

Comparison Study on Characterization of Various Fly Ashes for Heavy Metal Adsorption

E. Moroydor Derun, N. Tugrul, N. Baran Acarali, A. S. Kipcak, S. Piskin

Abstract—Fly ash is a waste material of coal firing thermal plants that is released from thermal power plants. It was defined as very fine particles that are drifted upward which are taken up by the flue gases. The emerging amount of fly ash in the world is approximately 600 million tons per year. In our country, it is expected that will be occurred 50 million tons of waste ash per year until 2020. The fly ashes can be evaluated by using as adsorbent material. The purpose of this study is to investigate the possibility of use of various fly ashes (Tuncbilek, Catalagzi, Orhaneli) like low-cost adsorbents for heavy metal adsorption. First of all, fly ashes were characterized. For this purpose; analyses such as XRD, XRF, SEM and FT-IR were performed.

Keywords—Adsorbent, fly ash, heavy metal, waste.

I. INTRODUCTION

FLY ash is one of the significant waste [1]. Large amounts of fly ash consist by burning of coal in thermal power plants. In recent years, different application areas started to be investigated due to the nature of fly ash waste and polluting the environment. The fly-ash is capable of removing organic contaminants in consequence of high carbon content, a large surface area per unit volume and contained various elements. Therefore, fly ash is used as an effective coagulant and adsorbent [2]-[4].

Heavy metals [5] are one of the most important contaminants in water and soil. Heavy metals are discharged to the environment by several industries, such as mining, metallurgical, electronic, electroplating and metal finishing. Heavy metals cannot be degraded nor destroyed [6].

The aim of this study is to compare the possibility of use of various fly ashes like low-cost adsorbents for heavy metal adsorption. Analysis such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning electron microscope (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR)

E. Moroydor Derun is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834756; fax: 0090-212-3834725; e-mail: moroydor@gmail.com).

N. Baran Acarali is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834766; fax: 0090-212-3834725; e-mail: nbaran@yildiz.edu.tr).

A. S. Kipcak is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834751; fax: 0090-212-3834725; e-mail: skipcak@yildiz.edu.tr).

S. Piskin is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834729; fax: 0090-212-3834725; e-mail: piskin@yildiz.edu.tr).

were performed to characterize fly ashes. Depending on the results of the analysis, morphology and chemical composition of fly ashes were investigated.

II. EXPERIMENTAL

A. Materials

The fly ashes were acquired from various Electricity Generation Companies.

B. Equipments

One of the equipments used for characterization in the present study is XRD where in this equipment crystalline structures of solids were determined.



Fig. 1 XRD

The X-ray analysis was carried out at an ambient temperature by using a Philips Panalytical X'Pert-Pro diffractometer with CuK α radiation ($k = 0.15418$ nm) at operating parameters of 40 mA and 45 kV with step size 0.02° and speed of $1^\circ/\text{min}$. Phase identification of solids was performed by inorganic crystal structure database (ICSD) (Fig. 1).

A Panalytical-Minipal 4 equipped with an array of 12 analyzing crystals and fitted with an Rh X-ray tube target was used. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles [7] (Fig. 2).



Fig. 2 XRF

Cam Scan-Apollo 300 Scanning Electron Microscope was used to take the micrograph of the sample. Sample was mounted on aluminum stubs using conductive glue and was then coated with a thin layer of carbon (Fig. 3).

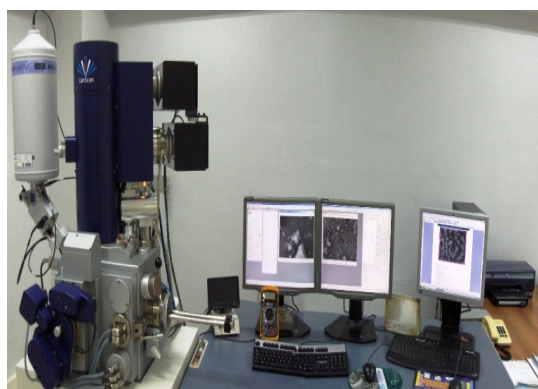


Fig. 3 SEM

Attenuated total reflectance (ATR) of FT-IR spectroscopy (Perkin Elmer Spectrum One) was used in identification of chemical bonds of the samples.

Before the analysis, the crystal area had been cleaned and the background collected; the solid material was placed over the small crystal area on universal diamond ATR top plate.

The FT-IR spectrum was achieved after force was applied to the sample, pushing it onto the diamond surface. The IR spectrum was recorded in the spectral range of 4000 to 650 cm^{-1} at ambient temperature and the resolution used was 4 cm^{-1} [8] (Fig. 4).

C. Methods

Fly ashes were characterized by XRD, XRF, SEM and FT-IR to before using for in the adsorption for waste water. Firstly, fly ashes (Fig. 5) were sieved by using 0.841 mm, 0.250 mm, 0.15 mm, 0.075 mm and fly ash was dried at 105°C for 24 hours.



Fig. 4 FT-IR



Fig. 5 Fly ash sample

III. RESULTS AND DISCUSSION

A. Characterizations

XRD, XRF, SEM and FT-IR analyses were carried out by using Philips Panalytical-X'Pert Pro, Panalytical-Minipal4, Cam Scan-Apollo 300 and Perkin Elmer-Spectrum One instrument, respectively.

XRD analyses were showed in Tables I-III. The results showed that the structures included Quartz. Chemical compositions of fly ashes were given in Tables IV-VI. The fly ash is substantial with silicon dioxide.

TABLE I
 XRD RESULTS OF TUNCBILEK FLY ASH

| PDF no | Mineral | Formula |
|-------------|----------|-------------------------|
| 01-089-1961 | Quartz | SiO_2 |
| 01-073-0603 | Hematite | Fe_2O_3 |

TABLE II
 XRD RESULTS OF CATALAGZI FLY ASH

| PDF no | Mineral | Formula |
|-------------|------------|---------------------------|
| 01-085-1780 | Quartz | SiO_2 |
| 00-022-0018 | Silimanite | Al_2SiO_5 |
| 01-089-7194 | Iron | Fe |

TABLE III
XRD RESULTS OF ORHANELI FLY ASH

| PDF no | Mineral | Formula |
|-------------|------------|----------------------------------|
| 01-089-1961 | Quartz | SiO ₂ |
| 01-073-0603 | Hematite | Fe ₂ O ₃ |
| 01-083-1566 | Silimanite | Al ₂ SiO ₅ |

TABLE IV
CHEMICAL COMPOSITION OF TUNCBILEK FLY ASH

| Compound | Amount (%) |
|--------------------------------|------------|
| MgO | 3,70 |
| Al ₂ O ₃ | 22,0 |
| SiO ₂ | 61,5 |
| SO ₃ | 0,84 |
| K ₂ O | 1,40 |
| CaO | 1,90 |
| TiO ₂ | 0,72 |
| Fe ₂ O ₃ | 8,00 |

TABLE V
CHEMICAL COMPOSITION OF CATALAGZI FLY ASH

| Compound | Amount (%) |
|--------------------------------|------------|
| SiO ₂ | 57,5 |
| Al ₂ O ₃ | 29,2 |
| Fe ₂ O ₃ | 4,85 |
| K ₂ O | 3,44 |
| MgO | 2,2 |
| TiO ₂ | 1,03 |
| CaO | 0,95 |
| Na ₂ O | 0,5 |
| SO ₃ | 0,28 |

TABLE VI
CHEMICAL COMPOSITION OF ORHANELI FLY ASH

| Compound | Amount (%) |
|--------------------------------|------------|
| SiO ₂ | 52,9 |
| Al ₂ O ₃ | 25,5 |
| Fe ₂ O ₃ | 8,7 |
| CaO | 4,75 |
| MgO | 3,1 |
| SO ₃ | 2,1 |
| K ₂ O | 2,0 |
| TiO ₂ | 0,63 |
| Na ₂ O | 0,4 |

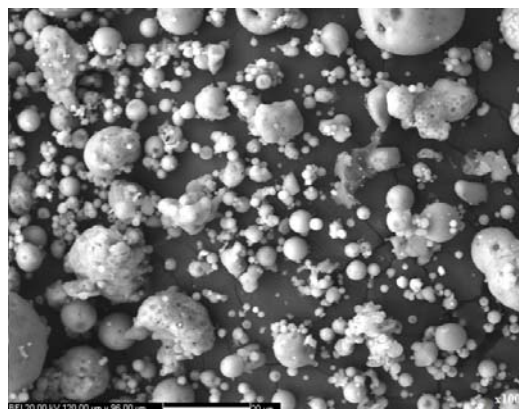


Fig. 7 SEM analysis of Catalagzi fly ash

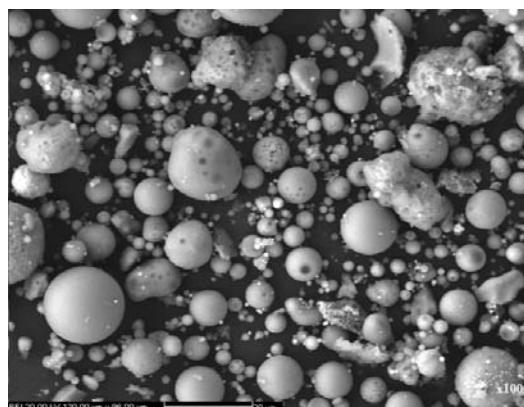


Fig. 8 SEM analysis of Orhaneli fly ash

SEM was used to determine morphological structure of products. The particle size of Tuncbilek changed in range 1.35 μm to 6.45 μm (Fig. 6). The particle size of Catalagzi changed in range 1.46 μm to 5.67 μm (Fig. 7). The particle size of Orhaneli changed in range 1.12 μm to 18.30 μm (Fig. 8).

The FT-IR spectrum of the fly ashes is shown in Fig. 9-11. The results show a broad band 800 cm^{-1} . Three characteristic bands centered at around 1100 has been identified. The strong and broad band at about 1100 cm^{-1} is due to (Si-O-Si) asymmetric stretching vibration.

Fly ash samples centered at this band has the highest SiO₂ content. The band at 850 cm^{-1} can be described for the SO₄²⁻ group (Figs. 9-11).

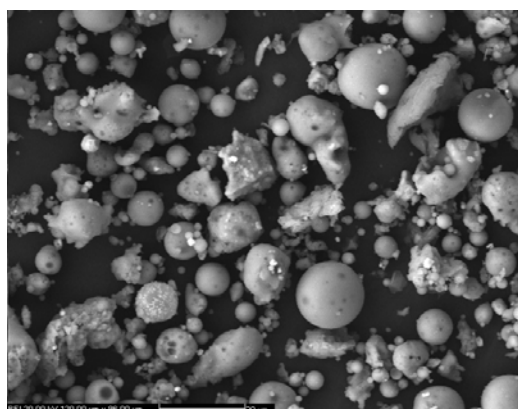


Fig. 6 SEM analysis of Tuncbilek fly ash

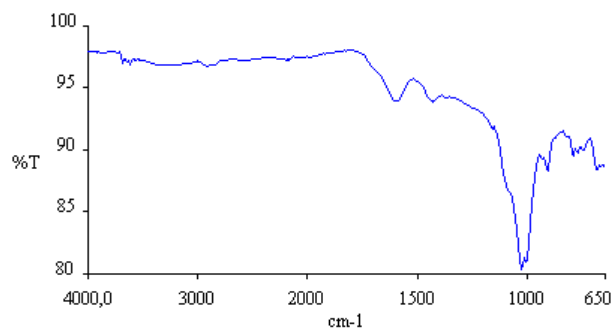


Fig. 9 FT-IR analysis of Tuncbilek fly ash

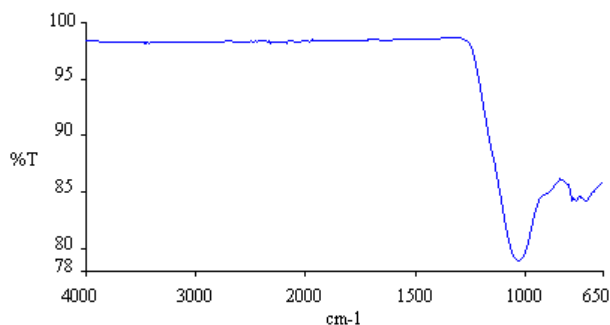


Fig. 10 FT-IR analysis of Catalagzi fly ash

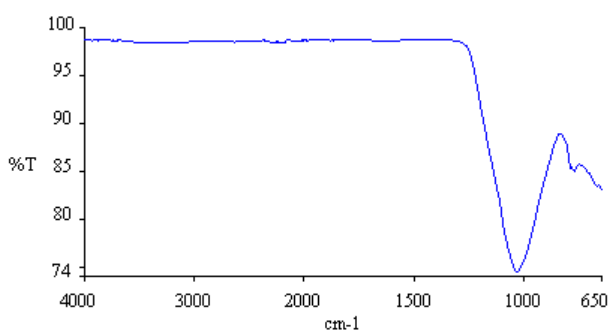


Fig. 11 FT-IR analysis of Orhaneli fly ash

Before the experimental studies, sieve analysis was performed with ASTM standard sieves and the mechanical shaker was used for sieve analysis (Fig. 12). These results indicate that size 20-200 mesh of the particles is the main fraction of fly ashes.



Fig. 12 Sieving procedure

IV. CONCLUSION

In this study, Tuncbilek, Catalagzi and Orhaneli fly ashes were characterized for the aim of heavy metal adsorption. Therefore, the selection of proper fly ash is very important. Sieve analysis, XRD, XRF, SEM and FT-IR analysis results

showed that fly ashes can be used as an adsorbent material for heavy metal adsorption. By this means, fly ashes are convenient for adsorption by pelletization.

ACKNOWLEDGMENT

This research has been supported by Yildiz Technical University Scientific Research Projects Coordination Department. Project Number: YTU-2011-07-01-KAP01.

REFERENCES

- [1] A. Bilodeau, and V. M. Malhotra, "High- volume fly ash system. Concrete solution for sustainable development", *ACI Mater.J.*, vol. 97, pp. 41-49, 2000.
- [2] P. K. Deb, A. J. Rubin, A. W. Launder, and K. H. Mancy, "Removal of COD from wastewater by fly ash", *Proceedings of 21st. Ind. Waste Conf., Purdue Univ., Indiana, Ext.Ser.*, vol. 121, 1967, pp. 848-860.
- [3] P. Cheremisinoff, "Coal fly ash: power plant waste or by-product", *Power Eng.*, vol. 92, pp. 40-41, 1988.
- [4] M. B. Vandebusch, and N. J. Sell, "Fly ash as a sorbent for the removal of biologically resistant organic matter", *Resour. Conserv. Recy.*, vol. 6, pp. 95-116, 1992.
- [5] H. Polat, and D. Erdogan, "Heavy metal removal from waste waters by ion flotation", *J. Hazard. Mater.*, vol. 148, pp. 267-273, 2007.
- [6] M. J. González-Muñoz, M. A. Rodríguez, S. Luquea, and J. R. Álvarez, "Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration", *Desalination*, vol. 200, pp. 742-744, 2006.
- [7] http://www.waternet.co.za/we/docs/vernon_removal_of_mercury_and_lead_ions.pdf
- [8] <http://www.scribd.com/doc/40053128/NaBH4-ulexite>



Emek Moroydor Derun was born in Istanbul in 1976. Moroydor Derun was graduated from B.Sc. in 1998, M.Sc. in 2000 and Ph. D. in 2005 from Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of waste management, lightweight concrete, semi conductive materials and boron technology. She has many articles and studies in international and national conference proceedings and articles.



Nurcan Tugrul was born in Gaziantep in 1973. Tugrul was graduated from B.Sc., M.Sc. and Ph.D. in Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of chemical technologies, evaluation of industrial wastes, food drying. She has many articles and studies in international and national conference proceedings and articles.



Nil Baran Acarali was graduated from B.Sc in Food Eng. Department at Trakya Univ., Edirne in 2000, both M.Sc. and Ph.D. in Chemical Eng. Department at Yildiz Tech. Univ., Istanbul in 2003 and 2008, respectively. The major field is boron technology. She has published ten articles in science citation index, over twenty nine studies in international conference proceedings and national proceedings. Her articles have forty two cited references. The research interests are supercritical fluids technology, polymer technology and boron technology. The research field in boron technology is zinc borate production. Dr. Baran Acarali is an online member of boron research.



Azmi Seyhun Kipcak was graduated from Department of Chemical Engineering in Ege University in 2002. After completing the university studies he graduated from Bilgi University from the department of Master of Business Administration in 2004. He worked in Kultur University from 2003 to 2007 as a research assistant then he transferred to Yildiz Technical University at 2008, where

he started his M.Sc. studies about Chemical Engineering in 2006. He completed his M.Sc. studies at Yildiz Technical University in 2009 and Ph.D. studies in 2013. Now he is studying on different types of borate synthesis from different raw materials and wastes.



Sabriye Piskin graduated from Istanbul Technical University on Chemical Engineering with M.Sc. degree in 1974. She completed a Ph.D. degree at the same department in 1983. Her research interests include boron minerals and compounds, hydrogen storage technologies, fuel cell applications, materials characterization, coal, waste management, corrosion, implants and synthetic materials production.