

The Cadmium Adsorption Study by Using Seyitomer Fly Ash, Diatomite and Molasses in Wastewater

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

Abstract—Fly ash is an important waste, produced in thermal power plants which causes very important environmental pollutions. For this reason the usage and evaluation the fly ash in various areas are very important. Nearly, 15 million tons/year of fly ash is produced in Turkey. In this study, usage of fly ash with diatomite and molasses for heavy metal (Cd) adsorption from wastewater is investigated. The samples of Seyitomer region fly ash were analyzed by X-ray fluorescence (XRF) and Scanning Electron Microscope (SEM) then diatomite (0 and 1% in terms of fly ash, w/w) and molasses (0-0.75 mL) were pelletized under 30 MPa of pressure for the usage of cadmium (Cd) adsorption in wastewater. After the adsorption process, samples of Seyitomer were analyzed using Optical Emission Spectroscopy (ICP-OES). As a result, it is seen that the usage of Seyitomer fly ash is proper for cadmium (Cd) adsorption and an optimum adsorption yield with 52% is found at a compound with Seyitomer fly ash (10 g), diatomite (0.5 g) and molasses (0.75 mL) at 2.5 h of reaction time, pH:4, 20°C of reaction temperature and 300 rpm of stirring rate.

Keywords—Heavy metal, fly ash, molasses, diatomite, adsorption, wastewater.

I. INTRODUCTION

HEAVY metals are one of the most important contaminants in water and soil which are discharged to the environment by several industries, such as mining, metallurgical, electronic, electroplating and metal finishing.

The removal of heavy metals from wastewater is of critical importance due to their high toxicity and tendency to accumulate in living organisms. Moreover, heavy metals cannot be degraded or destroyed [1]. In recent years, heavy metal pollution has become one of the most serious environmental problems. The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb and Zn etc... [2].

Adsorption is preferred for the removal of these pollutants due to easy handling and removal performance. On the other

hand, the economy and efficiency of the adsorption process are limited by the physicochemical characteristics and the cost of the adsorbent. In this context, several works have reported the adsorption of dyes and heavy metals in mono-component solutions using low-cost adsorbents of inorganic origin such as: clays [3], egg shell [4], fly ash [5], sandstone [6], rice husk ash [7], zeolites [8], shells of lentil, wheat and rice [9] among others.

Fly ash is the by-product of thermal power stations and is a waste material available in large quantities free of cost. Chemical and physical properties of fly ash differ according to the nature of the coal used in thermal power stations. Heavy metals like Zn, Pb, Cd, Ni and Cu have been removed from municipal solid waste leachate by fly ash [10] of thermal power plant.

Diatomite, also known as diatomaceous earth or kieselguhr, is a fine sedimentary rock of biogenetic origin, which mainly consists of amorphous hydrous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) that derives from the skeletons of aquatic plants called diatoms. In addition to bound water, varying between 3.5 and 8.0%, the siliceous skeleton may also contain, in solid solution or as part of the SiO_2 complex, small amounts of associated inorganic components – alumina, principally – and lesser amounts of iron, alkaline earth, alkali metals and other minor constituents [11].

Molasses, 23% of the hemicellulose formed by nitrogen-free organic nitrogenous substances with pectin, 12% of potassium, sodium, iron minerals such as organic matter composition, constitute 15% of water. pH is between 5.5 and 10 [12].

The purpose of this study is to investigate the possibility of the usage of Seyitomer fly ash as low-cost adsorbents for cadmium adsorption. Differently from the literature, molasses which is a waste of sugar production process is evaluated with Seyitomer fly ash.

Seyitomer fly ash was characterized by using XRF and SEM techniques, to determine the chemical composition and morphology. It was seen that adsorption yield (in percent) was affected by amounts of diatomite (in percent) and molasses (in milliliter).

II. EXPERIMENTAL

A. Raw Materials

The Seyitomer fly ash (Fig. 1 (a)), diatomite (Fig. 1 (b)) and molasses (Fig. 1 (c)) were supplied by Areas Cement Construction Incorporated Company, Kutahya Cement Factory, Konya sugar refinery, respectively.

N. Tugrul and N. Baran Acarali are with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834776; fax: 0090-212-3834725; e-mail: ntugrul@hotmail.com, nilbaran@gmail.com).

E. Cinar is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834790; fax: 0090-212-3834725; e-mail: ekin_cinar_5@hotmail.com).

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 / seyhunkipcak@gmail.com).

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).

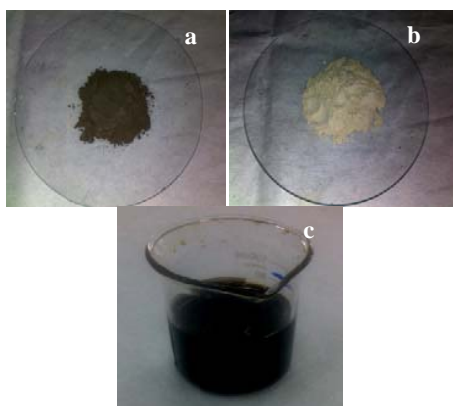


Fig. 1 Raw materials: (a) Seyitomer fly ash (b) Diatomite (c) Molasses

B. Methods and Characterizations

Seyitomer fly ash dried at 105°C for 24 h, then they were analyzed by using XRF (Panalytical-Minipal4) and SEM (Cam Scan- Apollo 300), respectively (Figs. 2, 3). SEM is one of the best and most widely used techniques for the chemical and physical characterization of fly ash [13]. Then, fly ash, diatomite (0 and 1% in terms of fly ash, w/w) and molasses (0, 0.25, 0.50 and 0.75 mL) were pelletized by Manfredi OL57 pellet machine with 4 cm diameter of pellets and under 30 MPa of pressure, where diatomite was used as a binder in the pelletization process for Seyitomer fly ash. Pellets were dried at 105°C for 24 h. Subsequently, the pellets were sintered in a high-temperature at 1200°C.

Five hundred parts per million of synthetic wastewater (5 ppm Cd solution) were prepared with a magnetic stirrer for 2 h prepared at 500 rpm of stirring rate and 20°C of temperature.



Fig. 2 Panalytical-Minipal4 XRF

Pellets were used at 20°C of reaction time, 300 rpm of stirring rate and 3 h of reaction time for Cd heavy metal adsorption. The effects of diatomite (in percent) and molasses (in milliliter) on adsorption yield were examined.



Fig. 3 Cam Scan- Apollo 300 SEM

III. RESULTS AND DISCUSSION

A. Characterization of the Raw Materials

Seyitomer fly ash was generally heterogeneous, consisting of a various identifiable crystalline phases such as quartz (SiO_2), iron oxide (Al_2O_3) and aluminum oxide (Fe_2O_3). The total amount of SiO_2 , Al_2O_3 , Fe_2O_3 Seyitomer fly ash exceeded 70% as previous study [14]. The iron (Fe_2O_3) content was found higher in Seyitomer fly ash. Then distribution of the compounds of Seyitomer fly ash used in this study is shown in Fig. 4. The SiO_2 and aluminum oxide (Al_2O_3) contents were 52 and 18%, respectively.

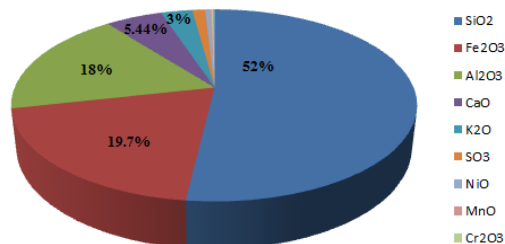


Fig. 4 Chemical compositions of the Seyitomer fly ash

The chemical analysis of diatomite was shown in Fig. 5. The main component of diatomite is SiO_2 , with a relatively small percentage of other oxides such as Al_2O_3 , Fe_2O_3 , MgO and others.

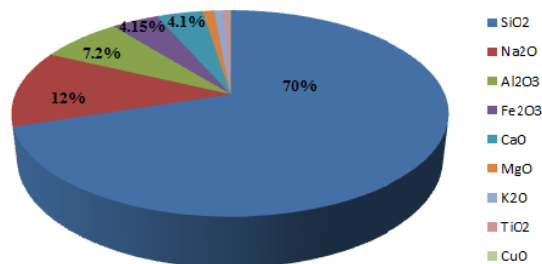


Fig. 5 Chemical compositions of the diatomite

Particle sizes of Seyitomer fly ash (Fig. 6 (a)) and diatomite (Fig. 6 (b)) were found between 2-10 μm and 4-37 μm , respectively under the SEM.

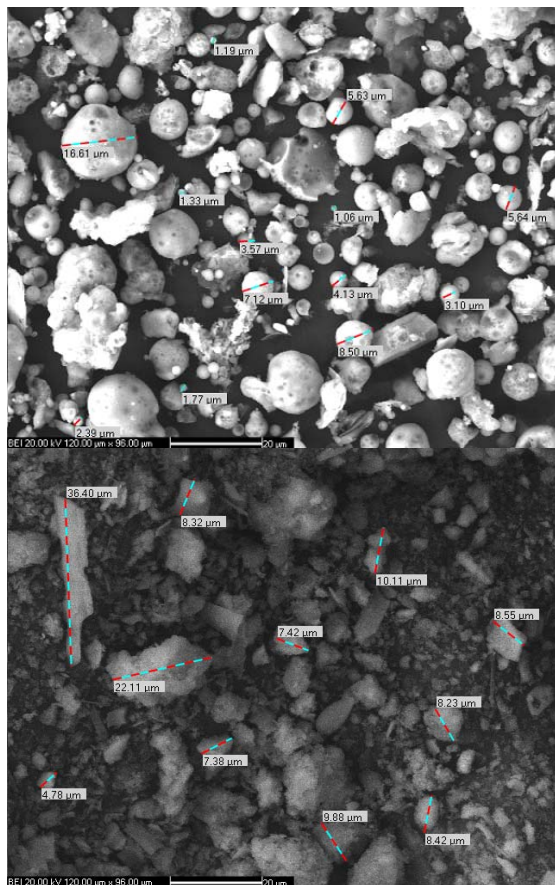


Fig. 6 SEM images: (a)Seyitomer fly ash ($\times 1000$ magnification) (b) Diatomite ($\times 1000$ magnification)

B. Methods and Characterizations

A series of pelletization experiments were conducted to show the effect of diatomite (in percent) and molasses (in milliliter) addition on the formation of fly ash pellets. The ratio of diatomite was used between 0-1%. The amount of molasses was selected between 0-0.75 mL (50% of molasses + 50% of distilled water). The pelletization results showed that molasses was a fundamental binder for Seyitomer fly ash. Pellets were fragile when molasses was not used.

C. Adsorption Experiments

Adsorption process was conducted between 30-180 minutes. Then samples were analyzed by ICP-OES instrument and results were shown in Table I.

The pelletization conditions were determined in terms of adsorption yield (in percent) as 10 g of Seyitomer fly ash, 0.5% of diatomite and 0.75 mL of molasses and the maximum adsorption yield was found 52% for 150 min. Optimum adsorption results were shown in at Fig. 7.

TABLE I
THE ICP-OES RESULTS FOR Cd^{+2} ADSORPTION OF SEYITOMER FLY ASH (10 G)
(20°C, 300 RPM, PH:4)

Diatomite (in terms of fly ash, w/w) (%)	Molasses (mL)	Formation of pellet	Adsorption yield (%)					
			30	60	90	120	150	180
0.5	0	-	-	-	-	-	-	-
0.5	0.25	+	38	37	44	33	33	33
0.5	0.50	+	3	5	47	33	33	33
0.5	0.75	+	5	2	-	45	52	47
1	0	-	-	-	-	-	-	-
1	0.25	+	-	-	-	-	-	-
1	0.50	+	-	-	-	-	-	-
1	0.75	+	-	-	-	-	-	-

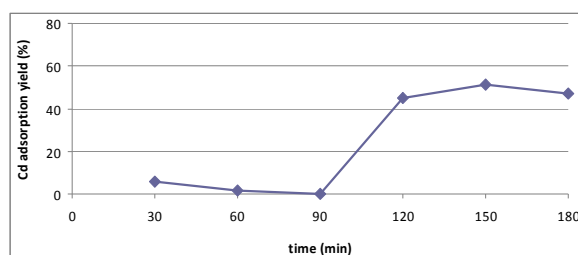


Fig. 7 Cd^{+2} adsorption yield depending upon time for optimum conditions by using Seyitomer fly ash (with diatomite and molasses)

IV. CONCLUSIONS

In this study, Seyitomer fly ash, diatomite and molasses were pelletized under determined conditions for Cd^{+2} adsorption where they are the wastes that can easily be found in Turkey. Characterization results showed that the SiO_2 and Al_2O_3 contents for Seyitomer fly ash were 52 and 18%, respectively.

Optimum adsorption yields of Cd^{+2} was found as 3, 5, 47, 33, 33, 33 (%) at 30, 60, 90, 120, 150, 180 minutes. Seyitomer fly ash was proper for Cd^{+2} adsorption and an optimum adsorption yield with 52% was found at a compound with Seyitomer fly ash (10 g), diatomite (0.5 g) and molasses (0.75 mL) at 2.5 h of reaction time, pH:4, 20°C of reaction temperature and 300 rpm of stirring rate.

From the results of this study, it was seen that molasses as and diatomite can be evaluated with fly ash.

ACKNOWLEDGMENT

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

REFERENCES

- [1] M.J. González-Muñoz, M.A. Rodríguez, S. Luquea, J.R. Álvarez, "Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration," *Desalination*, vol. 200, 2006, pp. 742-744.
- [2] D. Nilanjana, R. Vimala, P. Karthika "Biosorption of Heavy Metals-An Overview," *Ind. J. Biotechn.* VITUniversity, School of biotechnology, chemical and biomedical engineering, India, Vol 7, 2008, pp 159-159.
- [3] S. Gupta, S.Bhattacharyya, Interaction of metal ions with clays: I. A case study with Pb (II). *Appl. Clay Sci.* 30, 199-208. 2005.

- [4] M. Arami, N.Y. Limaee, N.M. Mahmoodi, Investigation on the adsorption capability of egg shell membrane towards model textile dyes, *Chemosphere* 65, 1999-2008, 2006.
- [5] J.X. Lin, S.L. Zhan, M.H. Fang, X.Q. Qian, H. Yang, Adsorption of basic dye from aqueous solution onto fly ash. *J. Environ. Manag.* 87, 193-200, 2008.
- [6] G. Atun, M. Tunçay, G. Hisarlı, R.Y. Talman, H. Görmez, Adsorption equilibria between dye and surfactant in single and binary systems onto geological materials. *Appl. Clay Sci.* 45, 254-261, 2009.
- [7] V.S. Mane, I.D. Mall, V.C. Srivastava, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. *J. Environ. Manag.* 84, 390-400, 2007.
- [8] M. Turan, U. Mart, B. Yüksel, M. S. Çelik, Lead removal in fixed-bed columns by zeolite and sepiolite. *Chemosphere* 60, 1487-1492, 2005.
- [9] H. Aydın, Y. Bulut, C. Yerlikaya, Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *J. Environ. Manag.* 87, 37-45, 2008.
- [10] S. Mohan, R. Gandgandhimathi, *J. Hazard. Mater.* 169, (1-3) 351-359, 2009.
- [11] H. Arik, Synthesis of Si_3N_4 by the carbo-thermal reduction and nitridation of diatomite, *J. Eur. Ceram. Soc.* 23 2005-2014, 2003.
- [12] B. Pekin, *Biyokimya Mühendisliği (Biyoteknoloji)*, 2. Kitap. Ege Üniversitesi Kimya Fakültesi Yayınları, 409, İzmir, 1983.
- [13] B. G. Kutchko, A. G. Kim, Fly ash characterization by SEM-EDS, *Fuel*, Vol. 85 (17), 2537-2544, 2006.
- [14] S. Turhan, I. H. Arıkan, B. Yücel, A. Varinlioğlu, A. Köse, Evaluation of the Radiological Safety Aspects of Utilization of Turkish Coal Combustion Fly ash in Concrete Production, *Fuel*, 89, 2528-2535, 2010.



Nil Baran Acarali was graduated from B.Sc. 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 eleven articles in science citation index, over thirty seven studies in international conference proceedings and national proceedings. Her articles have fortyfive cited references. The research interests are supercritical fluids technology, polymer technology, heavy metal adsorption and boron technology. The research field in boron technology is zinc borate production. Dr. Baran Acarali is an online member of boron research.



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. She has more than sixty articles and hundred conference manuscripts pressed at the international area.



Nurcan Tugrul was born in Gaziantep in 1973. Tugrul was graduated from B.Sc., M.Sc. and Ph.D. in Chemical Eng. 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.



Emek Moroydor Derun was born in Istanbul in 1976. Moroydor Derun 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.



Ekin Cinar was graduated from Department of Chemical Engineering in 2012. At this year, she started her M.Sc. studies about Chemical Engineering her interested area is consisting of fly ash and heavy metal adsorption.



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.