Removal of Heavy Metals from Aqueous Solution Using Fly Ash: Çan Thermal Power Plant, NW Turkey as a Case Study

**Abstract**

This study was conducted to investigate use of fly ash created by fluidized bed combustion Çan Thermal Power Plant for the removal of heavy metals from aqueous solutions as a low-cost adsorbent. The adsorption capacity of metal ions (Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn) from aqueous solution onto coal fly ash was studied in batch experiments, which were carried out at room temperature to investigate the efficiency of the adsorbent for removing selected metals. The highest adsorption capacities of fly ash were determined for Cu and Cd metals, with values of 67.29% and 53.66%, respectively. The following metal removal capacity of fly ash was determined: Cu > Cd > Pb > Zn > Cr > Co > Mn > Ni. The ash originating from coal combustion thermal power plant may be considered a viable adsorbent for metal ions from aqueous solutions at neutral pH conditions and with small amounts of fly ash.

**Keywords:** Adsorption, Aqueous solution, Can thermal power plant, Fly ash

**1. Introduction**

The increasing demand for energy has resulted in construction of many coal-fired power plants in different parts of the World (Cokca 2001). These power plants usually create large quantities of by-products, which if strategies for safe disposal or beneficial use are not developed, can be very harmful (Cokca 2001). Disposal of a growing amount of waste from thermal power plants such as fly and bottom ash creates environmental problems. Fly ash contains several toxic elements, which can leach out and contaminate soils, as well as water resources, and this contamination can lead to health and land-use problems (Deborah and Ernest 1981, Gehrs et al. 1981, Inyang 1992, Fernandez-Turiel et al. 1994, Georgakopoulos et al. 1994, 2002, Laumakis et al. 1996, McMurphy et al. 1996, Kamon et al. 2000, Mandal and Sengupta 2002, Baba 2003, Baba et al. 2003, Bilski et al. 2013). In Turkey, about 20 billion tons of coal was burned in coal-fired power plants between 1970 and 2013 (Osmanlioglu 2014). From this, about 2 billion tons of coal combustion products were produced, including about 150 million tons of fly ash (Osmanlioglu 2014). Annually, in Turkey 1% of fly ash is utilized in the cement and brick industry (Celik et al. 2008). Most fly ash is stored without taking chemical properties into consideration.

Water contamination by heavy metals has received attention in recent years (Azzam and Lambarki 2004). But, a matter of concern is the removal of heavy metals using a low-cost...
adsorbent. The potential of fly ash use in water treatment processes is obvious as it can be obtained at low-cost in large quantities and can be used both as an adsorbent and as a neutralization agent (Weng and Huang 2004). Fly ash has potential use in water treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area (Cetin and Pehlivan, 2007, Banerjee et al. 2014). Many studies have been performed on the metal adsorption of fly ash from aqueous solution previously reported by Lin and Chang 2001, Bayat 2002, Erol et al. 2005, Alinnor 2007, Tofan et al. 2008, Luo et al. 2011, Naiya and Das 2016. This study was conducted to investigate the use of fly ash created by a coal combustion thermal power plant for the removal of some selected metal ions from aqueous solutions as a low-cost adsorbent. For this purpose, fly ash samples were collected from fluidized bed combustion Can Thermal Power Plant (CTPP).

CTPP is located in the province of Canakkale within Can Coal Basin, NW Turkey (Figure 1). Low calorific value (i.e. 1500-4500 kcal/kg, average around 2000 kcal/kg) and high sulfur content (i.e, an average of about 6%) coal (Gunduz and Baba 2008) is being extracted by General Directorate of Turkish Lignite (TKI in Turkish abbreviation), as well as a number of private mining companies. Mining areas include Can, Comakli, Etili, Yayakoy and Yeniceri, and total coal reserves are over 100 Mt in the Can Coal Basin (Bozcu et al. 2008). Coals are consumed for domestic heating and as feed in the coal-fired CTPP in operation since 2005 and the first power plant in Turkey utilizing fluidized bed combustion technology (Baba et al. 2008). CTPP has two units with a total energy generation capacity of 2x160 MW, is designed to operate using local coals with an average of 2400 kcal/kg calorific value and the annual average coal requirement of the plant is 1.82 million tons (Baba et al. 2010). The annual production capacity of this power plant is 2.25 billion kWh, which is used to supply energy to the Northern Aegean, Thrace and Marmara regions (Baba et al. 2008). Nowadays, CTPP production capacity can contribute approximately 1% of Turkish electricity production.

The ash disposal site for CTPP is about 1 km NE of the plant, with ash carried to the area by closed-lid conveyors. Every year approximately 453440 tons of fly ash is produced by the CTPP (Ozmen 2011). According to satellite images from March 2007, the ash disposal site covered about 22 hectares (Figure 2a), with this site calculated to have increased to 72 hectares on satellite images from 2013 August (Figure 2b). This areal increase of the ash disposal site indicates a significant risk for environmental health.

2. Material and Methods

2.1. Fly Ash

Chemical composition of fly ash samples were determined by inductively coupled-plasma mass spectrometry (ICP-MS, PerkinElmer SCIEX-ELAN 9000) at ACME Labs, Canada. X-ray diffraction (XRD) analysis of fly ash samples was performed by using Philips PW 1830 at the General Directorate of Mineral Research and Exploration Analysis Laboratories in Ankara. The structure and morphology of fly ash was scanned with scanning electron microscopy (SEM, FEI Philips XL30 sFEG, Oregon) coupled with energy dispersive X-ray spectrometry (EDX) to determine surface features and local chemical contents at the Center for Material Science in Izmir Institute of Technology.

2.2. Batch Adsorption Experiments

The fly ash samples were dried in an oven (105 °C) overnight before batch experiments were conducted. Fly ash samples were mixed with ultra-pure water in conical flask to obtain fly ash slurry. The pH of the slurry was adjusted to the desired value of pH 7 with 0.1 M HCl. The slurry was agitated with an orbital shaker at 25 ± 2 °C until the pH of the solution stabilized to 7. Then in order to complete adsorption experiments 100 ppm concentration of Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn synthetic solutions (100 ml) were combined with 1 g/L ash dose (dry weight) and mixed in a orbital shaker (constant speed of 145 rpm) at room temperature for 24 hours. All chemicals used were of analytical reagent grade and were obtained from Merck, Germany. The fly ash particles were separated from suspension by filtration through a 0.45 µm membrane filter. The residual concentration of the metal ions in the supernatant was determined by ICP-MS in ACME Analytical Laboratories in Canada. The amount of metal ions adsorbed by fly ash was calculated as the difference between the initial and residual concentration of the metal ions. The reported value of all metal ions adsorbed by fly ash in each test was repeated at least three times.

3. Results

3.1. Characterization of Fly Ash

The mineralogical, physical and chemical properties of fly ash depend on the nature of the parent coal, conditions of combustion, type of emission control devices and storage
and handling methods (Shreya and Paul 2012). According to the XRD analyses, mineralogical composition of fly ashes includes anhydrite, quartz, hematite, cristobalite, lime, calcite, feldspar and magnetite. The chemical composition of the fly ash from the CTPP contained 58.54% SiO₂+Al₂O₃+Fe₂O₃ and CaO was 21.51% (Table 1). According to the American Society for Testing Materials (ASTM 2008) the ash is classified as “C class fly ashes”, which have high calcareous and pozzolanic characteristics. The contents of As, Ba, Co, Cu, Ni, Pb, Sr, Zn and Zr in fly ash are 445.20, 305, 21.90, 32.10, 15.30, 27.50, 358.10, 67 and 135.70, respectively.

The size and shape of the fly ash particles were scanned with SEM images shown in Figure 3a-d. Generally, fly ash particles have an irregular, porous and rarely spherical microscopic structure. Particles of fluidized bed combustion fly ash are very irregular in shape because of the combustion temperature. The EDX analysis results show that the major
constituents of irregular fly ash particles are O (63.1 wt.%), Ca (12.5 wt.%), Si (9.2 wt.%), C (8.3 wt.%), Al (4.3 wt.) and S (2.4 wt.%). On the other hand, McCrone and Delly (1973) and Weng and Huang (2004) stated that extended exposure time during combustion renders the particle more spherical in shape or crystal in form. During combustion, calcium oxide forms from the decomposition of carbonate minerals and combines with sulfur dioxide to form anhydrite

Table 1. Chemical composition of CTPP fly ash.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>wt. %</th>
<th>Constituent</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>32.24</td>
<td>As</td>
<td>445.20</td>
</tr>
<tr>
<td>CaO</td>
<td>21.51</td>
<td>Sr</td>
<td>358.10</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.73</td>
<td>Ba</td>
<td>305.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.57</td>
<td>Zr</td>
<td>135.70</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.21</td>
<td>Zn</td>
<td>67.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.97</td>
<td>Cu</td>
<td>32.10</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.67</td>
<td>Pb</td>
<td>27.50</td>
</tr>
<tr>
<td>MgO</td>
<td>0.55</td>
<td>Co</td>
<td>21.90</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.33</td>
<td>Ni</td>
<td>15.30</td>
</tr>
<tr>
<td>MnO</td>
<td>0.11</td>
<td>Mo</td>
<td>8.50</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.005</td>
<td>Se</td>
<td>1.20</td>
</tr>
<tr>
<td>LOI</td>
<td>5.10</td>
<td>Sb</td>
<td>0.60</td>
</tr>
<tr>
<td>Sum</td>
<td>88.99</td>
<td>Cd</td>
<td>0.30</td>
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</table>

Figure 3. Selected SEM images of fly ash
A) irregularly shaped, B) spherical particle, C) anhydrite, D) iron oxide (Fe 36.81%, O 55.83%).
4. Discussion

The abundance of sulfur minerals especially pyrite in Can Basin coals presents some environmental and human health concerns (Sanliyuksel Yucel and Baba 2013). Acid mine drainage/lakes with low pH (<3) and high metal and sulfate concentrations which formed around abandoned coal mines in Can Coal Basin transport long distances by local streams, create a great risk in terms of environmental quality (Okumusoglu and Gunduz 2013, Sanliyuksel Yucel et al. 2014, 2016, Sanliyuksel Yucel and Yucel 2016, Yucel and Turan 2016). Several studies have been performed on using fly ash to prevent acid mine drainage generation by Stouraiti et al. 2002, Xenidis et al. 2002, Gitari et al. 2006, 2008a, b, 2010, Perez-Lopez et al. 2007a, b, Yeheyis et al. 2009, Bäckström and Sartz 2011, Sahoo et al. 2013 and Qureshi et al. 2016. CTPP fly ash is a strong alkali material, which has a pH of 12.40 when added to ultra-pure water (1:2 solid:solution ratio) at the end of 24 hour. The alkaline nature of CTPP fly ash makes it a good neutralizing agent. Because the carbon has micro-porous form, high carbon content of fly ash increase the removal efficiency of metal ions from aqueous solution. Future work should be treatment of acid mine drainage/lakes is the filtration of water near mining lakes through buffering and neutralizing fly ash from the CTPP.

5. Conclusions

Nowadays, it is important to develop new areas of utilization for fly ash as a low-cost adsorbent which is produced in large quantities from coal combustion in thermal power plants. Increasing concerns about the environmental consequences of fly ash disposal have led to investigations regarding other possible areas of utilization. In this study, fly ash was used for the removal of some selected metal ions from aqueous solutions by adsorption has been intensively studied. The ash originating from CTPP may be considered a viable adsorbent for heavy metal ions (especially Cu and Cd) from aqueous solutions.

Table 2. Metal removal from aqueous solution using fly ash, %.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Ni</th>
<th>Mn</th>
<th>Co</th>
<th>Cr</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
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<tbody>
<tr>
<td>1st</td>
<td>11.35</td>
<td>18.15</td>
<td>20.17</td>
<td>25.70</td>
<td>28.92</td>
<td>35.24</td>
<td>53.76</td>
<td>67.33</td>
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<tr>
<td>2nd</td>
<td>12.18</td>
<td>17.60</td>
<td>18.07</td>
<td>23.14</td>
<td>27.72</td>
<td>36.92</td>
<td>55.21</td>
<td>65.61</td>
</tr>
<tr>
<td>3rd</td>
<td>12.79</td>
<td>15.21</td>
<td>21.68</td>
<td>23.50</td>
<td>29.65</td>
<td>34.10</td>
<td>52.01</td>
<td>68.95</td>
</tr>
<tr>
<td>Mean</td>
<td>12.10</td>
<td>16.98</td>
<td>19.97</td>
<td>24.11</td>
<td>28.76</td>
<td>35.42</td>
<td>53.66</td>
<td>67.29</td>
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<tr>
<td>SD</td>
<td>0.72</td>
<td>1.56</td>
<td>1.81</td>
<td>1.38</td>
<td>0.97</td>
<td>1.41</td>
<td>1.60</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Figure 4. Removal of heavy metals from aqueous solution using fly ash.
aqueous solutions at neutral pH conditions and using small amounts of ash. The fly ash with high calcium content in CTPP was found to be a metal adsorbent; therefore, there may be a good prospect for the use of fly ash for adsorption of heavy metals in practical applications.

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7. References


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