ADSORPTION OF METAL IONS FROM AQUEOUS SOLUTION BY USING FLY ASH AS A LOW-COST ADSORBENT: CASE STUDY CAN THERMAL POWER PLANT, NW TURKEY

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ABSTRACT

Metals like cadmium (Cd), chrome (Cr), lead (Pb) and zinc (Zn) in the aquatic environment are a matter of major concern as they are extremely toxic to aquatic life and human beings. These metals accumulate in the food chain and can be persistent in nature. Therefore, it is necessary to remove toxic metals from waste. The potential of solid waste from coal combustion thermal power plant for use as adsorbent for the removal of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn ions from aqueous solutions has been thoroughly investigated. The adsorption characteristics of these heavy metals by the solid waste from Can Thermal Power Plant (CTPP), which is the first power plant utilizing fluidized bed combustor technology (2x160 MW) in Turkey, was examined. The results show that the particle size and surface area of the ash are the most important factors affecting the extent of metal removal. The order of adsorption capacity of fly ash was determined as follows: Cu> Cd> Pb> Zn> Cr> Co> Ni> Mn. Bottom ash and slag, which have bigger particle sizes, have the ability to remove heavy metals and they also show similar behavior to fly ash. The ash resulting from burning to create energy of a thermal power plant may be considered a reasonable adsorbent for metal ions in diluted aqueous solutions and suggest that ash adsorption is a progression towards a prospective method especially at acid mine sites.

Keywords: Adsorption, bottom ash, fly ash, metal, slag

1. Introduction

The increasing demand for energy has resulted in construction of many coal-fired power plants in different parts of the world. But these power plants (Cokca, 2001) usually create large quantities of by-products, which if strategies for safe disposal or beneficial use are not made, can be very harmful. Disposal of a growing amount of waste from thermal power plants such as fly and bottom ash creates environmental problems due to the leachability of their metal contents. Fly and bottom ash originating from coal combustion in thermal power plants contains several toxic elements, which can leach out and contaminate soils as well as surface and ground water. The contamination can lead to health and land-use problems (Baba, 2003; Baba *et al*., 2003; Deborah and Ernest, 1981; Georgakopoulos *et al*., 1994; Georgakopoulos *et al*., 2002; Inyang, 1992).

The amount of metals released into the environment has increased continuously as a result of industrial activities (electroplating, metal finishing and metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, etc.) and technological development (Tofan *et al*., 2008).

Removal of metals from contaminated aquatic systems is deemed important for the protection of environmental health (Weng and Huang, 2004). Conventional technologies for the removal of metals are chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis and bio-sorption and emulsion per traction technology (Tiravanti *et al*., 1997; Zhou *et al*., 1993). Numerous approaches have been made to develop cheaper and cost effective techniques which can remove metals from waste. However, adsorption is by far the most versatile and an effective method for removal of metal if combined with appropriate regeneration steps (Naiya *et al*., 2009). Generally, the adsorption process can have many advantages over chemical precipitation; it can better meet strict effluent discharge standards, allow metal recovery, and generate less sludge. Adsorbents such as activated carbon and oxides generally have high metal adsorption capacities, but they are generally expensive (Weng *et al*., 2001). With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of metals from waste waters (Weng and Huang, 1994). The application of low-cost adsorbents such as scrap rubber, peat, corn-cob, coconut shell, bituminous coal, sludge ash, activated sludge, fly ash, and wood fines has been demonstrated to be effective in removing heavy metals from waste water (Tofan *et al*., 2008; Weng *et al*., 2001; Weng, 2002).

In Turkey, about 20 billion tonnes of lignite were burned in lignite-fired power plants between 1970 and 2013. From this, about 2 billion tonnes of lignite combustion products were produced, including about 150 million tonnes 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 has been stored without taking into consideration engineering properties. Therefore, fly ash has affected the ecosystem but this waste can be used to remove toxic metals. Toxic metals have received attention in recent years, especially in Turkey. But, a matter of concern is the removal of toxic metals using a low-cost adsorbent. In this study, an attempt has been made to investigate the use of fly ash, bottom ash and slag from a coal combustion thermal power plant for the removal of toxic metals from aqueous solutions. For this purpose, ash samples were collected from Can Thermal Power Plant.

2. Study area

The Can basin has been in operation since 1980s and low calorific value and high sulfur content (mean 6%) lignites of the area are being extracted by General Directorate of Turkish Lignites (TKI in Turkish abbreviation) as well as a number of private mining companies. In the Can basin total coal reserves are over 100 Mt (Baba *et al*., 2008) and are consumed for domestic heating and as feed coals in the coal-fired Can Thermal Power Plant (CTPP). CTPP, in operation since 2005, is located southwest of Kulfal village, approximately 12 km west of the county of Can of Canakkale province in northwest Turkey (Figure 1).

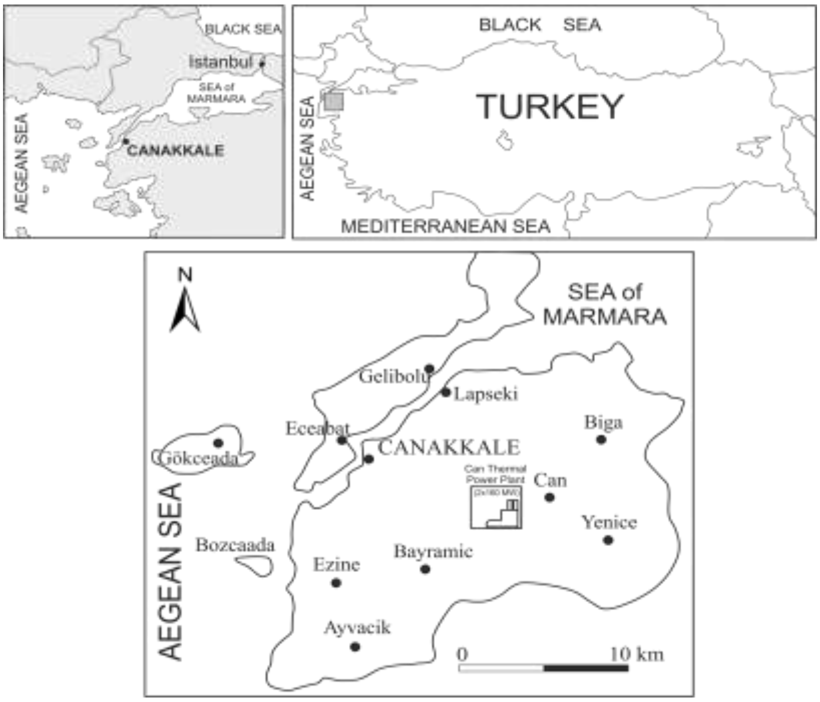

Figure 1: Location map of the study area

CTPP is the first power plant in Turkey utilizing fluidized bed combustion technology. The thermal power plant has two units with a total energy generation capacity of 2x160 MW and is designed to operate on local lignites with an average of 2400 kcal/kg calorific value. The annual average lignite requirement of the plant is 1.82 million tons. 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 1.5-2.5% of Turkish electricity production. At the CTPP approximately 5000 tons of coal is burnt and approximately 1500 tons of fly ash is produced every day. This power plant currently produces almost half a million tons of fly ash per year.

3. Geological background

The study area, Can lignite basin, is of Early-Middle Miocene-age and is located in the northwest of Anatolia, to the north of the Kazdag Horst in the Biga Peninsula which consists of mainly volcano-clastics, fluviatile and lacustrine clastic sediments (Gurdal and Bozcu, 2011). During early to middle Miocene, the Can basin unconformably overlay the Oligocene-aged Can volcanics. The sediments of the Can lignite basin are composed of bituminous shale and claystone with intercalated lignite, sandstone, siltstone and tuff. Within the sequence of the Can formation, the lignite levels are commonly overlain by dark green or greenish colored well-laminated claystone. This claystone level contains rich organic matter and can be assumed to be a key horizon/reference layer in the field. In the basin, one main coal seam is mined which has a thickness ranging from 17 to 35 m and is contained within this claystone horizon. This organo-sedimentary level is interpreted as a low-energy lacustrine or lake-shore/swamp depositional environment. Depositional characteristics, lithological content and sedimentary structures of the Can formation indicate a change from a fluvial to a lacustrine depositional environment. The basin resembles a caldera developed by volcanic and tectonic activities (Gurdal and Bozcu, 2011).

Results of XRD analyses indicate that in general, major mineral contents of Can basin coals are clay minerals, gypsum, pyrite, quartz and mica/illite (Sanliyuksel Yucel, 2013). The moisture and ash content (as received basis) of the Can basin coals vary between 8.76-32.56 and 2.46-41.19 wt. %, respectively. The presence of high sulfur content (max: 14.36) may be attributed to the peat environment and regional volcanic activity (tuff deposits are interbedded in the coal-bearing sequences) as well as to alkaline depositional environments with intensive sulfide mineralization. The results of sulfur form show that the sulfur contents are mainly of organic and pyritic sulfur (Gurdal and Bozcu, 2011).

4. Materials and methods

The solid waste (fly ash, slag and bottom ash) samples from CTPP were taken in March and May 2012. The ash samples were dried at 105 °C for two hours then ground and sieved to a particle size of 1000 µm before tests were conducted. Ultra pure water (TKA GenPure) was used for washing and adsorption processes. $CoCl_2 . 6H_2O$ (Merck), $CuCl_2 . 2H_2O$ (Aldrich), $NiCl_2 . 6H_2O$ (Merck), $PbCl_2$ (Aldrich), $CrCl_3 . 6H_2O$ (Merck), $MnCl_2 . 4H_2O$ (Aldrich), $CdCl_2$ (Aldrich), and $ZnCl_2$ (Aldrich) salts with analytical purity were used as metal sources. The Memmert universal oven model UF55 was used for drying and the Sartorius CPA analytical balance was used for weighing.

In order to complete adsorption experiments of the ashes for Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn metals, 100 ml and 100 ppm of solution with 1 gram of ash sample was taken and mixed in the magnetic mixer at room temperature for 2 hours. At the end of the duration, the upper sides of the solutions were sampled. After sampling, they were filtered at 0.2 µm and analyzed with inductively coupled plasma-mass spectroscopy (ICP-MS) in ACME Analytical Laboratories in Canada.

5. Results and discussions

5.1. Characterization of fly ash

Chemical composition of fly ash varies depending on the quality of parent coal source and the operating conditions of the thermal power station. The chemical composition of the fly ash from the CTPP contained less than 70% SiO_2 +Al_2O_3 (%)+Fe_2O_3 (%) values (average 53.30%) and CaO (%) was more than 10% (on average 22%). 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 experimental results of XRD analysis on CTPP fly ash samples are: hematite, calcite, anhydrite, quartz and cristobalite (Ozay *et al*., 2005).

Generally, fly ash particles have a characteristic spherical and rarely irregular and porous microscopic structure. As the molten droplets of inorganic coal residues cool down, fly ash particles solidify and separate out as spheres, while solidifying around trapped hollow gas bubbles. On the other hand, particles of fluidized bed combustion fly ash were very irregular in shape because of the combustion temperature. During combustion, calcium oxide forms from the decomposition of carbonate minerals and combines with sulfur dioxide to form anhydrite. The occurrence of hematite results from oxidation of pyrite in the combustion units.

5.2. Adsorption characteristics of fly ash

There is a high positive linear correlation (> 0.90) between adsorption of metals and ashes. The fly ash originating from coal combustion in CTPP may be considered a reasonable sorbent for Cu and Cd ions from diluted aqueous solutions. The retention percentages increased rapidly to 49.75% for Cd and 63.71% for Cu with the initial pH =7 (Figure 2). The results show that the particle size and surface area of the ash are the most important factors affecting the extent of metal removal. The following adsorption capacity of fly ash was determined: Cu> Cd> Pb> Zn> Cr> Co> Ni> Mn. Bottom ash and slag, which have bigger particle sizes, also have the ability to remove heavy metals and show similar behavior to fly ash.

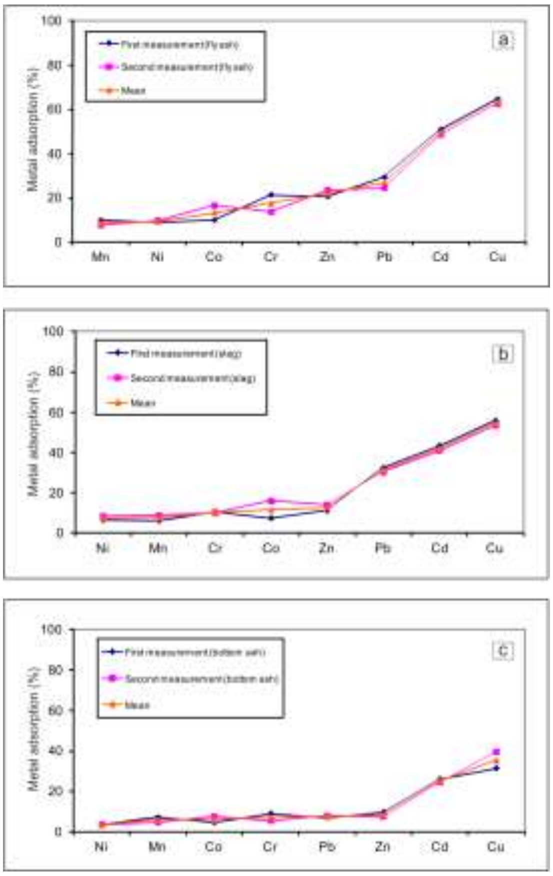

Figure 2: Metal removal from aqueous solution **a)**. fly ash, **b)**. slag, **c)**. bottom ash

6. Conclusions

Today, it is important to develop new areas of utilization for fly ash which is produced in large quantities as a result of 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, the adsorption of dissolved metals by different kind of ashes has been determined. The ash originating from CTPP may be considered a viable sorbent for metal ions (Cu, Cd, Pb and Zn) from diluted aqueous solutions. The fly ash with high calcium content in CTPP was found to be a metal adsorbent as effective as activated carbon and, therefore, there are good prospects for the adsorption of toxic metals by fly ash in practical applications.

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