

Article

A Case Study of Landfill Leachate Using Coal Bottom Ash for the Removal of Cd^{2+} , Zn^{2+} and Ni^{2+}

Julia Ayala and Begoña Fernández *

Laboratorio de Metalurgia, Escuela de Minas Energía y Materiales, Universidad de Oviedo, Independencia 13, 33004 Oviedo, Spain; jayala@uniovi.es

* Correspondence: fernandezbegona@uniovi.es; Tel.: +34-98-5104235

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Abstract: The removal of Cd^{2+} , Zn^{2+} and Ni^{2+} by coal bottom ash has been investigated. In single metal system, metal uptake was studied in batch adsorption experiments as a function of pH (2–3), contact time (5–180 min), initial metal concentration (50–400 mg/L), adsorbent concentration (5–40 g/L), particle size, and ionic strength (0–1 M NaCl). Removal percentages of metals ions increased with increasing pH and dosage. Removal efficiency at lower concentrations was greater than at higher values. The maximum amount of metal ion adsorbed in milligrams per gram was 35.4, 35.1 and 34.6 mg/g for Zn^{2+} , Cd^{2+} and Ni^{2+} , respectively, starting out from an initial solution at pH 3. Simultaneous removal of Zn^{2+} , Cd^{2+} and Ni^{2+} ions from ternary systems was also investigated and compared with that from single systems. Cd^{2+} uptake was significantly affected by the presence of competing ions at pH 2. The results obtained in the tests with landfill leachate showed that bottom ash is effective in simultaneously removing several heavy metals such as Ni, Zn, Cd, As, Mn, Cu, Co, Se, Hg, Ag, and Pb.

Keywords: bottom ash; heavy metal; removal; landfill leachate; wastewater treatment

1. Introduction

Some industrial activities like mining, smelting and refining of non-ferrous metals, fertilizer industries, the manufacture of batteries, and paper industries discharge heavy metal wastewaters directly or indirectly into the environment. The presence of these metals has a potentially damaging effect on human and other biological systems because heavy metals are not biodegradable and tend to accumulate in living organisms [1].

The most widely used techniques for removing metal ions from wastewater include chemical precipitation, ion exchange, reverse osmosis and solvent extraction and adsorption [2–14]. Several studies have reported that significant amounts of heavy metals are removed from solution by adsorption on fly ash [15–29].

Coal bottom ash consists of heavy particles that fall to the bottom of coal power plants. According to the American Coal Ash Association (ACAA), the U.S. industry generated 14.4 million metric tons of bottom ash during 2013 [30].

Bottom ash properties are influenced by the design and type of power plant, the source and feed of fuels and by the type of coal and secondary fuels. The chemical composition of bottom ash is determined by the chemistry of the coal and the combustion process. Bottom ash is mainly composed of silica, alumina, and iron with small amounts of calcium, magnesium, sulfate, etc. The chemical composition of bottom ash is similar to that of fly ash, but typically contains greater quantities of carbon.

The properties of bottom ash are similar in form and composition to fine aggregates like sand and gravel, making them useful for applications in the construction industry. This by-product

is predominantly used for the following applications: road base and sub-base layers under rigid and flexible pavements, structural fill, backfill, aggregate for concrete, asphalt and masonry, abrasives, etc. [31–35]. Bottom ash is also often used as a sorbent for pollutants in synthetic water. However, few studies have been conducted using this by-product to remove Ni, Cd and Zn from real wastewaters [36–43].

According to Ecoba, about 2.4 million metric tons of bottom ash were used in the construction industry in Europe (EU 15) in 2008 Joint EURELECTRIC/ECOPA [44].

The aims of this study are to examine the removal of Zn^{2+} , Cd^{2+} and Ni^{2+} ions from an aqueous solution by bottom ash and to investigate the feasibility of using a low-cost treatment for the removal of heavy metals from landfill leachate. The removal of heavy metal ions by bottom ash was evaluated under various conditions such as pH, contact time, initial concentrations, particle sizes and bottom ash dosages. This paper also presents the results of the removal of Zn^{2+} , Cd^{2+} and Ni^{2+} from multicomponent solutions and landfill leachate.

An important environmental problem that arises in the landfills of abandoned mines is the leachates discharge that can contaminate soil and groundwater with heavy metals. Utilization of some industrial wastes, such as bottom ash, for the treatment of these wastes, entails many benefits in both economic and environmental terms. Materials used in this study come from local industries in northern Spain.

2. Materials and Methods

2.1. Materials

The coal bottom ash used in this research study comes from a power plant burning very low quality coal, mine tailings and biomass using a fluid bed technology.

This by-product was dried in an oven at 105 °C overnight before use. It was characterized by means of two different instrumental techniques: X-ray fluorescence (Phillips PW2404, Phillips, Eindhoven, The Netherlands) and X-ray diffraction analysis (Phillips PW1430 system with Cu $K\alpha$ radiation, Phillips, Eindhoven, The Netherlands). The diffractometer was operated at 45 kV and 40 mA, over the range of 2θ from 5° to 80°, with a detector speed of 1°/min.

The loss on ignition (LOI) was calculated by heating a pre-weighed dry sample to 900 °C for 3 h, using a gravimetric technique to analyze the sulfate content. The bottom ash was screened to give different particle sizes: >3.15 mm, 3.15–1 mm, 1–0.5 mm, 0.5–0.3 mm, 0.3–0.1 mm, and <0.1 mm. The real density of the waste was determined using the pycnometer method (UNE Standard 80105), employing water as the immersion liquid.

All the chemical solutions used in this study were prepared using deionized water and analytical grade chemicals. Stock solutions respectively containing 1000 mg/L of cadmium, nickel, and zinc were prepared by dissolving the metal sulfate in deionized water. Solutions with the desired metal concentrations were prepared by successive dilutions of the stock solution.

Landfill leachate was analyzed by Inductively Coupled Plasma (ICP) techniques, pH, redox potential and electrical conductivity. Preparing and analysis were in accordance with EN (European norms).

2.2. Leaching Test

There are numerous standard test methods [45]. The leachability of heavy metals from bottom ash was carried out by mixing bottom ash with deionized water ($W:V$ ratio = 1:10) and shaking (75 rpm) at room temperature for 180 min. The leachate was then filtered, the pH was measured, and metal concentrations were determined by atomic absorption spectroscopy. Two leachant solutions were used for the experiments: solution 1 was deionized water, while solution 2 was prepared by diluting 1 M H_2SO_4 with deionized water to achieve a pH of 2.

2.3. Batch Adsorption Experiments

Batch adsorption experiments were carried out by mechanically shaking series of bottles containing bottom ash samples and metallic solutions prepared in the laboratory. Twenty-five milliliters of the solutions was mixed with 0.25 g of bottom ash in polyethylene bottles, the samples were stirred at room temperature at 75 rpm, and the two phases were subsequently separated by centrifugation. The pH was measured and the concentrations of metal in the resulting supernatant were analyzed by atomic absorption spectroscopy. For each metal solution, one sample was reserved for analysis to determine the initial metal concentration.

The amount of metal removed was determined by mass balances according to the following equation:

$$\% \text{ Metal removal} = \frac{C_{\text{Initial}} - C_{\text{Final}}}{C_{\text{Initial}}} \times 100 \quad (1)$$

The amount of metal ion removed in milligrams per gram by bottom ash was calculated according to Equation (2).

$$q = \frac{(C_0 - C_e) \times V}{W_s} \quad (2)$$

where q is the amount of removed metal ion (mg/g), W_s the amount of bottom ash (g), C_0 and C_e the metal ion concentration (mg/L) before and after removal, respectively, and V the sample volume (L).

Different series of batch experiments were carried out to determine the influence of pH, contact time, initial metal concentration, adsorbent dosage, particle size, and ionic strength.

The effect of the initial pH of the solution on the adsorption process was analyzed using different solutions, adjusting the pH to between 2 and 6 with NaOH and H₂SO₄ to determine the optimum pH for maximum adsorption. The effect of the initial metal concentration was determined by varying the concentrations of Zn²⁺, Cd²⁺ and Ni²⁺ ions (50–400 mg/L). The effect of ionic strength and particle size on metals removal was studied using a solution with an initial concentration of 300 mg/L at different pH. Finally, the influence of the adsorbent dosage was determined using a solution with an initial concentration of 400 mg/L.

Industrial wastewater can contain several heavy metal ions that may interfere with one another. A series of trials were carried out to investigate the effect of other heavy metal ions on the removal of each metal. Finally, the effectiveness of bottom ash in removing heavy metals from landfill leachate was studied.

3. Results and Discussion

3.1. Characterization of the Bottom Ash Sample

The main components were Al₂O₃, SiO₂ and CaO with others at low concentrations. SiO₂ and Al₂O₃ contents make up about 79% of the bottom ash, while Fe₂O₃, CaO and K₂O comprise about 14%, the loss of ignition being 2.22%. However, the concentration of CaO in the finest fraction is much higher, around 37%, a small amount is associated with sulfur as calcium sulfate, and the other is a free oxide, Table 1.

Table 1. Chemical composition of the Bottom ash and <100 μm particle size.

Sample	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	TiO ₂ (%)	P ₂ O ₅ (%)	L.O.I. (%)	SO ₃ (%)
B. ash	54.1	24.1	6.0	0.06	1.56	4.11	0.58	4.05	0.92	0.13	2.22	2.4
<100 μm	20.8	10.6	3.4	0.05	0.86	36.9	0.31	1.58	0.40	0.06	9.84	15.2

Table 2 shows the distribution of the bottom ash sample and LOI by size. It can be seen that the major part (42.20%) falls within the 3.15–1 mm range. Loss on ignition was less than 1.3% for particles larger than 0.1 mm, increasing to 9.84% for the smaller fraction.

Table 2. Bottom ash particle size distribution and LOI.

Size (mm)	wt. %	LOI %
>3.15	14.01	1.3
3.15–1	42.20	1.15
1–0.5	13.23	1.16
0.5–0.3	8.90	1.12
0.3–0.1	17.50	0.92
<0.1	4.16	9.84

The real density value, 2.6489 g/cm³, was determined using the pycnometer method.

The XRD analysis of the bottom ash employed in this study is shown in Figure 1. The bottom ash was found to contain crystalline phases: Quartz (Q), Anhydrite (A), Muscovite (M), and Hematite (H).

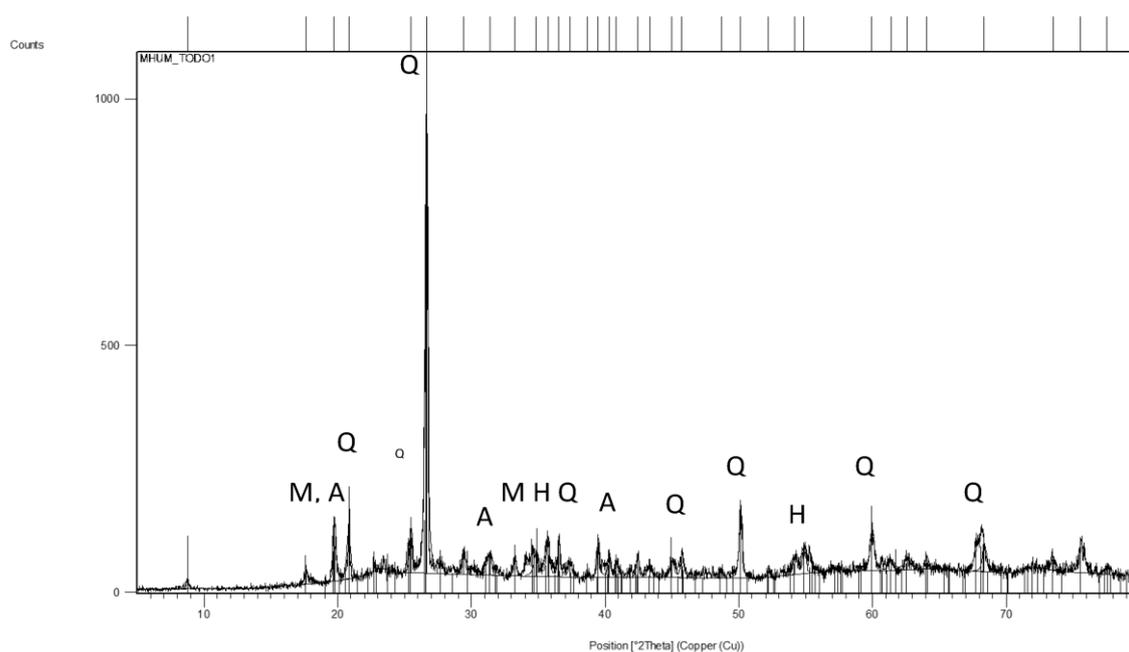


Figure 1. X-ray diffraction pattern of the bottom ash: M, Muscovite; A, Anhydrite; Q, Quartz; and H, Hematite.

3.2. Leaching Test

The chemical characteristics of the analyzed leachate samples are shown in Tables 3 and 4.

Table 3. Soluble concentration of some elements in water from Bottom ash.

Water Solution	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Ni mg/L	Cd mg/L	Zn mg/L	Cu mg/L	Mn mg/L	Fe mg/L	pH _{final}
Deionized	5.2	5.8	416	0.1	0.1	0	0–0.1	0.1	0.2	0	12.71
Deionized-pH-2	5.8	6.6	506	0.3	0.2	0	0.1	0.1	0.3	0.1	11.57

Table 4. Leachate analysis of different particle size.

Size (mm)	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	Ni mg/L	Cd mg/L	Zn mg/L	Cu mg/L	Mn mg/L	Fe mg/L	pH _{final}
>3.15	12.5	20.1	132	28.5	0.1	0–0.1	0.4	0.1	1.3	70	4.05
3.15–1	11.6	19	228	24	0.2	0	0.5	0.2	0.6	2.1	4.51
1–0.5	6.9	12.2	360	0.1	0–0.1	0	0	0–0.1	0	0	11.89
0.5–0.3	5.3	8.4	490	0.2	0.1	0	0	0	0	0	11.69
0.3–0.1	5.0	7.0	1160	0.1	0.1	0	0.1	0	0	0	12.52
<0.1	4.6	5.9	1500	0.1	0.1	0	0.1	0.1	0	0	12.98

The final pH value of the leachate was above 11.5; this can be attributed to the leaching of alkali metals, mainly calcium. The lime content of bottom ash neutralizes acidic solutions. The amounts of heavy metals leached from the bottom ash were relatively small.

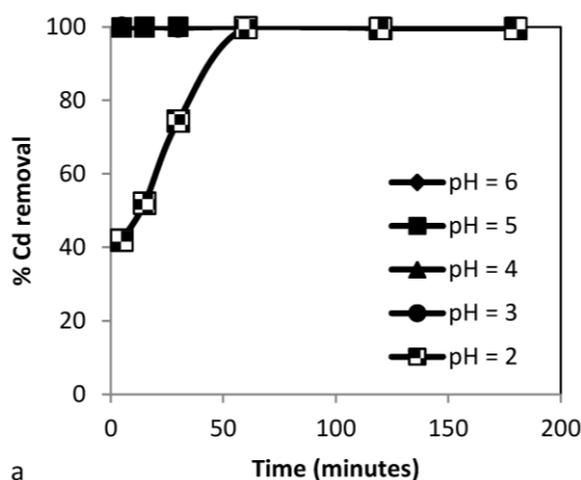
During the leaching test, the amount of Mn and Fe leached from the bottom ash decreased with decreasing particle size, whereas the amount of dissolved Ca increased. The leaching concentrations of heavy metals (Ni, Cd, Zn and Cu) are higher for coarser fractions. The final pH value of the leachate increased with decreasing particle size.

3.3. Batch Adsorption Experiments

3.3.1. Effect of pH

A series of experiments were carried out to examine the influence of initial pH on the removal of metal ions employing a 50 mg/L solution concentration and a bottom ash concentration of 10 g/L. The initial pH of the solutions was adjusted from 2 to 6 using H₂SO₄ and NaOH solutions.

The capacity of bottom ash to remove heavy metals was not significantly affected by increases in pH in the 3–6 range, Figure 2. Removal efficiency decreased as pH decreased below 3. The removal of Cd²⁺, Zn²⁺ and Ni²⁺ ions can be seen to start shortly after stirring commences and increases over time at pH 2. The removal of Cd²⁺ ions was found to be 42% in the first 5 min, reaching a value of 99.8% after about 60 min. Similar results were also obtained for Zn²⁺ and Ni²⁺ ions. A similar influence of pH has been previously reported for Zn²⁺ and Ni²⁺ adsorption onto fly ash [19,24,29].

**Figure 2.** Cont.

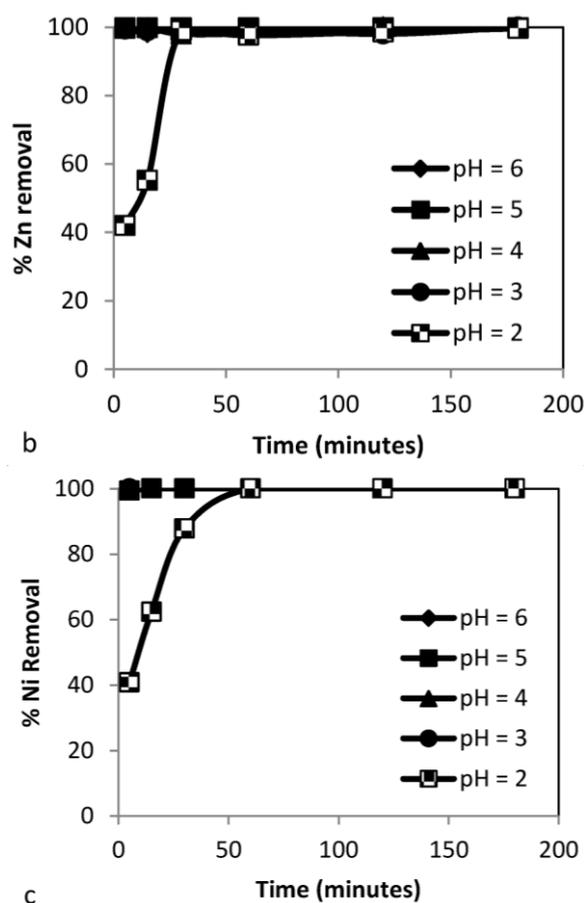


Figure 2. Metals removal by bottom ash as a function of time at different initial pH: (a) Cd; (b) Zn; and (c) Ni.

The final pH of the solution after the removal of heavy metals was found to differ significantly from the initial pH. The difference between the initial and final pH of the sample depended on the stirring time and initial pH. Thus, for tests performed at $\text{pH}_{\text{initial}} 2$, the solutions showed a pH_{final} (6.3–7.3) after 5 min of stirring depending on the metal being removed. The pH_{final} value was between 10 and 12 in all cases after 180 min of reaction time. The high pH value is attributed to the leaching of alkalis. In the previously performed leaching test (Table 3), a high calcium content (506 mg/L) was observed in the leachate. This is due to the dissolution of CaO according to Equation (3).



The dissolution of CaO contributes to increasing the pH of the solution. At these pH values, a higher degree of precipitation of metal ions can be expected, thereby enhancing removal.

The same effect has been reported by other authors. For instance, Erol et al. [46] investigated the capacity of fly ash to remove Cu^{2+} and Pb^{2+} finding it to be directly proportional to the CaO content, as the dissolution of oxides such CaO and MgO contribute to increasing in solution pH. Gitari et al. [28] reported the importance of precipitation reactions in this process in elements such as Mn, Al, Zn and Cu. Bayat [24] found that fly ash with a high soluble calcium oxide content is more effective than fly ash with a low CaO content at equilibrium conditions for removing Ni^{2+} , Cu^{2+} and Zn^{2+} metals due to the formation of Ca and Si complexes such as calcium silicates ($2\text{CaO} \cdot \text{SiO}_2$).

In very acidic solutions (pH 2) and with a short stirring time (5–30 min), the removal is performed by adsorption, since the final pH is around 8.4. For greater stirring time or solutions with higher initial pH values (3–6), the removal is by precipitation, as in these cases final pH value is over 10.

The removal mechanism for heavy metals by bottom ash may include both adsorption and precipitation reactions.

3.3.2. Effect of the Initial Concentration

The removal experiments were carried out in the 50–400 mg/L heavy metal concentration range employing an adsorbent concentration of 10 g/L at pH 2 and 3.

It was found that the amount of metal ions uptake by bottom ash increased with time (Figure 3). The results indicate that removal was nearly 100% for almost all the initial concentrations at pH 3. For initial concentrations of 400 mg/L, the removal efficiency was respectively 88.5%, 87.8% and 86.5% after 180 min for Zn²⁺, Cd²⁺ and Ni²⁺. The maximum amount of metal ion adsorbed in milligrams per gram was 35.4, 35.1 and 34.6 mg/g for Zn²⁺, Cd²⁺ and Ni²⁺, respectively, at pH 3.

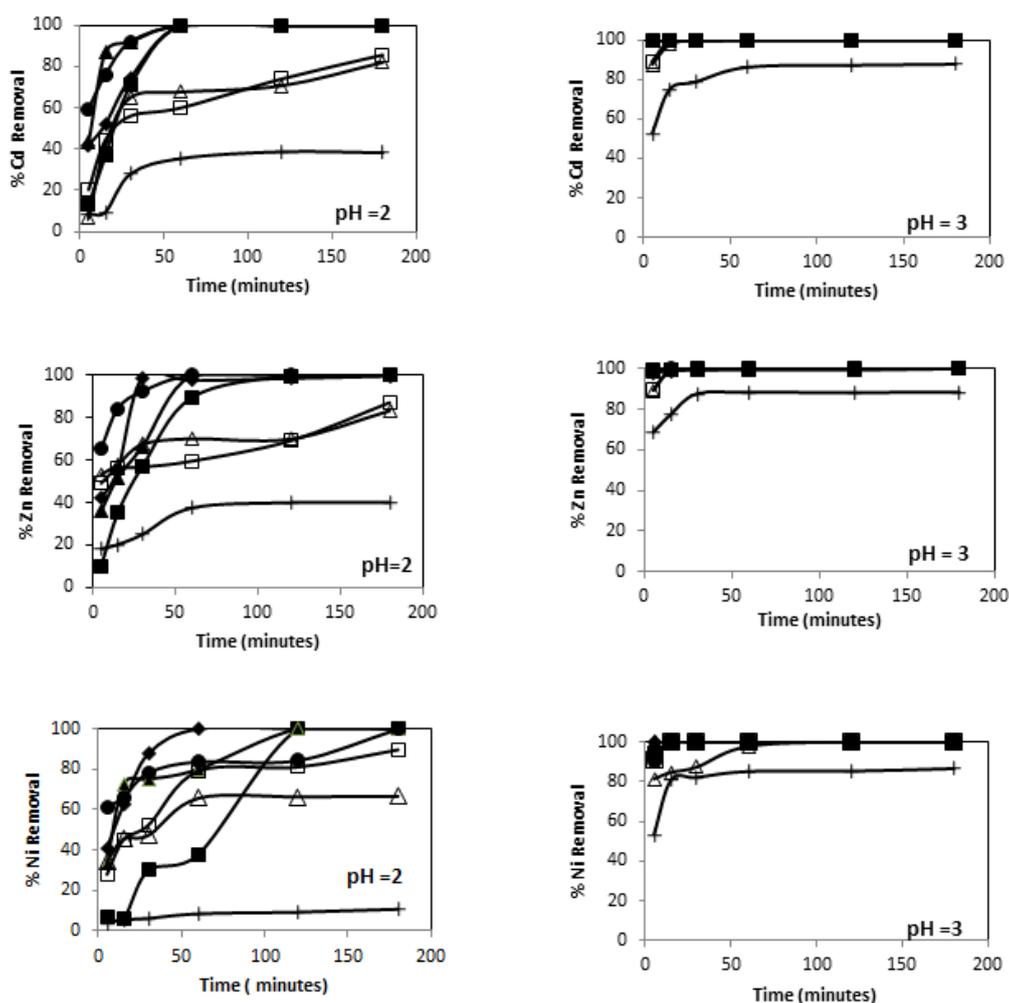


Figure 3. Removal of Zn, Cd, and Ni by bottom ash as a function of initial concentrations at different initial pH: ◆ 50 mg/L; ■ 100 mg/L; ▲ 150 mg/L; ● 200 mg/L; □ 250 mg/L; △ 300 mg/L; and † 400 mg/L.

The results indicate that the percentage of heavy metal removal at pH 2 decreases with increasing initial concentration during the first minutes of stirring. In trials with an initial concentration of 400 mg/L, metal removal after 180 min was 38.3%, 40% and 10.8% for Cd, Zn and Ni ions, respectively.

The bottom ash used in this study is much more effective in removing Zn, Cd than the bottom ash used by Sukpreabprom et al. and V. Asokbunyarat et al. [42,43]. These authors reported that

the amount of metal ion adsorbed in milligrams per gram was just over 12, 10 mg/g of Zn and Cd respectively and 4.3 mg/g of Cd.

Effectiveness of removal of the bottom ash used in this study, compared to those cited above, is due to its higher final pH which facilitates precipitation of heavy metals.

Experimental results show that this bottom ash has a similar capacity to remove Cd and Zn ions and has less ability to remove Ni ions in solutions at the pH studied in this paper.

Bayat [22,24] found that the adsorption capacity of the high-calcium Turkish fly ash for metal ions followed the order: $Cd^{2+} > Zn^{2+} > Ni^{2+}$; Mohan et al. [20] reported that the uptake behavior of fly ash for heavy metal cations follows the order: $Cd^{2+} > Zn^{2+}$; and, for Cetin (19), $Zn^{2+} > Ni^{2+}$. However, the adsorption studies carried out by M. Visa et al. [27] to estimate heavy metal removal from wastewater using activated fly ash showed that the efficiency follows the order: $Pb^{2+} > Zn^{2+} \geq Cd^{2+}$, while Ricou et al. [47] studied the removal of heavy metals by fly ash and a mix of fly ash/lime, reporting the order: $Ni^{2+} > Zn^{2+} > Cd^{2+}$.

3.3.3. Effect of Dosage

The effect dosage was studied by shaking 400 mg/L solution with different doses of bottom ash, ranging from (5–40 g/L), for 180 min at pH 2 and 3.

It was observed that the percentage of metal removal gradually increased as the dose of adsorbent increased from 5 to 40 g/L (Figure 4). The uptake from Zn^{2+} , Cd^{2+} and Ni^{2+} solutions was 67.5%, 47.5% and 54.7%, respectively, at an adsorbent concentration of 5 g/L, increasing to 100% at 20 g/L when the initial solutions had a pH of 3. In the case of a solution with pH 2, when the adsorbent concentration increased from 5 to 40 mg/L, the loading capacity of bottom ash increased from 22.8% to 96.3% for Zn^{2+} , from 10.8% to 92.8% for Cd^{2+} , and from 5.6% to 73.5% for Ni^{2+} .

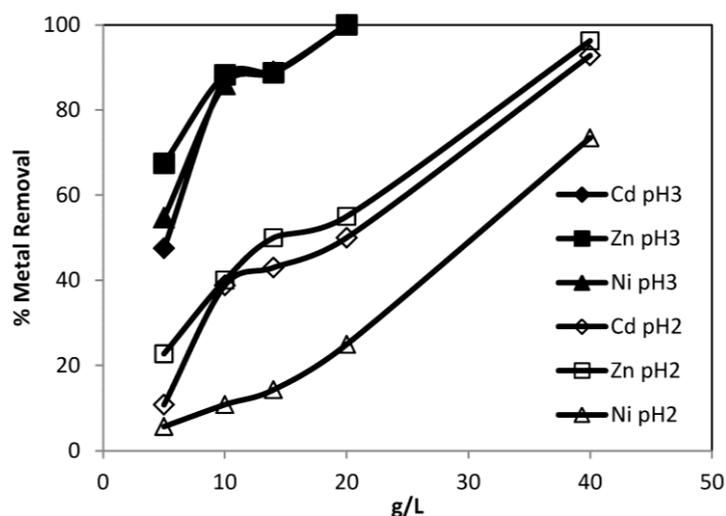


Figure 4. Effect of Bottom ash dosage on the removal of heavy metals.

3.3.4. Effect of Ionic Strength

The effect of ionic strength on metal removal was studied employing a heavy metal concentration of 300 mg/L, varying the background electrolyte of the solution (0–1 M NaCl) with an adsorbent concentration of 10 g/L at pH 2 and 3.

In the tests performed with solutions at pH 3, it was found that the presence of different concentrations of NaCl did not decrease the effectiveness in removing heavy metals. At pH 2, however, the results indicate that small amounts of NaCl (0.01 to 0.1 M) decreased the removal of heavy metals, while increasing NaCl to 1 M enhanced the amount of metal removed (Figure 5).

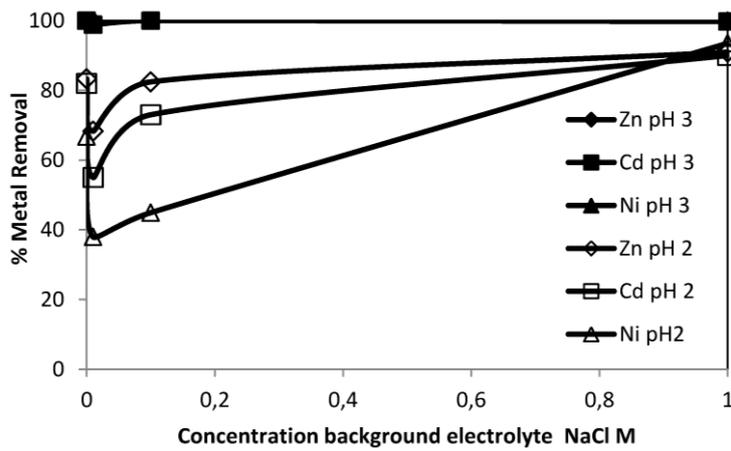


Figure 5. Effect of ionic strength on the removal of Zn, Cd and Ni.

3.3.5. Effect of Particle Size

A series of experiments were carried out to examine the effect of particle size employing a solution concentration of 300 mg/L and a bottom ash concentration of 10 g/L (Figure 6).

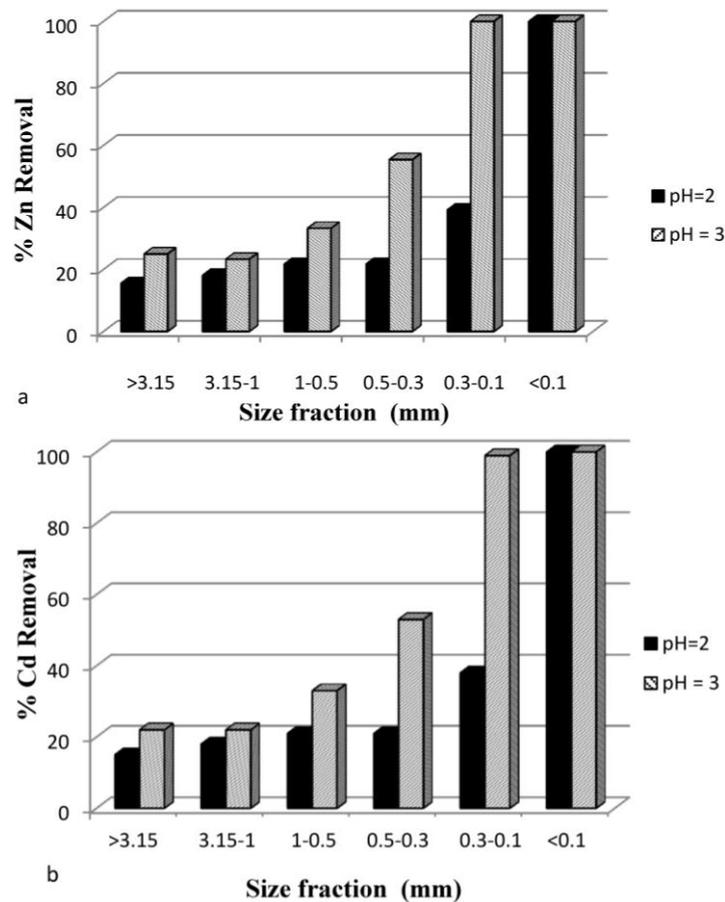


Figure 6. Cont.

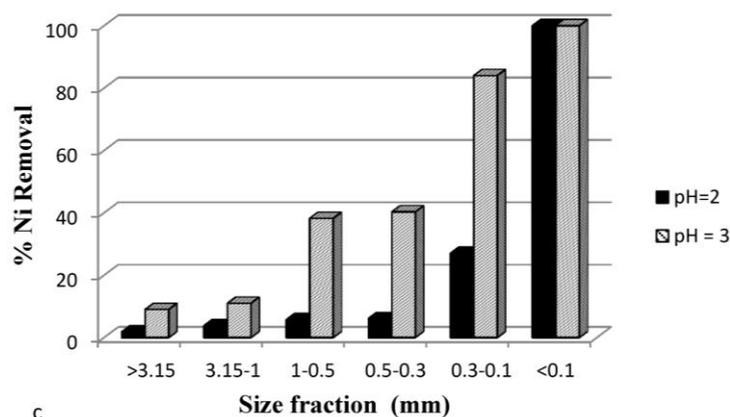


Figure 6. Metal removal by bottom ash as a function of particle size at different initial pH: (a) Zn; (b) Cd; and (c) Ni.

It is clear from the results that the uptake of heavy metal ions increased with decreasing bottom ash particle size. Cd^{2+} removal efficiency increased from 22% and 15% to 100% for an initial solution at pH 3 and pH 2, respectively, as the particle sizes decreased from >3.15 mm to <0.1 mm. The smallest particle size afforded the greatest uptake of heavy metal ions, removal efficiency being 100% for all metals.

The leaching test (Table 4) shows the concentrations of soluble metals and the final pH obtained. Few alkali metals were dissolved in the coarsest fraction. However, the finest fraction had a high lime content, 1500 mg/L of dissolved Ca, leading to a higher pH_{final} and precipitation of metal ions.

In coal power plants, coals are combusted along with ground limestone to enhance its specific surface area as much as possible for gas desulfurization. For this reason, the CaO content in the bottom ash increases as the particle size decreases [48].

Heavy metals removal can be achieved by precipitation and/or adsorption. On the one hand, as particle size decreases, effective surface area and the adsorption capacity increase. On the other hand, it has been observed that, as the particle size decreases, the final pH of the solution increases, increasing the removal efficiency by precipitation (Table 4 and Figure 6).

Others researchers working with different adsorbents have reported that heavy metal removal efficiency increased with fine particle size because of the increase in the effective contact area of the adsorbent and adsorbate [36,49]. In the present study, it should also be borne in mind that the finest fraction had much higher lime content, 36.9%, which promotes precipitation by increasing the pH of the solution (Table 1).

3.3.6. Multi-Component Systems

Industrial wastewater can contain several heavy metal ions. A series of trials were performed to investigate how the presence of other metal ions affected the removal of one particular metal ion.

Ternary systems (Cd–Ni–Zn) with 100 ppm of each metal at pH 2 and pH 3 were used in the multi-component systems trials (Table 5).

In the tests performed with solutions at pH 3, it was found that the presence of other metal ions did not significantly affect the removal of heavy metals due to the precipitation process. More reaction time was needed to complete the total removal of Cd. The results of multi-component removal from ternary mixtures at pH 2 showed a substantial decrease in Cd removal compared to that of a single solution containing an equal concentration. The elements Ni and Zn showed lower sensitivity to the presence of other metals. A similar result has been found by other researchers [17,29,50,51].

Table 5. Comparison of single and multi-component removal of Cd²⁺, Ni²⁺, and Zn²⁺ by bottom ash.

Time (min)	pH _i	pH _f	% R _{Cd}			% R _{Ni}			% R _{Zn}			% R Total
			100 mg/L	300 mg/L	Multi	100 mg/L	300 mg/L	Multi	100 mg/L	300 mg/L	Multi	
5	3	6.67	99.8	87.7	45.6	94.3	81.3	89.1	99.5	89.3	100	78.23
15	3	6.93	100	97.7	60.6	100	84.7	95.9	99.7	99.3	100	85.5
30	3	7.98	100	99.8	73.2	100	87.3	98.9	99.7	100	100	90.7
60	3	9.62	100	100	88.7	100	97.7	99.7	99.8	100	100	96.13
120	3	10.71	100	100	99.9	100	100	99.8	99.8	100	100	99.9
180	3	11.32	100	100	100	100	100	99.9	100	100	100	99.97
5	2	6.83	11	6.7	11.7	6.8	34.7	17.9	30	53.3	35	21.53
15	2	6.88	34.7	42	11.2	6	45.5	20.4	40	58	38	23.2
30	2	7.04	60.8	65	14.5	30.2	47.3	25.5	60	67.5	48	29.33
60	2	7.04	90	67.6	16.6	37.9	65.7	34.9	89.6	70.1	53	34.83
120	2	7.07	100	70	21.1	100	66.3	35.9	99.8	70	68.6	41.87
180	2	7.27	100	82	27.6	100	66.7	56.9	100	83.3	92	58.83

At pH 2 and initial concentrations of 100 mg/L and 300 mg/L for a single component, Cd²⁺ removal was found to be 100% and 82%, respectively, after 180 min. The final solutions reached high pH values; hence, there is a high degree of precipitation. However, with initial concentrations of 100 mg/L Cd²⁺ + 100 mg/L Ni²⁺ + 100 mg/L Zn²⁺, Cd removal was only 11.7% and the pH_{final} was 6.83, the influence of precipitation being lower.

In the case of Zn at pH 2 for a single component, the removal efficiency was 100% and 83.3% for an initial concentration of 100 mg/L and 300 mg/L Zn²⁺, respectively, and 92% in the multi-component solution.

Comparing the removal of metals in single and multi-component systems for an initial concentration of 300 mg/L, a very low removal value (58.8%) was obtained after 180 min in the trial with the multi-component system, mainly due to Cd.

Total removal was calculated as:

$$\% \text{ Removal}_{\text{Total}} = \frac{27.6 \text{ mg/L Cd}^{2+} + 56.9 \text{ mg/L Ni}^{2+} + 92 \text{ mg/L Zn}^{2+}}{300 \text{ mg/L}} \times 100 = 58.8\%$$

The interpretation of the multi-component systems may be a function of one or all of the following parameters: ionic radii, electronegativity, system pH, and the availability of active sites on the adsorbent. Metals that have smaller ionic radius can be adsorbed onto a fixed surface area of adsorbent more quickly. Metal ions that are more electronegative can be more strongly attracted to the surface. The acidity of the solution affects the speciation of ions and the surface properties of the adsorbents [52–55].

3.3.7. Treatment of Industrial Wastewater

The wastewater used in this study was taken from the landfill leachate of a company located in northern Spain and analyzed for various physico-chemical characteristics and heavy metal concentrations. The pH (5) and redox potential (358 mV) were determined using a PH2002 meter (Crison[®], Barcelona, Spain) and electrical conductivity (501 μS/cm) using an EC-Meter Basic 30 device (Crison[®]).

Metal concentrations in the leachate were analyzed by Inductively Coupled Plasma (ICP) techniques (Table 6.) The leachate contained significant amounts of heavy metals such as Ni, Zn, Cd, As in addition to lower amounts of Pb, Cu, Se, Mn, Mo, Cr and Hg.

The removal experiments were carried out at different reaction times using an adsorbent concentration of 10 g/L, the mixtures being stirred at 75 rpm. The concentrations of heavy metals in the resulting supernatant were analyzed by atomic absorption spectroscopy (Table 7). Removal efficiencies were close 100% in the first 15 min of contact time. These results were expected, as the leachate had a pH 5 before treatment with bottom ash.

Table 6. Metal concentrations analyzed by ICP of untreated leachate and leachate treated with bottom ash during 15 min.

Element	Major Component (ppm)		Element	Minor Component (ppb)	
	Untreated	Treated		Untreated	Treated
Ni	17.4	0.003	Mn	9.23	0.3
Zn	14.8	0.003	Cu	41.5	5.9
Cd	47.5	0.006	Co	0.45	0.07
As	5.9	0.002	Se	5.5	1.2
Na	10.37	12.79	Hg	4	0.34
Mg	0.9	0.95	Ag	17.2	0.2
K	10.7	11.84	Pb	1.9	1.47
Ca	51.04	207.5	U	0.04	0
			Tl	0.04	0.02
			Fe	0.67	1.14
			Sb	28	9
			B	20	25
			Al	460	9
			Ti	0.06	0.33
			V	1	1
			Cr	11	8
			Mo	3.4	4.7
			Sr	171	629
			Sn	0.06	0.17
			Ba	8	38

Table 7. Percentage of heavy metals removal from landfill leachate treated with bottom ash.

Time (min)	% Cd Removal	% Ni Removal	% Zn Removal
5	61.54	54.4	91.45
15	99.99	99.98	99.98
30	100	100	100
60	100	100	100
120	100	100	100
180	100	100	100

Leachate treated with bottom ash for 15 min was also analyzed by ICP in order to determine the effect of the treatment on other elements present in the landfill leachate (Table 6). After only 15 min of contact time between the bottom ash and leachate, the concentrations of other metals such as As, Mn, Cu, Co, Se, Hg, Ag, and Pb were also seen to decrease. However, the concentrations of Ca, Na, Mg and K increased. Gitari et al. [28] found similar results when treating acid mine drainage with fly ash.

4. Conclusions

Bottom ash can be employed for the removal of Cd^{2+} , Zn^{2+} and Ni^{2+} from wastewater.

Heavy metals are rapidly removed by bottom ash. Removal increases with increasing pH, reaching almost 100% removal of Cd, Ni and Zn ions at pH 3 for nearly all initial concentrations. For an initial concentration of 400 mg/L at pH 3, the removal efficiency was 88.5%, 87.8% and 86.5% after 180 min for Zn^{2+} , Cd^{2+} and Ni^{2+} , respectively.

The percentage of metal removal gradually increases as the dose of adsorbent increases from 5 to 40 g/L in the case of a solution with pH 2, increasing from 22.8% to 96.3% for Zn^{2+} , from 10.8% to 92.8% for Cd^{2+} , and from 5.6% to 73.5% for Ni^{2+} .

The smallest particle size showed the highest uptake rate of metal ions due to the fact that the finest fraction had a high content of CaO.

The main mechanisms involved in the removal of heavy metal ions were adsorption at the surface of the bottom ash and precipitation.

The lime content of the bottom ash seems to be an important parameter governing the use of this waste as an adsorbent, neutralizing agent for acidic wastewater or for the immobilization of heavy metals in a solid matrix.

In multi-component systems at pH 3, the presence of other metals does not significantly affect the removal of heavy metals due to the fact that the high final pH reached induces a precipitation reaction. However, the removal of Cd at pH 2 decreased due to the presence of other ions.

Bottom ash is effective in simultaneously removing various heavy metals such as Ni, Zn, Cd, As, Mn, Cu, Co, Se, Hg, Ag, and Pb from industrial wastewater.

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