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Synthesis of Zeolitic-type Adsorbent Materials from Municipal Solid Waste Incinerator Bottom Ash and its Application in Heavy Metal Adsorption

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ABSTRACT

Municipal solid waste incinerator (MSWI) bottom ash (BA) was converted to zeolitic-type adsorbent materials by hydrothermal conversion under strongly alkaline conditions. The conversion product was determined to be a mixture of sodium aluminum silicate hydrate (SASH) ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.68\text{SiO}_2\cdot 1.73\text{H}_2\text{O}$) and tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2\cdot 4\text{H}_2\text{O}$). The BET specific surface area was $22.1\text{ m}^2/\text{g}$, which represented a significant gain compared to the BA ($4.6\text{ m}^2/\text{g}$) due to the formation of micropores and mesopores. The converted BA demonstrated promising performance for application as a sorbent towards several heavy metals (oxyanions of As(V), and Cd^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+}). Its performance was found to be generally superior to that of a mainly-clinoptilolite natural zeolite, achieving greater sorption extents and better stabilizing capability of contaminated sediments. At a lower dosage rate (50 mg sorbent per gram sediment) to that of natural zeolite, converted BA achieved greater than 80% reduction of cationic heavy metal concentrations in sediment porewater. These results suggest a promising route for reutilization of MSWI-BA, which can greatly enhance the sustainability of waste incineration technology.

Keywords: Heavy metals, Adsorption, Sorbent, Zeolite, Bottom ash, Sediment

1. Introduction

Rising prices of raw materials and growing awareness for environmental issues has led to a change in perception of the value of waste materials. Waste recycling and re-utilization are potentially favorable routes towards development of environment-friendly, sustainable and cost effective industrial processes. Therefore, it is of great interest to explore the possibilities of turning wastes into valuable products. Conversion of thermal waste ashes into zeolitic-type materials has been shown to be a promising approach due to the compositional similarity of the ashes to some volcanic materials, precursors of natural zeolites [1]. Compared to high-grade zeolites, which have fully connected tetrahedral framework, frameworks of waste-derived zeolitic-type materials are less condensed and present large numbers of hydroxyl groups. Hydrothermal treatment is the most widely used synthesis method for these materials [2-6], and

various types can be obtained based on different combinations of ash sources, activation solution/ash ratios, temperatures, pressures and reaction times. Typical zeolitic-type materials include: analcime, cancrinite, herschelite, NaP1, sodalite, and tobermorite [1].

Waste-derived zeolites can be used as catalysts or catalyst supports; for example Zeolite Y prepared from fly ash has been reported to show good activity for cumene cracking, whilst fly ash generated zeolite and amorphous silica alumina catalysts have been found to be active for pyrolysis of waste plastics [7]. Properties of synthesized zeolites can also be tailored by the incorporation of exchangeable cations through ion exchange, broadening its functionality. For instance, the introduction of rare earth elements is known to increase the acidity of zeolites and can result in enhanced structural resistance to severe reaction conditions; their high thermal stability also makes them suitable as a stable solid acid catalyst [8,9].

Alternatively, the use of these materials as sorbents has attracted much attention [10], given their large specific surface area, high sorption capacity and good cation exchange capability that help to adsorb heavy metals from aqueous media [11]. Potential applications of these sorbents include direct treatment of heavy metal laden streams (e.g. wastewater, groundwater, soil, and sediments) [12-14]. Based on available literature, the maximum sorption capacities reported for waste-derived zeolites are: $\text{Cd}^{2+} = 0.85 \text{ mmol/g}$ [15], $\text{Pb}^{2+} = 2.53 \text{ mmol/g}$ [16], $\text{Zn}^{2+} = 1.53 \text{ mmol/g}$ [16]. In comparison, sorption capacities reported for natural zeolites are: $\text{As(V)} = 0.05 \cdot 10^{-3} \text{ mmol/g}$ [14], $\text{Cd}^{2+} = 0.12 \text{ mmol/g}$ [17], $\text{Pb}^{2+} = 0.89 \text{ mmol/g}$ [18], $\text{Zn}^{2+} = 0.20 \text{ mmol/g}$ [19]. These values suggest zeolites are versatile towards cationic heavy metals, but less suitable for oxyanionic metalloids.

In Europe, incineration is the key treatment process for solid municipal wastes, generating vast amounts of hazardous ashes [20]. Hence the urge to better utilize the waste ashes and minimize landfill burden is paramount. Municipal solid waste incineration bottom ash (MSWI-BA) mainly consists of melt products formed during the incineration process, including mainly silicate-based glass phases and melilites, pseudowollastonite, spinels, and metallic inclusions, which play an important role in concentration of heavy metals [21]. MSWI-BA is considered hazardous as it contains: (i) fine particulate matter; (ii) heavy metals (transition metals, As, Pb...) [22,23]; and (iii) organic compounds (polychlorinated dibenzodioxins, furans...) [24]. Conversely, it also contains oxides of silicon and aluminum, and has intrinsic basicity [25],

which are required for a sol-gel synthesis reaction leading to the formation of micro- and mesoporous aluminosilicate materials.

While previous works have demonstrated several routes for waste-to-zeolite synthesis using coal and incineration fly ashes [12,16,26-28], literature on the synthesis of zeolitic-type materials from MSWI-BA is scarce [29-31], and little results are provided on the efficacy of the derived materials for sorbent or ion-exchange use. Bac et al. [10] synthesized a mixture of Na-P1, tobermorite, hydroxysodalite, hydroxy-cancrinite and pectolite-1 A from MSWI ashes with high silica and alumina and moderate lime contents (47, 12, 16 wt%, respectively) by hydrothermal treatment (HT) and found optimum reaction condition to be: 200 °C, 1:30 (grams ashes to ml NaOH), 2 M NaOH concentration, and 24 hours reaction time. Jing et al. [31] primarily obtained tobermorite from steam-mediated HT treatment of compacted MSWI-BA/NaOH disk specimens at 180 °C and 1 MPa for 12 hours. A reduction in the leaching of heavy metals (As, Cd, Cr, Pb and Se) from the converted material compared to the original material was observed. Sallam et al. [32] adjusted the SiO₂/Al₂O₃ ratio of a high silica MSWI ash (67 wt%) with sodium aluminate to promote zeolite A synthesis by fusion.

The most comprehensive works to date on the synthesis and the use of zeolitic-type materials from MSWI-BA can be attributed to Penilla et al. [29] and Peña et al. [30]. In the first study they obtained sodium aluminium silicate hydrate (SASH) and aluminum tobermorite, and increased surface area (from 0.8 to 12.4 m²/g) of the MSWI-BA (consisting of 34.1 wt% SiO₂, 19.3 wt% Al₂O₃ and 21.9 wt% CaO), using HT at 200°C, with 1N NaOH solution at a solution/ash ratio of 10, for 12 hours. Subsequently they tested this material's performance for retention of heavy metals from a multi-element synthetic solution (0.0002 N of Cs⁺, Cd²⁺, Pb²⁺, Cr³⁺), achieving 31% retention of Cs⁺ and ~99% retention of the other elements. However, the pH of the solution was not controlled, reaching values over 10, signifying that precipitation rather than adsorption was the dominant removal mechanism.

This work aims to characterize the sorption performance of zeolitic-type materials synthesized from MSWI-BA by alkaline hydrothermal treatment towards four heavy metals, oxyanions of As(V), and cationic forms of Cd²⁺, Pb²⁺, and Zn²⁺, using both synthetic solutions and contaminated sediments. Sorption performance is compared against a common, widely available, industrially used natural zeolite. The intention is to assess the potential of converted MSWI-BA

as a sorbent for wastewater treatment and soil/sediment remediation applications, with a view of finding sustainable routes for the re-utilization of the ashes.

2. Experimental Procedures

2.1. Preparation and characterization of sorbent material

Fresh bottom ash samples were obtained from a municipal solid waste incinerator in Flanders, Belgium, produced from a moving-grate furnace. Fresh samples were chosen as it has been shown in literature that aging may transform reactive crystalline silica compounds (e.g. quartz) into more stable but less reactive amorphous species [33]. Samples, having been water quenched, were dried in an oven at 105 °C for 24 hours prior to use. Prior to characterization and synthesis, particles larger than 2 mm, which constitute mostly inorganic debris (e.g. metallics, ceramics), were sieved out.

Hydrothermal conversion of MSWI-BA was conducted in slurry using a Buchi Ecoclave 300 Type 3E autoclave reactor (Büchi Glas Uster AG) of 1.1 litre internal volume, equipped with cyclone impeller stirrer (0 to 2000 rpm), electric-heating/water-cooling jacket, and capable of operating at pressure between 0 to 60 bar (gauge) and temperature between 20 to 250 °C. Optimal synthesis conditions utilized, chosen based on reported findings in Querol et al. [1] were: 3M NaOH, 150 °C, autogenous pressure, 24 hours reaction time, liquid-to-solid ratio (L/S) = 5 (120g BA in 600 ml 18.2 MΩ·cm water). The cooled slurry was filtered (589/3 filter paper), rinsed, and dried at 105 °C for four hours to recover the converted material. A natural zeolite sample (ZeoChem) was also acquired for comparison of performance as a sorbent.

Mineralogical analysis was conducted by X-ray diffraction (XRD) (Philips PW1830), equipped with a graphite monochromator and a gas proportional detector, using Cu K α radiation at 30 mA and 45 kV, step size of 0.02° 2 θ and counting time 2 s per step, over 5 to 70° 2 θ range; mineral identification was done in DiffracPlus EVA (Bruker) software and quantitative phase analysis by full profile Rietveld method was implemented in Topas Academic v4.1 software. ZnO was added at 10 wt% to samples for calibration of their crystalline content. BET nitrogen adsorption–desorption isotherms were performed on a Micromeritics TriStar 3000. Chemical

composition of solid samples was determined by X-ray Fluorescence (XRF, Panalytical PW2400). Morphological assessment was performed by imaging with a scanning electron microscope (SEM) (Philips XL30 FEG). Aqueous samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo Electron X Series) and Atomic Absorption Spectroscopy (AAS) for determination of the equilibrium concentration of heavy metals in solution.

2.2. Sorption experiments

2.2.1. Sorption isotherms

Experiments were carried out with sorbents in aqueous solutions of varying concentrations (1, 5, 20 and 100 mg/l) of each heavy metals of interest at pH = 5.5, to determine the equilibrium heavy metal concentrations (adsorbed and in solution) and the adsorption isotherms. Standard solutions of each heavy metal (As(V), Cd²⁺, Pb²⁺ and Zn²⁺) were used to make up the test solutions. Sorbent dosage of 1 g/l was compatible with expected sorption capacities from literature; solutions were shaken at 160 rpm and 20°C (Gerhardt Laboshake) over five days, filtered (0.45 µm membrane), and analyzed by ICP-MS in triplicates. The pH of the test solutions was maintained by adjustment with 5M KOH. To assess competition for adsorption sites, multi-element solutions were also be prepared and tested; solutions containing equal amounts of the four heavy metals were prepared (ranging from 1 to 100 mg/l individually) and mixed with 4 g/l sorbent over five days. To assess sorption kinetics, samples were taken from the multi-element solutions at intermediate time intervals (from 30 minutes to 120 hours).

2.2.2. Contaminated sediment immobilization test

To better assess the adsorption behavior of the sorbents, sorption tests were performed with sediments taken from a brook in northern Belgium that runs through an area contaminated with historical mining activity pollution. The heavy metal contamination level of this sample was characterized by XRF and ICP-MS. The objective was testing the zeolitic-type sorbents as amendments to the sediment to assess the heavy metal immobilization efficacy of the sorbents.

Porewater solution was extracted from the fresh sampled sediment slurry by filtration. Sorption tests consisted in mixing porewater solution with untreated sediment at a fixed L/S ratio of 5, together with varying amounts of single sorbents (5, 10 and 50 g/l). The mixtures were agitated for seven days, with intermediate sampling and pH measurement to obtain kinetic information. The slurry pH was also measured before sorbent addition and at the end of the experiment to assess sorbent pH-buffering effect. Aqueous filtered (0.45 μm membrane) samples from the sorption tests were tested in triplicates by ICP-MS to determine equilibrium heavy metal concentrations in solution. These results were used to calculate sorption performance by comparison with original porewater values.

3. Results and Discussions

3.1. Bottom Ash Characterization

Municipal solid waste incinerator bottom ash is characteristically composed of wide varying particle sizes, from fine particulate matter to chunky fragments, both of which result from inorganic fractions of the burnt waste. The particle size distribution, obtained from weighing of dry sieved fractions, is shown in Fig. 1. The largest size fraction, which includes material up to several centimeters in size, was removed prior to hydrothermal conversion as it was considered too coarse to effectively participate in the synthesis reaction (small reactive surface area for dissolution) and to be mixed in the one liter volume autoclave (potentially damaging to the high-speed impeller blade). Furthermore, from an industrial perspective, this coarse material fraction can be readily reutilized as a secondary raw material in applications such as road construction [34], given that environmental leaching of heavy metals is not a particular concern for this fraction due to the smaller surface area, unlike its finer counterpart.

The chemical composition of the fresh bottom ash, expressed as oxides, is given in Table 1 as determined by XRF. For zeolite synthesis, the most relevant components are silica (SiO_2) at 28.6 wt% and alumina (Al_2O_3) at 8.3 wt%. The Si to Al ratio is 3.0 on a molar basis. Wu et al. [6] found that the Si:Al ratio affects the type of zeolite formed from hydrothermal treatment of fly ash. They observed a shift from hydroxi sodalite at low Si:Al ratio (= 1) to NaP1 zeolite at Si:Al ratio up to 3.5. In comparison, for the natural zeolite, whose composition is also listed in

Table 1, the Si:Al ratio is 5.5, though this value should be taken with caution as this natural material possibly is not composed of a single crystalline zeolite phase. The bottom ash also contains 40.9% calcium oxide; the molar ratio of CaO to SiO₂ is 1.52. Jing et al. [35] found that tobermorite was formed using a municipal incineration bottom ash with CaO:SiO₂ ratio of 0.83, which is the same as the CaO:SiO₂ ratio in tobermorite (5CaO.6SiO₂.5H₂O). They also reported formation of tobermorite with a ratio of 0.95 indicating possibility of synthesizing the mineral at various ratios.

The mineralogical composition of the materials, limited to the crystalline phases, was determined by XRD and is presented in Fig. 2. MSWI bottom ash (< 2 mm) is characteristically amorphous, which is accredited to its reaction in the high temperature moving grate incineration furnace (> 1500 °C) followed by the rapid water quenching process. The detectable phases are quartz (SiO₂) and calcite (CaCO₃). The XRD result shows the natural zeolite material is a mixture of clinoptilolite zeolite ((Ca,Na,K)₂₋₃Al₃(Al,Si)₂Si₁₃O₃₆·12H₂O) and levyne zeolite ((Ca,Na₂,K₂)Al₂Si₄O₁₂·6(H₂O)). Since the Si:Al ratios of these two identified minerals are respectively 4.5 and 2; the excess silica as determined by XRF (5.5) is likely present as quartz, and other minor silicate phases.

3.2. Sorbent Characterization

Bottom ash treated by hydrothermal conversion was analyzed by XRD and SEM to determine crystallographic and morphological characteristics of the synthesized products. Fig. 2 shows two major phases produced: sodium aluminum silicate hydrate (SASH) (Na₂O·Al₂O₃·1.68SiO₂·1.73H₂O) and tobermorite (Ca₅Si₆O₁₆(OH)₂·4H₂O). Rietveld analysis indicated 41 wt% SASH and 29 wt% tobermorite in the product. SASH, also called NaP1 zeolite, has been reported as a zeolitic product synthesized from coal fly ash [1,36]. Tobermorite, belonging to a mineral family of cation exchangers, has been previously synthesized from MSWI bottom ash by hydrothermal treatment [29,31]. The disappearance of quartz peaks confirms good conversion extent of the main silica source for the reaction.

Fig. 3 compares the morphology of untreated bottom ash particles (sub-figures a and b) with those after conversion (sub-figures c and d). It is clear that after synthesis the appearance of

crystalline structure can be confirmed. Due to the stirred slurry reaction condition it appears the crystalline material forms porous particles upon precipitation.

Nitrogen adsorption testing was used to determine the pore size distribution and surface area of the untreated and converted bottom ashes. Fig. 4 presents the adsorption and desorption branches of the nitrogen adsorption isotherms. There is a substantial increase in nitrogen adsorption capacity after hydrothermal conversion, further confirming the formation of zeolitic-like crystalline structures, giving the material potential for heavy metal adsorption. The sorption isotherms can be classified as Type IV, with hysteresis loop Type H3 [37]. The hysteresis loop (i.e. disconnect between adsorption and desorption curves) at the relative pressure range $P/P_0 > 0.4$ is characteristic of materials with mesoporous structure, and the adsorption capacity at low relative pressure ($P/P_0 < 0.01$) indicates presence of micropores [38]. The manifestation of these two features for the treated bottom ash sample is evidence of significant presence of zeolitic material. The BET surface area of the bottom ash increased from $4.6 \text{ m}^2/\text{g}$ to $22.1 \text{ m}^2/\text{g}$ after zeolitization treatment. In comparison, the natural zeolite sample had a BET surface area of $31.6 \text{ m}^2/\text{g}$.

3.3. Metal Sorption Isotherms

Heavy metal adsorption onto zeolitic materials is best described by the Langmuir equation (1), where c is the solute concentration in solution (mmol/l); D is the solute uptake onto the sorbent (e.g. mmol/g); D_m is the empirically derived maximum sorption capacity (mmol/g); and k is an empirically derived constant (l/mmol).

$$D = \frac{D_m k c}{1 + k c} \quad (1)$$

As can be seen from Fig. 5, which shows modeling results performed with Visual MINTEQ for six heavy metal elements (including two As oxidation states), at the isotherm pH of 5.5, all heavy metals involved are soluble. Hence removal performance achieved herein can be dominantly attributed to adsorption mechanism rather than pH induced precipitation.

Fig. 6. shows adsorption isotherms for converted bottom ash and natural zeolite conducted with mono-element and multiple-element solutions. Experimental data were fitted by least

squares method to the Langmuir equation, and the Langmuir coefficients obtained are shown in Table 2. Sorption capacities (D_m) of the converted BA for Cd^{2+} , Pb^{2+} and Zn^{2+} are significantly higher (200-300%) than those for natural zeolite in the case of mono-element adsorption. Natural zeolite achieves higher As(V) sorption capacity. Converted BA sorption capacity is the highest for lead, followed by zinc, cadmium and arsenic.

In the case of multi-element adsorption, sorption capacity of the individual elements decreases, indicating competition for adsorption sites. Arsenic sorption capacity is the least affected, possibly due to it being an anionic species rather than a cationic species like the other three elements; in fact a higher capacity is estimated in the case of converted BA, the reason for which is unknown. Sorption capacity of the converted BA for the other three elements decreases by an average of 80%. Given that the multiple-element solutions contained higher amounts of Zn^{2+} and Cd^{2+} compared to Pb^{2+} , as they were prepared on an equal-mass (mg/l) rather than molar basis, the similar drops confirm a greater adsorption affinity for Pb^{2+} . Natural zeolite also sees similar decreases in capacity, except for a more moderate 20% decrease in zinc capacity. Nonetheless, the total sorption capacity for the three cationic heavy metals is still higher for the converted BA (0.185 mmol/g) compared to the natural zeolite (0.113 mmol/g).

3.4. Sorption Kinetics

The adsorption kinetics were observed by analyzing samples taken over time during isotherm sorption testing. Fig. 7 presents adsorption kinetics data of converted bottom ash for the four tested heavy metals. Solution concentrations over time are presented along with overall percent removal values. As indicated by the isotherms, adsorption extents of Cd^{2+} and Zn^{2+} are small (0-13%), with most of the solution concentration reduction taking place in the first 30 minutes. Lead adsorption reaches higher extents (54-83%), and is distributed over longer times. While the concentration of the highest dosage solution does not change significantly after the first 30 minutes, the more dilute solutions continue to see concentration reduction up to 120 hours. Behavior of arsenic is similar to that of lead, except for less adsorption extent of the more concentrated solutions (20-47%).

3.5. Sorption Performance in Sediment

3.5.1. Sediment Contamination Level

The sediment, once filtered and dried, was analyzed by semi-quantitative XRF to determine the chemical composition. Results are presented in Table 3. The matrix of the sediment is mainly composed of iron and siliceous compounds. The concentrations of zinc and cadmium are particularly high, though arsenic and lead are present in significant amounts as well.

The porewater of the sediment was analyzed by ICP-MS and AAS to determine the concentration of the heavy metals of interest in solution at equilibrium. Results are presented in Table 3 in ppb ($\mu\text{g/l}$) together with the solution pH. Similarly to the solid composition, zinc is present in solution at the largest amount, though in this case its concentration is roughly two orders of magnitude greater than cadmium. Arsenic and lead are present in significantly smaller, though still environmentally problematic, concentrations. Cobalt and nickel, though present in the sediment solids in significantly less quantities than arsenic and lead, are more abundant in solution; this can be explained by the solution pH being significantly lower than the precipitation pH of Co and Ni hydroxides as shown in Fig. 5 (approx. 7.5 and 7.0 respectively), and closer to that of Pb hydroxide (approx. 5.5-6.0). In the case of arsenic, it has been found that the sediment, made up of naturally formed hematite, magnetite and goethite, acts as a sorbent for arsenic at its natural pH [27], which explains the low arsenic porewater concentration and the high solid concentration. Given the natural pH of the sediment (5.2), which is significantly lower than the dissolution pH of As(III) ($\text{pH} > 7$), it can be expected that the dissolved As in porewater is mostly in the form of As(V). The porewater values serve as a basis for comparison of post-treatment equilibrium values to determine sorption efficiency of the zeolitic materials.

3.5.2. Sorbent Performance

Both sorbents (natural zeolite and converted bottom ash) were mixed with sediment at three sorbent-to-sediment ratios (25, 50 and 250 mg/g) in slurry (20 g sediment in 100ml porewater), and shaken for seven days to reach equilibrium. Filtered solutions were analyzed by ICP-MS and compared to porewater values (Table 3) to determine percentage removal of six heavy metals (As(V), Cd^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}). Final pH was measured to assess its influence on the results. Detailed results are presented in Fig. 8.

Natural zeolite was successful in fully attenuating arsenic and achieved nearly as high percent removal of lead, independent of mixture ratio. Removal of cobalt and nickel was proportional to sorbent addition amount, doubling for a ten-fold increase in sorbent concentration and reaching roughly 50% removal for both contaminants. Cadmium and zinc removal, the two contaminants present at by far the largest amounts in original porewater, was on a percentage basis less successful. Only with the largest sorbent dosage removals of 9% (Cd^{2+}) and 37% (Zn^{2+}) were reached. Final solution pH values were only marginally higher than the original porewater (5.2), varying between 5.3 and 5.5, signifying that heavy metal removal mechanism can be attributed solely to adsorption rather than pH-induced precipitation.

In comparison, the converted bottom ash had strikingly different, and mainly superior, performance. For five of the six contaminants (Cd^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) percent removals superior to 80%, and in many cases at or near 100% were achieved. In fact, such percentages were already reached with the intermediate sorbent dosage (50 mg/g). Increasing the dosage to 250 mg/g led to better removal results for Co^{2+} , Ni^{2+} and Zn^{2+} . However in the case of lead the removal percentage reduced at the highest dosage. Moreover, in the case of arsenic, increased leaching was observed, in proportion to the sorbent dosage, reaching nearly a four-fold increase of As in solution when 250 mg/g was used.

The negative As result can be directly attributed to the pH effect. At the highest converted BA dosage, the equilibrium pH was 7.8, which is a substantial increase from the original porewater. Based on the geochemical model already discussed (Fig. 5), it can be expected that As(III) begins to leach at pH over 7. Therefore the strong buffering effect of the converted BA, though suitable for attenuation of other heavy metals susceptible to precipitation at this pH range (in order: $\text{Pb}^{2+} \approx \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$; theoretical, based on the VM model), is detrimental to arsenic treatment. As such, the more moderate sorbent dosage of 50 mg/g would appear most suitable for eventual application of this material in the field. At this dosage the pH rises to 6.2, which though only contributing partially to precipitation of Pb^{2+} (according to the VM model), is not as favorable to As(III) leaching.

The high percentage removal figures of converted bottom ash at 50 mg/g and pH 6.2 can be attributed mainly to the adsorption performance of the synthesized zeolitic phases (SASH and tobermorite). It is likely that different zeolitic phases have different affinity and capacity for

different heavy metals. In fact, it appears clinoptilolite is most suitable for arsenic adsorption. Given the inaptitude of converted BA towards arsenic, a possible optimized sediment remediation route can include the combined use of converted BA with natural zeolite (or other natural, synthetic or waste-derived amendments). Extensive research has been conducted in this area by our group and will be presented in a following paper.

4. Conclusions

The zeolitic-type materials synthesized by hydrothermal conversion of MSWI-BA demonstrated promising sorption performance for the six heavy metal contaminants tested (As(V), Cd²⁺, Co²⁺, Ni²⁺, Pb²⁺, and Zn²⁺). The key findings of this study are:

- The synthesized zeolitic-type material consisted of a mixture of 41 wt% sodium aluminum silicate hydroxide (SASH) (Na₂O·Al₂O₃·1.68SiO₂·1.73H₂O) and 29 wt% tobermorite (Ca₅Si₆O₁₆(OH)₂·4H₂O).
- The conversion process significantly increased the BET surface area of MSWI-BA from 4.6 to 22.1 m²/g due to increased presence of micropores and mesopores.
- Sorption isotherms indicated higher affinity for Cd, Pb and Zn for converted MSWI-BA, while natural zeolite had good affinity for As.
- The sorption performance of converted MSWI-BA was generally superior to that of the natural zeolite for both synthetic heavy metal solutions and contaminated sediments. MSWI-BA achieved greater than 84% removal of Cd, Co, Ni, Pb and Zn from sediment porewater at 50 mg/g sorbent dosage; while natural zeolite proved efficient only for As and Pb.

Given the positive results found in this study, further work aims to optimize the performance of the converted BA for sediment remediation. The affinity of this material for heavy metals, its flexibility and low-cost, also open the possibility for its application in other industrial processes, including chemical and catalyst synthesis. In any case, the reutilization of MSWI bottom ash achieves the goal of reducing the burden of industry on its safe disposal and improves the sustainability of waste incineration technology.

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References

- [1] X. Querol, J.C. Umaña, F. Plana, A. Alastuey, A. Lopez-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, *Fuel* 80 (2001) 857-865.
- [2] C.A. Ríos R., C.D. Williams, C.L. Roberts, *Fuel* 88 (2009) 1403-1416.
- [3] N. Shigemoto, H. Hayashi, K. Miyaura, *J. Mater. Sci.* 28 (1993) 4781-4786.
- [4] C.-F. Wang, J.-S. Li, L.-J. Wang, X.-Y. Sun, *J. Hazard. Mater.* 155 (2008) 58-64.
- [5] M. Inada, H. Tsujimoto, Y. Eguchi, N. Enomoto, J. Hojo, *Fuel* 84 (2005) 1482-1486.
- [6] D. Wu, B. Zhang, L. Yan, H. Kong, X. Wang, *Int. J. Miner. Process.* 80 (2006) 266-272.
- [7] M. Balakrishnan, V.S. Batra, J.S.J. Hargreaves, I.D. Pulford, *Green Chem.* 13 (2011) 16-24.
- [8] B. Thomas, B.B. Das, S. Sugunan, *Microporous and Mesoporous Mater.* 95 (2006) 329-338.
- [9] P. Liu, Y. Yao, X. Zhang, J. Wang, *Chin. J. Chem. Eng.* 19 (2011) 278-284.
- [10] B.H. Bac, Y. Song, Y. Moon, M.H. Kim, I.M. Kang, *Waste Manage. Res.* 28 (2010) 714-722.
- [11] S. Dimović, I. Smičiklas, I. Plečaš, D. Antonović, M. Mitrić, *J. Hazard. Mater.* 60 (1998) 217-226.
- [12] C.-F. Lin, S.-S. Lo, H.-Y. Lin, Y. Lee, *J. Hazard. Mater.* 60 (1998) 217-226.
- [13] S. Shevade, R.G. Ford, *Water Res.* 38 (2004) 3197-3204.
- [14] F. Ruggieri, V. Marín, D. Gimeno, J.L. Fernandez-Turiel, M. García-Valles, L. Gutierrez, *Eng. Geol.* 101 (2008) 245-250.
- [15] R. Shawabkeh, A. Al-Harashsheh, M. Hami, A. Khlaifat, *Fuel* 83 (2004) 981-985.

- [16] W. Qiu, Y. Zheng, *Chem. Eng. J.* 145 (2009) 483-488.
- [17] M.R. Panuccio, A. Sorgonà, M. Rizzo, G. Cacco, *J. Environ. Manage.* 90 (2009) 364-374.
- [18] P.H. Jacobs, U. Förstner, *Water Res.* 33 (1999) 2083-2087.
- [19] J. Perić, M. Trgo, N.V. Medvidović, *Water Res.* 38 (2004) 1893-1899.
- [20] T. Van Gerven, D. Geysen, L. Stoffels, M. Jaspers, G. Wauters, C. Vandecasteele, *Waste Manage.* 25 (2005) 75-87.
- [21] Y. Wei, T. Shimaoka, A. Saffarzadeh, F. Takahashi, *J. Hazard. Mater.* 187 (2011) 534-543.
- [22] A. García-Sánchez, A. Alastuey, X. Querol, *Sci. Total Environ.* 242 (1999) 179-188.
- [23] Y. Wei, T. Shimaoka, A. Saffarzadeh, F. Takahashi, *J. Hazard. Mater.* 187 (2011) 534-543.
- [24] Y.-S. Lin, K.-S. Chen, Y.-C. Lin, C.-H. Hung, G.-P. Chang-Chien, *J. Hazard. Mater.* 154 (2008) 954-962.
- [25] T. Van Gerven, E. Van Keer, S. Arickx, M. Jaspers, G. Wauters, C. Vandecasteele, *Waste Manage.* 25 (2005) 291-300.
- [26] M. Ahmaruzzaman, *Prog. Energy Combust. Sci.* 36 (2010) 327-363.
- [27] J. Giménez, M. Martínez, J. de Pablo, M. Rovira, L. Duroc, *J. Hazard. Mater.* 141 (2007) 575-580.
- [28] M. Miyake, C. Tamura, M. Matsuda, *J. Am. Ceram. Soc.* 85 (2002) 1873-1875.
- [29] R.P. Penilla, A.G. Bustos, S.G. Elizalde, *J. Am. Ceram. Soc.* 86 (2003) 1527-1533.
- [30] R. Peña, A. Guerrero, S. Goñi, *J. Hazard. Mater.* B129 (2006) 151-157,
- [31] Z. Jing, F. Jin, N. Yamasaki, E.H. Ishida, *Ind. Eng. Chem. Res.* 46 (2007) 2657-2660.
- [32] M. Sallam, R.P. Carnahan, A. Zayed, S. Sunol, Recycling of Municipal Solid Waste Ash through an Innovative Technology to Produce Commercial Zeolite material of High Cation Exchange Capacity, in: *Proceedings of NAWTEC16 16th Annual North American Waste-to-Energy Conference, Philadelphia, USA, 19-21 May 2008*, pp. 73-79.
- [33] A.P. Bayuseno, W.W. Schmahl, *Waste Manage.* 30 (2010) 1509-1520.
- [34] A. Van Brecht, A. Konings, Innovative and BREF proven material recycling of MSWI bottom ashes, in: P.T. Jones, Y. Pontikes, J. Elsen, Ö. Cizer, L. Boehme, T. Van Gerven,

- D. Geysen, M. Guo, B. Blanpain (Eds.), Proceedings of the Second International Slag Valorisation Symposium, Leuven, Belgium, 18-20 April 2011, pp. 215-227.
- [35] Z. Jing, N. Matsuoka, F. Jin, T. Hashida, N. Yamasaki, *Waste Manage.* 27 (2007) 287–293.
- [36] T. Klamrassamee, P. Pavasant, N. Laosiripojana, *Eng. J.* 14 (2010) 37-44.
- [37] I. Majchrzak-Kuceba, W. Nowak, *Thermochim. Acta* 437 (2005) 67-74.
- [38] Q. Tan, X. Bao, T. Song, Y. Fan, G. Shi, B. Shen, C. Liu, X. Gao, *J. Catal* 251 (2007) 69-79.

List of Figures

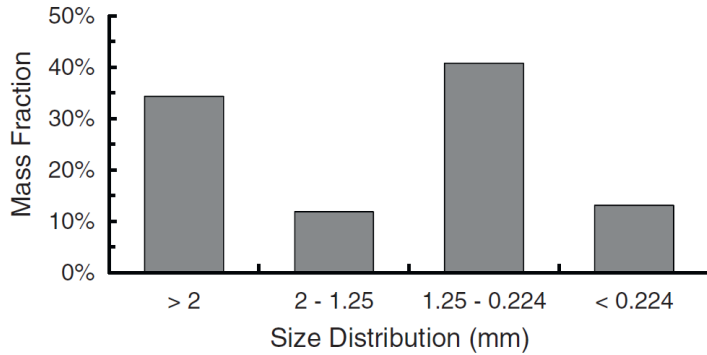


Fig. 1. Particle size distribution of fresh bottom ash determined by dry sieving.

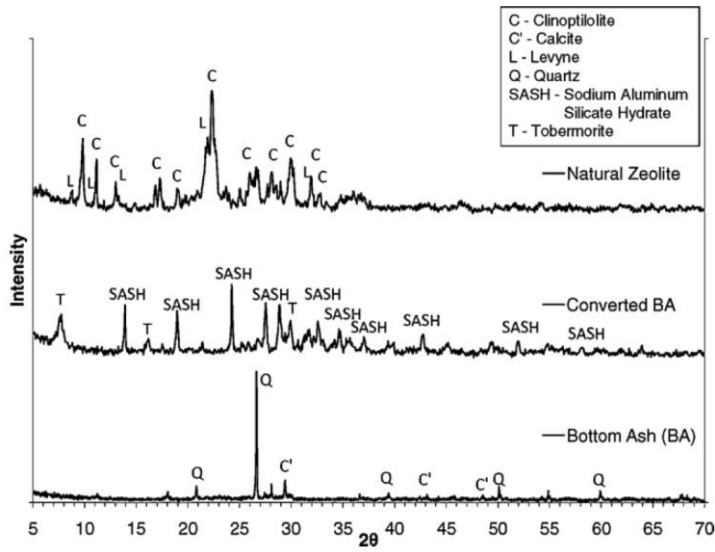


Fig. 2. Crystallographic composition of fresh bottom ash (bottom), converted bottom ash (middle), and natural zeolite (top) samples determined by XRD.

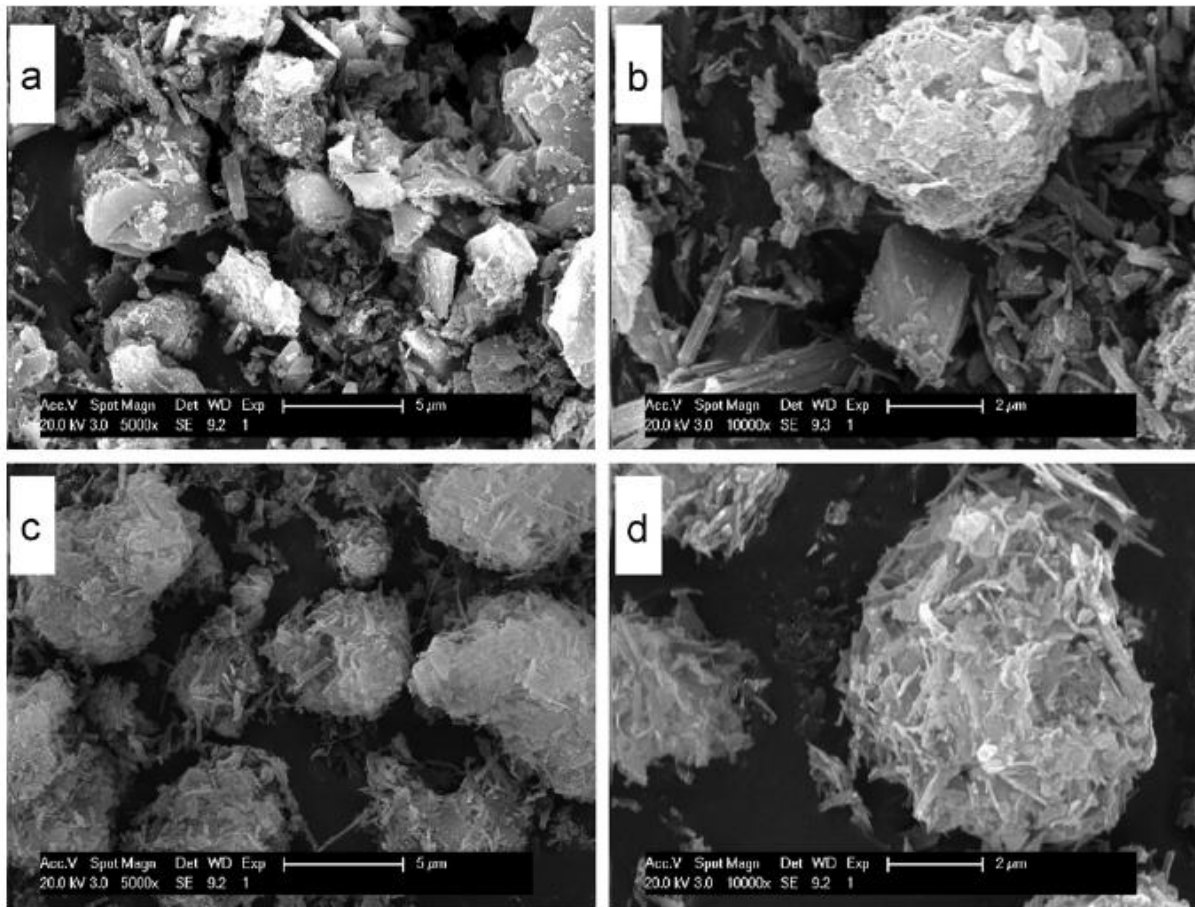


Fig. 3. Morphology of fresh bottom ash (a-b), and converted bottom ash (c-d) inspected by SEM.

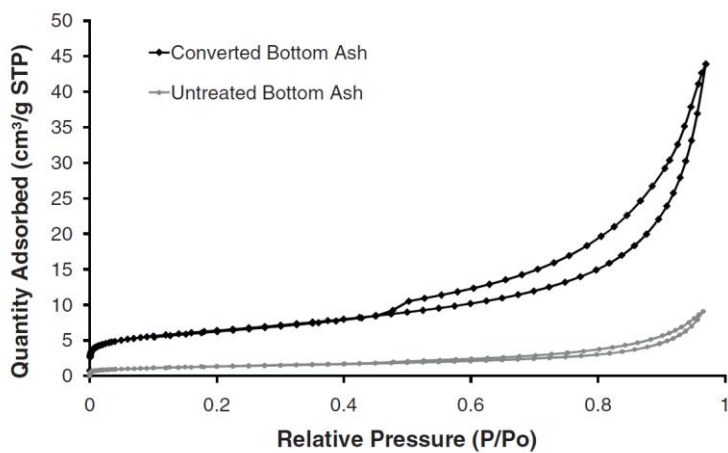


Fig. 4. Nitrogen adsorption/desorption isotherms of untreated and converted bottom ashes.

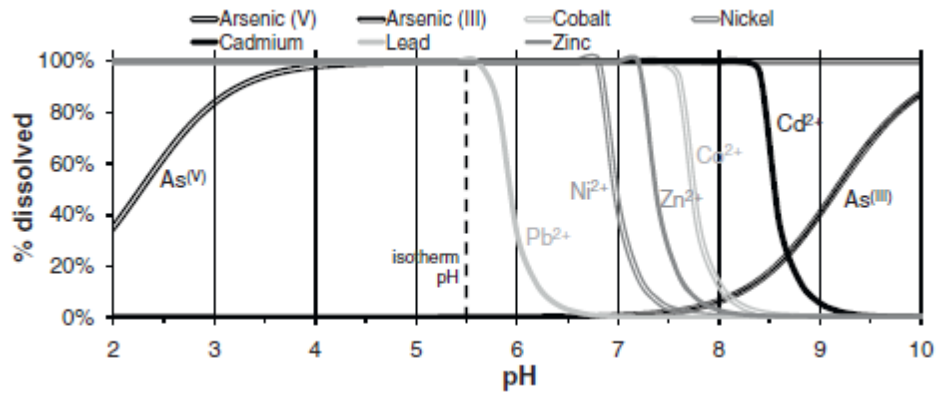


Fig. 5. Precipitation behavior of heavy metals (As (III,V), Cd^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) as a function of pH, determined by geochemical modeling (Visual MINTEQ).

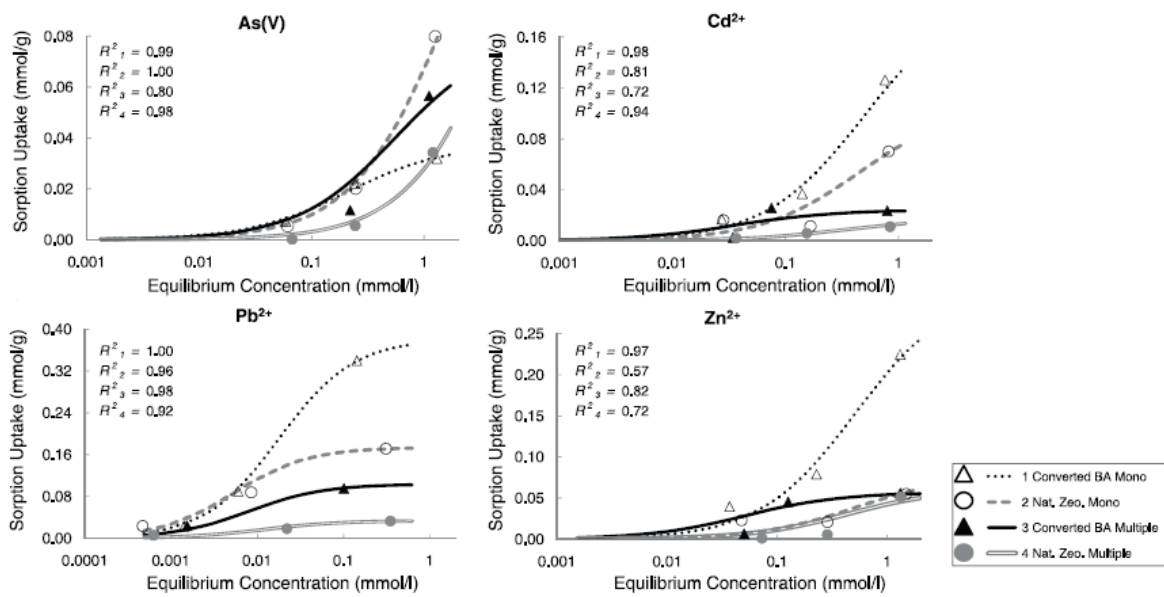


Fig. 6. Adsorption isotherms of converted bottom ash and natural zeolite for four heavy metals (As(V) , Cd^{2+} , Pb^{2+} , Zn^{2+}).

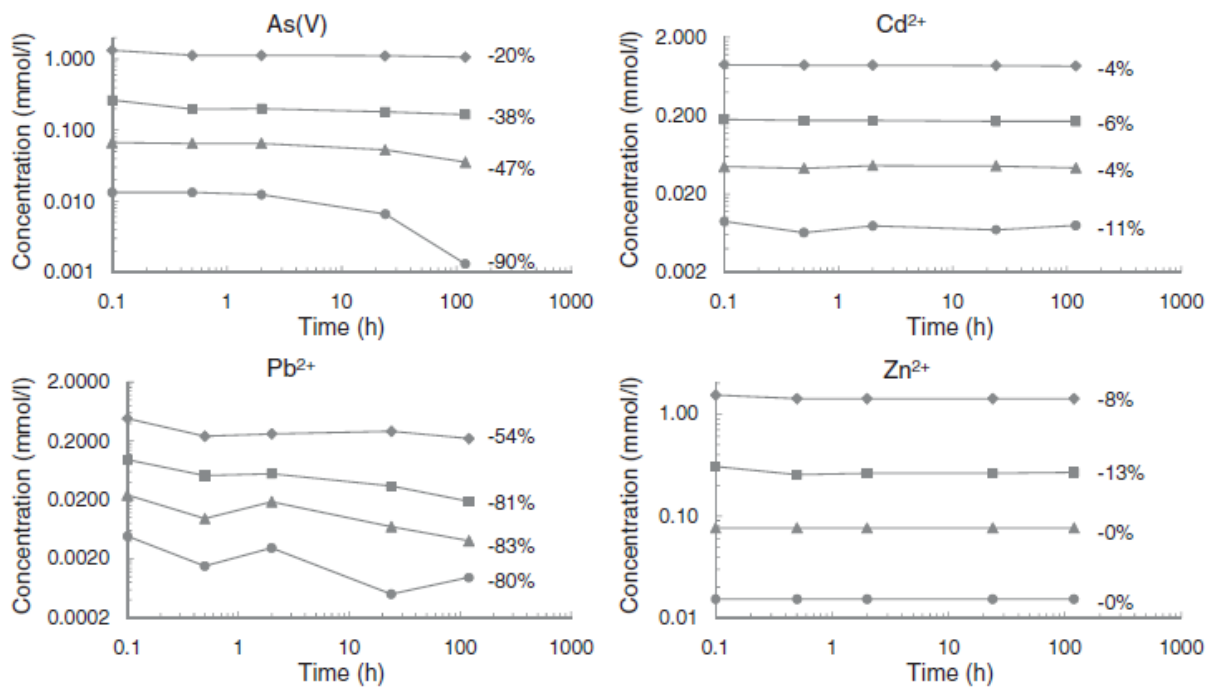


Fig. 7. Adsorption kinetics of converted bottom ash for four heavy metals (As(V), Cd²⁺, Pb²⁺, Zn²⁺) for different initial concentrations (100, 20, 5, 1 ppm); percent values indicate overall removal.

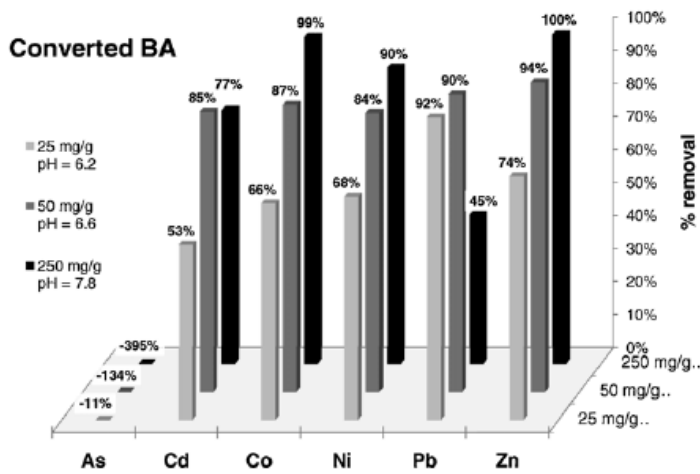
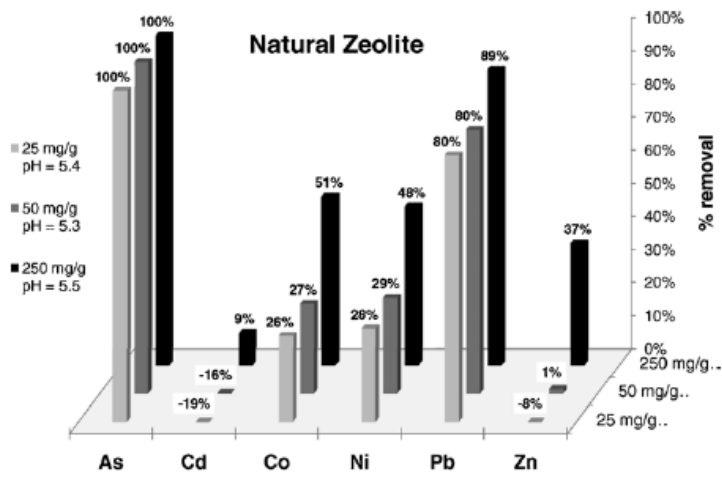


Fig. 8. Sediment remediation results expressed as percentage removal of heavy metals (As, Cd, Co, Ni, Pb, Zn) from porewater and equilibrium pH, for treatment with natural zeolite (top) and converted bottom ash (bottom) at three sorbent-to-sediment ratios (25, 50, 250 mg/g).

List of Tables

Table 1

Chemical composition of fresh bottom ash (< 2 mm) and natural zeolite determined by XRF.

Component	Bottom Ash (wt%)	Natural Zeolite (wt%)
Al₂O₃	8.3	12.4
BaO	0.5	0.1
CaO	40.9	3.0
Cr ₂ O ₃	0.2	-
CuO	0.4	-
Fe ₂ O ₃	8.9	1.8
K ₂ O	2.0	4.3
MgO	3.0	0.7
MnO	0.3	0.03
Na ₂ O	2.0	0.3
P ₂ O ₅	1.1	-
SiO₂	28.6	77.1
TiO ₂	3.0	0.2
ZnO	0.7	-

Table 2

Langmuir equation parameters of converted bottom ash and natural zeolite for four heavy metals (As(V), Cd²⁺, Pb²⁺, Zn²⁺).

	<i>D_m</i> (mmol/g)				<i>k</i>			
	As ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺	As ²⁺	Cd ²⁺	Pb ²⁺	Zn ²⁺
C.BA Mono	0.037	0.196	0.381	0.306	4.87	2.02	55.9	1.96
Nat.Zeo. Mono	0.187	0.107	0.174	0.076	0.56	2.25	186.5	1.96
C.BA Multiple	0.080	0.024	0.104	0.057	1.80	28.1	124	19.6
NZ Multiple	0.214	0.018	0.034	0.061	0.15	2.81	82.9	2.29

Table 3

Chemical composition of dry sediment (by XRF) and sediment porewater (by ICP-MS and AAS).

Sediment	As	Cd	Co	Ni	Pb	Zn
heavy metals						
(g/kg)	8.53	20.6	0.04	0.06	1.21	42.6
Sediment	Al	Fe	S	Si		
major elements						
(wt%)	4.5	30.1	5.2	11.7		
Porewater	As	Cd	Co	Ni	Pb	Zn
heavy metals	18	3.3	597	215	13	272
	($\mu\text{g/l}$)	(mg/l)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	($\mu\text{g/l}$)	(mg/l)
pH				5.2		