reliant upon lignite combustion, it is necessary to design novel pathways for lignite fly ash utilization, able to offer immediate industrial solutions. In this sense, the current study investigates the potential of highly calcareous and siliceous fly ash to be utilized as sorbents in mine wastewater treatment. Representative fly ash samples were collected from the lignite-fired power stations of Kardìa & Megalopolis, Greece and tested for their pH regulation capability as well as their heavy metal-uptake capacity. Fly ash performance was tested by the use of actual wastewater samples from: a) an abandoned ore mine in Ermioni, eastern Peloponnese, Greece and b) leachates, prepared in the laboratory, of FeS₂ from the active mixed sulphidemine of Kassandra, Chalkidiki, northern Greece. The initial & remaining concentration of Hg, Fe, Zn, Cd, Cu, Pb, Mn, Ni, Co and Cr (total), was determined by means of Flame Atomic Absorption Spectroscopy (FAAS). For both fly ash types, their performance was tested as a function of reaction time and solid-to-liquid ratio. Both Kardìa (high-CaO) and Megalopolis (SiO₂) ash showed promising results in heavy metal-uptake, with the first being clearly preferable when Fe, Zn, Cd, Cu, Pb, Mn, Ni, Co precipitation is the primary target of the process. Both sorbents are activated fast enough, having uptake the bulk amount of pollutants in the very first hour of solid-liquid reaction. Finally, as expected by its highly calcareous nature, Kardìa fly ash has been more efficient in neutralizing acid mine water drainage, achieving pH=7 within short reaction times. The differentiation of flyash performance is attributed to the different physical, chemical, and mineralogical properties of Kardìa and Megalopolis flyash, which were determined by means of a series of analytical techniques, incl. SEM, XRF, XRD, and N₂-porosimetry.

INTRODUCTION

Liquid waste management remains a primary challenge for metallurgical industry, mainly in the case of sulfurous ores. Components such as pyrite/marcasite (FeS_2), galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS) etc, due to their high exposure in atmospheric conditions, both in active & abandoned mines, may form acid drainage (a self-catalytic process), harming the eco-system due to its low pH (1.5-3.5) and high heavy metal concentration. Soils and groundwater contaminated with acid drainage may in turn pose a great threat to public health, as heavy metals (HM) discharged in wastewaters are extremely toxic to aquatic life and cause natural waters to be unsuitable as potable water sources. The safe and cost-effective management of toxic metal-containing wastewater remains a challenging task for industrialists and environmentalists. The traditional treatment methods of HM-contaminated aquatic discharges, such as reduction precipitation, ion exchange, electrochemical reduction, reverse osmosis etc, are methods involving large exposed liquid surface area and long detention periods as well as high capital cost, usually not-affordable for small-scale industries [1, 2, 3].

In general, to handle acid drainage, alkaline components such as NaOH , Na_2CO_3 , CaO , CaCO_3 , $\text{Ca}(\text{OH})_2$ etc, are added, so to neutralize the initially acidic solution and let the insoluble metals precipitate. The quantity and quality of alkaline addition depends on a number of technological factors, incl. flow velocity of waters, pH of acid drainage, nature and concentration of toxic metals, among others. Fly ash (FA) from coal- and lignite-fired power stations can be a cheap alternative to the established liquid-phase sorbents, as it has been successfully used in the past for water de-contamination processes [4-10]. This work is one of the few examining its usage in mine-wastewater treatment, focusing on the comparison between high-Ca- & Si- ashes, generated in lignite-fired power stations. Greece is quite rich in several minerals, such as P.B.G. porphyry Cu. V.M.S etc, while lignite fly ash is also available in abundant quantities, rendering this work a quite interesting precursor for the industrial application of this concept in Greece, provided it can be an economically feasible procedure. It is noted that there are several active & abandoned mines currently in Greece; this work has been focused on two of the most important, based on the environmental disturbance they may cause.

MATERIALS AND METHODS

Raw materials: acid drainage & fly ash

Pyrite ore samples were collected from the active mine of Kassandra, Chalkidiki (Northern Greece) while acid drainage was sampled from the abandoned mine of Ermioni, Eastern Peloponnese (Southern Greece). In the first case, so to produce an artificial solution of acid drainage, 80g of pure pyrite have been mixed with 400 ml of potable water and the solution pH was being monitored for five consecutive days before it could be used for experimental purposes (LMWW: Laboratory Mine Waste Water, pH

vs. time: Table 1). In the second case, acid drainage was used as collected from the mine (EAD: Ermioni Acid Drainage). The concentration of selected heavy metals in both solutions (Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) has been determined by means of Flame Atomic Absorption Spectroscopy (FAAS); and in the case of Hg, FAAS coupled with hydride generation system.

Table 1. pH vs. time until stabilization: Laboratory Mine Waste Water (LMWW).

Time (h)	pH
0.5	4.95
10	3.55
24	3.48
25	3.45
48	3.20
72	3.17
96	3.07

Representative FA samples were collected from the electrostatic precipitators of two different lignite-fed power plants of Greece [Kardia (1250MW) and Megalopolis (850MW) thermal power stations], under maximum electricity load. Kardia FA (KFA) is highly calcareous, strongly Class C, according to ASTM C618, while Megalopolis FA (MFA) is generally siliceous, barely classified as Class C, according to same protocol. Chemistry and mineralogy of fly ash samples has been examined by means of X-Ray Fluorescence (XRF, X-Lab 2000 EDAX) & Diffraction (XRD, Siemens D-5005), respectively, while ash microstructure was investigated by means of Scanning Electron Microscopy (SEM, JSM-6300 JEOL).

Acid drainage treatment tests

The analytical test procedure involved filling a series of glass tubes with 50mL of solution (a. LMWW and b. EAD), adding 10/1/0.5/0.1 g of adsorbent to them and then implementing mechanical stirring at 250 rpm. The incubation period was set at 24 h. pH was being measured (by applying ISO 6588) each 30 min until 12 h and each 1 h between 12 and 24 h. Then, the supernatant solution was filtered and subjected to flame atomic adsorption spectroscopy (FAAS). The process was repeated for three times and the average measured values are given as the final results of the (%) heavy-metal uptake by the different ash samples and solid-to-liquid ratio (10/1/0.5/0.1 g FA / 50 ml acidic drainage).

RESULTS AND DISCUSSION

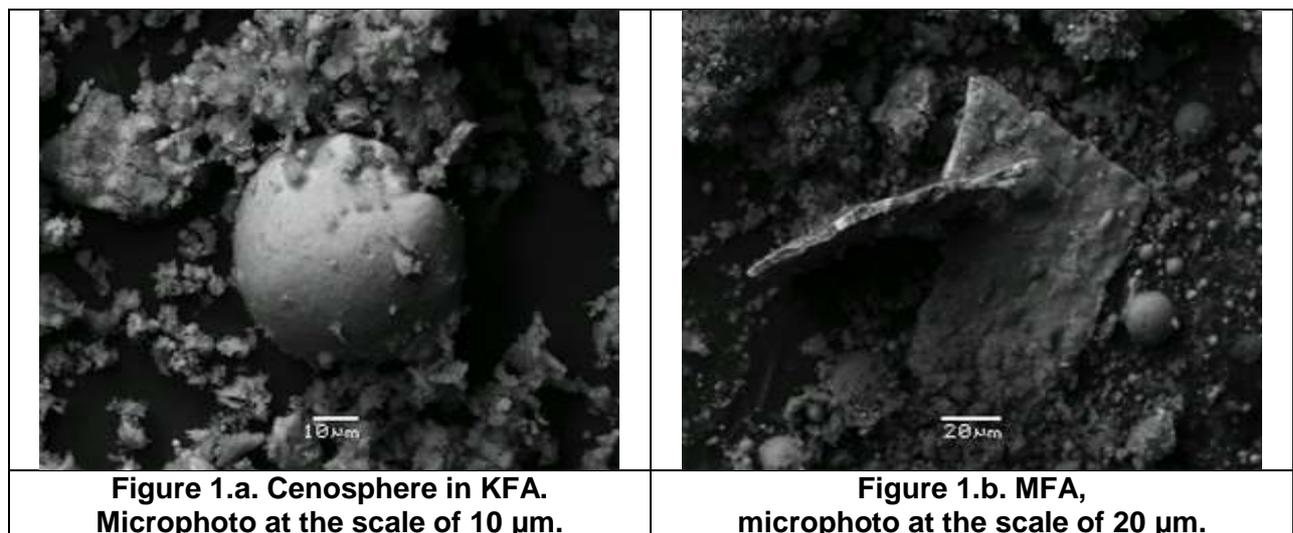
Fly ash characterization

Table 2. Oxides (%) in KFA and MFA

Oxide	KFA	MFA
SiO ₂	30.1	49.5
Al ₂ O ₃	14.9	19.2
Fe ₂ O ₃	5.10	8.45
CaO	34.5	11.8
Na ₂ O	1.01	0.53
K ₂ O	0.40	1.81
MgO	2.69	2.27
P ₂ O ₅	0.34	0.37
TiO ₂	0.60	1.35
SO ₃	6.28	2.91

Table 2 shows the concentration of major oxides in KFA and MFA. Figures 1.a & b show selected microphotos of Kardia and Megalopolis fly ash, respectively. In KFA-microphoto, a cenosphere has been targeted, while in this of MFA, an individual mineral phase is demonstrated. It is noted that cenospheres are more likely to form in Kardia power station rather than in Megalopolis, due to the higher applied combustion temperatures in the latter. Table 3 summarizes the findings from interpreting the X-Ray Diffractograms of KFA & MFA. As expected, in

high-Si MFA quartz is predominant, while calcareous compounds such as anhydrite, calcite and lime are only present in limited quantities. Fe in MFA is basically present in the form of hematite. On the other hand, KFA is dominated by calcite and lime. KFA is rich in free CaO as calcite thermally decomposes to CaO and CO₂. A fraction of calcite can be autogenic and give microcrystals, as it first decomposes in the boiler and it can there form as microcrystalline secondary calcite, during KFA particle-flue gas co-transfer to the chimney.



**Figure 1.a. Cenosphere in KFA.
Microphoto at the scale of 10 μ m.**

**Figure 1.b. MFA,
microphoto at the scale of 20 μ m.**

Table 3. Minerals and their relative presence in MFA and KFA.

Mineral	Chemical Type	MFA	KFA
Feldspar	(Na,K)AlSi ₃ O ₈	+	+
Andalusite	Al ₂ (SiO ₄)O	-	+
Anhydrite	CaSO ₄	+	++
Augite	(Ca,Na)(Mg,Fe ²⁺ ,Al,Fe ³⁺ ,Ti)[(Si,Al) ₂ O ₆]	-	+
Calcite	CaCO ₃	-	+++
Cristobalite	SiO ₂	+	-
Gehlenite	Ca ₂ Al(AlSiO ₇)	-	+
Gismondite	CaAl ₂ Si ₂ O ₈ ·4H ₂ O	+	+
Gypsum	CaSO ₄ ·2H ₂ O	+	-
Hematite	Fe ₂ O ₃	++	+
Lime	CaO	-	+++
Magnetite	Fe ₃ O ₄	+	-
Muscovite	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	-	+
Portlandite	Ca(OH) ₂	+	++
Quartz	SiO ₂	+++	+
Glass			

(+++ : intense, ++ : strong, + : presence, - : absence)

Drainage treatment tests: Effect on pH

Table 4 refers to the treatment of LMWW & EAD samples by both KFA & MFA and it shows how pH changes vs. time, until t=24 h, for a solid-to-liquid ratio =10 g FA / 50 ml LMWW & EAD. In the case of KFA - LMWW solution, it is quite clear that pH can get well into the alkaline region after less than one hour of solid-liquid reaction. On the other hand, MFA can achieve almost neutral pH in the same solution, and with the same adsorbent load, not earlier that t = 24 h. Concerning EAD, the trend can be better for MFA, but overall not significantly different. Again, after only 1 h of treatment, KFA solution pH is well into the alkaline region (12.58), while MFA needs 5.5 h to neutralize (7.11 after 5.5 h). As also shown in the same Table, pH of blank aquatic solution of KFA is bigger by over 2 units than the respective of MFA and this trend is kept virtually stable vs. time, explaining, to some extent, the observed effect of ash-drainage reaction on the final solution pH.

Table 5 refers to the treatment of LMWW with KFA and MFA in lower solid-to-liquid ratios (1, 0.5, 0.1 g FA / 50 ml LMWW) and it shows how pH changes vs. time, until t = 72 h. We can observe that pH of MFA-treated drainage solution remains well into the acidic region, and in specific cases as low as 4.37 (0.1 g MFA/ 50 ml LMWW). On the other hand, in almost all cases of KFA-to-LMWW ratio (exception: 0.1 g / 50 ml), pH is alkaline and quite stable after a maximum 1.5 h of treatment. Only insignificant changes in solution pH may occur between 1.5 and 72 hours. Unlike KFA, treatment of 50 ml drainage solution with 0.5 or 1 g MFA cannot lead to desirable results. It should be noted that although higher solution pH is preferable for the removal of most heavy

metals (by regulating their solubility), treatment with MFA may be preferable when Cr (in its hexavalent form) is the main issue, as it is normally mobile at higher pH values [11]. Limited adsorption of Cr(VI) at higher pH is generally attributed to the abundance of OH⁻, resulting in increased hindrance to the diffusion species and/or to neutralization of negative surface charge by an excess of hydrogen ions, which may facilitate diffusion of dichromate ions and their adsorption by the sorbent [12–14].

Table 4. pH vs. time, 10 g MFA; KFA / 50 ml LMWW; EAD. pH of blank solutions.

Time (h)	pH MFA (LMWW)	pH KFA (LMWW)	pH MFA (EAD)	pH KFA (EAD)	pH MFA blank	pH KFA blank
0	3.07	3.07	2.7	2.7	-	-
0.1	3.15	4.78	2.95	4.66	10.01	12.38
1	5.53	12.50	5.71	12.58	11.30	12.76
2	5.69	12.52	5.97	12.48	11.32	12.62
2.5	5.81	12.45	6.31	12.52	11.35	12.62
3.5	5.92	12.44	6.48	12.45	11.31	12.60
4	5.98	12.40	6.71	12.42	11.26	12.54
4.5	5.98	12.37	6.85	12.40	11.29	12.52
5.5	5.97	12.38	7.11	12.41	11.26	12.50
6.5	6.03	12.35	7.38	12.40	11.23	12.50
7.5	6.07	12.41	7.64	12.42	11.20	12.54
8.5	6.11	12.41	7.72	12.51	11.23	12.59
9.5	6.06	12.42	7.84	12.45	11.18	12.55
10.5	6.03	12.40	7.88	12.43	11.20	12.53
11.5	6.06	12.41	7.99	12.42	11.15	12.52
24	6.54	12.51	9.41	12.54	11.01	12.70

Table 5. pH vs. time for different g FA / ml LMWW ratios.

Ratio	1gr/50ml		0.5gr/50ml		0.1gr/50ml	
Time (h)	pH MFA	pH KFA	pH MFA	pH KFA	pH MFA	pH KFA
0	3.07	3.07	3.07	3.07	3.07	3.07
0.1	4.85	5.88	5.04	5.00	4.20	5.26
0.5	6.60	12.18	5.54	11.77	4.74	6.17
1	6.30	12.16	6.30	11.66	4.69	6.10
1.5	6.80	12.15	6.40	11.60	4.66	6.12
2	6.85	12.25	6.35	11.50	4.62	6.02
2.5	6.91	12.16	6.30	11.40	4.62	6.02
24	6.45	12.16	5.20	10.78	4.39	5.87
48	5.82	12.02	nm	nm	4.37	5.76
72	5.84	11.97	nm	nm	nm	nm

(nm: not measured)

Drainage treatment tests: Removal of heavy metals

Tables 6-9 show the percentage capacity of MFA and KFA in uptaking specific trace pollutants from LMWW solutions. Table 6 compares MFA and KFA, as far as their HM-uptake capacity from LMWW is concerned, under the heaviest solid load examined in this study (10 g / 50 ml). Overall, KFA proved more efficient, but in most cases the variation was rather insignificant. Exceptions were Cd, Zn and Cr, with the latter also demonstrating the biggest spread between the two adsorbents. Table 7 demonstrates the same values for a smaller adsorbent loading ratio (1 g / 50 ml). It is obvious that MFA capacity may dramatically diminish when reducing adsorbent load, especially in the cases of: Cd (dropped to 69% from 95%), Cr (dropped to 21.84% from 47.13%), Mn (33.44% from 99.37%), and Ni (57.55 % from 99.65%). On the other hand, no important decline in HM-removal capacity is presented by such an important reduction of adsorbent load, probably thanks to its highly alkaline pH. Tables 8 & 9 show the same values for even smaller solid-to-liquid ratios, i.e. 0.5 & 0.1 g FA / 50 ml LMWW. In most metals, MFA demonstrates a linear drop in uptake capacity. On the other hand, we observe that KFA maintains its relevant ability almost to a full potential, even for a ratio as low as 0.5 g / 50 ml, while it expectedly severely diminishes for load = 0.1 g FA / 50 ml LMWW. Table 10 compares MFA to KFA, as far as their HM-uptake capacity from EAD is concerned, under the heaviest adsorbent load examined in this study (10 g / 50 ml). Again, KFA appears more efficient, with the exception of mercury. However, in a direct agreement to pH measurements, KFA superiority in this case appears quite marginal, rather than clear and solid as in the case of LMWW, actually reflecting the different nature of samples, i.e. Volcanogenic Massive Sulfides (VMS) (the case of Ermioni Acidic Drainage) and mixed sulfide Pb-Zn (\pm Ag) (\pm Au) carbonate-hosted (Kassandra ore samples).

Table 6. HM-uptake capacity of KFA & MFA from LMWW (ratio: 10 g FA / 50 ml LMWW).

Element	Initial Solution	KFA	Removal (%)	MFA	Removal (%)
pH	3.07	12.52	-	6.53	-
Cd (ppm)	1	b.d.l	100.00	0.05	95.00
Co (ppm)	116	b.d.l	100.00	0.50	99.57
Cr (ppm)	0.87	0.09	89.65	0.46	47.13
Cu (ppm)	0.58	b.d.l	100.00	b.d.l	100.00
Fe (ppm)	546	b.d.l	100.00	b.d.l	100.00
Hg (ppb)	28.3	b.d.l	100.00	b.d.l	100.00
Mn (ppm)	317	b.d.l	100.00	2	99.37
Ni (ppm)	80	b.d.l	100.00	0.28	99.65
Pb (ppm)	2.60	b.d.l	100.00	b.d.l	100.00
Zn (ppm)	245	0.06	99.97	15.7	93.60

(bdl: below detection limit)

Table 7. HM-uptake capacity of KFA & MFA from LMWW (ratio: 1.0 g FA / 50 ml LMWW).

Element	Initial Solution	KFA	Removal (%)	MFA	Removal (%)
pH	3.61	11.97	-	5.84	-
Cd (ppm)	1	b.d.l	100.00	0.31	69.00
Co (ppm)	116	b.d.l	100.00	122	0
Cr (ppm)	0.87	0.04	95.40	0.68	21.84
Cu (ppm)	0.58	b.d.l	100.00	b.d.l	100.00
Fe (ppm)	546	b.d.l	100.00	1.08	99.80
Mn (ppm)	317	b.d.l	100.00	211	33.44
Ni (ppm)	80	b.d.l	100.00	34	57.50
Pb (ppm)	2.60	b.d.l	100.00	b.d.l	100.00
Zn (ppm)	245	0.62	99.75	227	92.65

Table 8. HM-uptake capacity of KFA & MFA from LMWW (ratio: 0.5 g FA / 50 ml LMWW).

Element	Initial Solution	KFA	Removal (%)	MFA	Removal (%)
pH	3.57	10.87	-	5.20	-
Cd (ppm)	1	b.d.l	100.00	0.53	47.00
Co (ppm)	116	b.d.l	100.00	86	25.86
Cr (ppm)	0.87	0.09	89.65	0.73	16.10
Cu (ppm)	0.58	b.d.l	100.00	b.d.l	100.00
Fe (ppm)	546	b.d.l	100.00	99	81.87
Mn (ppm)	317	b.d.l	100.00	133	58.04
Ni (ppm)	80	b.d.l	100.00	30	62.50
Pb (ppm)	2.60	b.d.l	100.00	b.d.l	100.00
Zn (ppm)	3.57	10.87	-	5.20	-

Table 9. HM-uptake capacity of KFA & MFA from LMWW (ratio: 0.1 g FA / 50 ml LMWW).

Element	Initial Solution	KFA	Removal (%)	MFA	Removal (%)
pH	3.57	6.09	-	4.37	-
Cd (ppm)	1	0.19	81.00	0.65	35.00
Co (ppm)	116	30	74.14	68	41.38
Cr (ppm)	0.87	0.44	49.43	0.76	12.64
Cu (ppm)	0.58	b.d.l	100.00	0.52	10.34
Fe (ppm)	546	1.38	99.75	194	64.47
Mn (ppm)	317	164	48.26	59	81.39
Ni (ppm)	80	8	90.00	76	5.00
Pb (ppm)	2.60	b.d.l	100.00	b.d.l	100.00
Zn (ppm)	245	33.6	86.30	46.60	81.00

Table 10. HM-uptake capacity of KFA & MFA from EAD (ratio: 10 g FA / 50 ml EAD).

Element	Initial Solution	KFA	Removal (%)	MFA	Removal (%)
pH	2.7	12.55	-	9.4	-
Cd (ppm)	0.05	b.d.l	100.00	0.02	100.00
Co (ppm)	1.95	0.07	96.41	0.09	95.38
Cr (ppm)	0.10	2.03	0	0.12	0
Cu (ppm)	5.63	b.d.l	100.00	b.d.l	100.00
Fe (ppm)	49.50	0.32	99.35	0.06	99.88
Hg (ppb)	0.70	0.40	42.86	b.d.l	100.00
Mn (ppm)	12.10	b.d.l	100.00	1.22	89.92
Ni (ppm)	0.48	0.09	81.25	0.12	75.00
Pb (ppm)	b.d.l	b.d.l	-	b.d.l	-
Zn (ppm)	27.20	b.d.l	100.00	0.03	100.00

CONCLUSIONS

The main conclusions of this study are summarized below:

- Highly calcareous fly ash (KFA) proved faster than siliceous ash (MFA) in regulating the pH of acidic drainage, in both cases of Laboratory Mine Waste Water and Ermioni Acidic Drainage;
- With the exception of mercury, highly calcareous fly ash (KFA) proved more efficient than siliceous fly ash (MFA) in uptaking a series of heavy metals from acidic drainage (% removal, Cd; Co; Cr; Cu; Fe; Mn; Ni; Pb; Zn), in both cases of Laboratory Mine Waste Water and Ermioni Acidic Drainage;
- KFA can be a fairly efficient adsorbent for most heavy metals in a solid-to-liquid ratio as low as 1 g / 50 ml LMWW; EAD. The respective optimum ratio for MFA cannot get lower 10 g / 50 ml.

REFERENCES

1. Godfrey M. et al., 2010. Fate of sulphate removed during the treatment of circumneutral mine water and acid mine drainage with coal fly ash: Modeling and experimental approach. *Minerals Engineering* (24): 1467-77.
2. Rao, M., Parwate, A.V, Bhole, A.G., 2002. Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash, *Waste Management* 22: 821–830.
3. Chauhary, A.J, Goswami, N.C., Grimes, S.M., 2003. Electrolytic removal of hexavalent chromium from aqueous solutions, *Journal of Chemical Technology and Biotechnology* 78: 877–883.

4. Wang, S., Wu, H., 2002. Environmental-benign utilisation of fly ash as low-cost adsorbents, *Journal of Hazardous Materials B136*: 482–501.
5. Koukouzas, N. Vasilatos, C, Itskos, G. Mitsis, I., Moutsatsou, A., 2010. Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials, *J. Hazardous Materials 173 (1–3)*: 581–588.
6. Bayat, B., 2002. Comparative study of adsorption properties of Turkish fly ashes II. The case of Cr (VI) and Cd (II), *Journal of Hazardous Materials*: 275–290.
7. Kantiranis, N., Filippidis, A., Georgakopoulos, A., 2005. Investigation of the uptake ability of fly ashes produced after lignite combustion, *Journal of Environmental Management 76*: 119–23.
8. Querol, X., et al. Synthesis of Na zeolites from fly ash in a pilot plant scale. Examples of potential environmental applications, *Fuel 80 (6)*: 857–865.
9. Kao, P.C., Tzeng, J.-H., Huang, L., 2000. Removal of chlorophenols from aqueous solutions by fly ash, *Journal of Hazardous Materials 76 (2000)* 237–249.
10. Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy-metals uptake from contaminated water: a review, *Journal of Hazardous Materials 97*: 219–43.
11. Itskos, G., Koukouzas, N., Vasilatos, Ch., Megremi, I and Moutsatsou, A., 2010. Comparative uptake study of toxic elements from aquatic media by the different particle size fractions of fly ash, *Journal of Hazardous Materials 183 (1-3)*: 787–92.
12. Rubio, B. Izquierdo, M.T., Mayoral, M.C., Bona, M.T. Andres, J.M., 2007. Unburnt carbon from coal fly ashes as a precursor of activated carbon for nitric oxide removal, *Journal of Hazardous Materials 143*: 561–566.