

ASH UTILIZATION IN WATER QUALITY MANAGEMENT

T. Viraraghavan
Faculty of Engineering, University of Regina
Regina, Saskatchewan, Canada, S4S 0A2

ABSTRACT

The potential for water pollution involving heavy metals and organics exists especially when wastewater treatment is either inadequate or non-existent. This paper reviews a number of investigations where coal ashes have been studied for the removal of organic matter (COD), color, organic compounds such as phenol, and heavy metals. Results of experimental studies conducted at the University of Regina, on the adsorption of 1) phenol and 2) heavy metals such as cadmium, chromium, mercury, copper, nickel and zinc by fly ash, are presented. The use of fly ash in sludge management is also examined.

Keywords: coal ash utilization, water treatment, wastewater treatment

INTRODUCTION

Increased reliance on coal as an energy source has led to significant by-product management problems of storage or disposal. These by-products include slag, bottom ash and fly ash. Commercial uses of coal ashes are limited and this paper examines the application of these by-products in water pollution control.

USE OF FLY ASH IN WATER TREATMENT

Ballance *et al.* used fly ash as a coagulant aid in water treatment (1). Fly ash from four sources and in certain proportions was found by the authors to assist in the chemical coagulation of turbid water and in the settling of chemically induced floc. A denser sludge was produced from coagulation with fly ash and alum than with alum alone. Laboratory tests using Neyveli lignite fly ash showed that it aids in the settling of turbid water when used along with alum (2).

USE OF COAL ASHES IN WASTEWATER TREATMENT

The use of bottom ash and fly ash in removing contaminants from wastewater (on-site and municipal) is examined with special reference to removal of COD, color, organic compounds, and heavy metals.

On-site Wastewater Treatment

Bottom ash was considered as an alternative medium for the mound type soil absorption systems used in on-site wastewater treatment. Laboratory work carried out at West Virginia University showed that the bottom ash filter had the ability to reduce BOD and SS (3, 4). Three bottom ash mound systems built in Monogalia County, West Virginia based on this work were reported to be operating well (5). Laboratory studies on four different recirculating filters using pea gravel, medium sand, bottom ash and fly ash-bottom ash mixture showed that there was no significant difference in the performance of different media with respect to reduction in COD and SS (6). A 23-month study examined 11 filters - five bottom ash filters, five sand filters treating septic tank effluent and one bottom ash filter treating aerobically treated effluent. The study data showed that sand media filters resulted in a higher quality effluent; noticeable improvement in the performance of all the filters was observed in the last five-month period with effluent BOD in the 10-14 mg/L range (5). The Southern Illinois Power Co-op used unscreened bottom ash in a single intermittent filter treating septic tank effluent. The filter

operation was monitored from January 1981 to April 1982; the average effluent BOD and SS values were 7 and 8 mg/L respectively (7). Detailed studies on a bottom ash recirculating filter treating septic tank effluent from a residence showed that the system performed consistently and produced an effluent with average BOD and SS less than 12 mg/L (8).

Municipal Wastewater Treatment

Batch tests showed that unsieved fly ash (6% carbon) removed in 24h 19 to 56% of COD, and 0 to 77% of ABS from secondary effluent depending upon the adsorbent dose (9). This study also showed that COD removal increased with an increase in the carbon content of fly ashes tested (9). Deb *et al.* found that the removal of COD is logarithmically related to three parameters - 1) time of mixing, 2) initial COD and 3) concentration of fly ash (10). Nelson and Guarino found that removals of COD, BOD and SS by the addition of fly ash to a municipal plant effluent were not appreciable (11). The investigations by Eye and Basu showed that fly ash was capable of reducing COD of a secondary effluent by about 30 percent at a fly ash concentration of about 1600 mg/L when the initial COD is around 60 mg/L and removal of SS containing fly ash by coagulation with lime was very efficient (12).

Removal of color. The removal of Metomega Chrome Orange GL, a commercial textile dye from wastewater was found to be nearly 99% under optimal conditions (pH = 3.0 and temperature =30°C) using fly ash as an adsorbent (13); the sorption data fitted the Langmuir isotherm model. The removal of Omega Chrome Red ME (a popular chrome dye) from its aqueous solution by adsorption on a mixture of fly ash and coal was studied; a 100% removal of the dye was achieved at 10 mg/L, 30°C, and 2.0 pH, using a 1:1 ratio of fly ash and coal (14). The equilibrium data was reported to fit well with the Langmuir model of adsorption.

Removal of organics. Fly ash was successfully used to recover phenol from industrial wastewater, by lagooning the mixture of fly ash and wastewater; phenol was reduced from 4500 mg/L to 280 mg/L (15). Fly ash was also used to remove TNT in both batch and column systems; in column systems 90% removal of TNT was reported (16). Bhargava *et al.* examined the removal of a detergent in a fixed-bed continuous flow fly ash column and developed a relationship for the design of such systems (17). Using 1000 mg/L of fly ash containing 23.27% carbon, 74% removal of ABS was obtained with a two-hour contact time (18). Khanna and Malhotra examined the kinetics and mechanism of phenol removal by fly ash and provided data for the design of phenol-fly ash adsorption systems (19). Jain *et al.* showed that the adsorption plot of oxalic acid from aqueous solution by fly ash has two linear components each following the Langmuir isotherm (20). Banerjee *et al.* examined the use of fly ash as a sorbent in the treatment of alcohols, aldehydes, ketones and aromatics (21). This study showed that immobilization of organic pollutants is feasible by adsorbing the contaminants onto fly ash. The residual carbon content was found to play a significant role in the adsorption process. Percent reductions of the aromatic compounds were found to be much higher compared to other functional groups such as alcohols, aldehydes and ketones.

Removal of heavy metals. Gangoli *et al.* performed batch tests by contacting 40 g of fly ash with 1 L of an aqueous solution of chromium (22). They concluded that the removal of hexavalent chromium using fly ash involved a chemisorption mechanism associated with the bonding between active alumina sites and the chromate anion. Grover and Narayanaswamy carried out batch experiments to study the effects of contact time, pH and fly ash dosage on the removal of hexavalent chromium (23). They explained the equilibrium data for chromium uptake by fly ash at different pH values on the basis of the Freundlich adsorption isotherm. They found that there was an improved adsorption of chromium at a pH less than 2.5. Yadava *et al.* (24) investigated the removal of cadmium by fly ash at different conditions by varying the

contact time, temperature and pH. They found that the removal of cadmium from aqueous solutions by adsorption on fly ash increased with time and that equilibrium is attained in 2 hours. On studying the kinetics of adsorption of cadmium on fly ash using the Lagergren equation, they concluded the adsorption process to be first order. They found that the adsorption of cadmium on fly ash could be explained by the Langmuir equation. Their results showed that an increase in temperature from 20°C to 40°C decreased the adsorption of cadmium on fly ash from 96.07% to 83.78%. The removal of cadmium by fly ash increased from 11.85% to 89.82% on increasing the pH of cadmium solution from 4.0 to 8.5. The ability of a homogenous mixture of fly ash and wollastonite (1:1) to remove Cr^{6+} from aqueous solution by adsorption was investigated by Panday *et al.* (25). Maximum removal was observed at pH 2.0 and 30°C. Studies were conducted to investigate the removal of copper from the metal cleaning wastes by adsorption on fly ash; these studies showed that adsorption can significantly increase copper removal (26). The removal of Cu^{2+} by adsorption on fly ash was found by Panday *et al.* to be concentration, pH and temperature dependent (27). Adsorption was found to be endothermic; the maximum removal was observed at pH 8.0. Prabhu *et al.* showed that fly ash was a good adsorbent for the removal of zinc from aqueous solutions; maximum removal was obtained in the pH range of 3 to 4 (28). They found that adsorption fitted the Freundlich isotherm. Studies by Gashi *et al.* showed that fly ash showed good adsorptive properties of removal of lead, zinc, cadmium and copper from effluents of battery industry and fertilizer industry (29). Removal efficiencies were greater than 70%. Adsorption studies carried out to estimate heavy metal removal using fly ash on wastewater at Varnasi, India showed that removal was in the following order: $Pb > Zn > Cu > Cr > Cd > Co > Ni > Mn$ (30). Adsorption of Cu^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} and Ag^+ on fly ash was investigated by Weng and Huang and they found that the process was spontaneous and endothermic (31). Sen and De found that fly ash was found to have a good adsorption capacity for Hg^{2+} ; they reported that the adsorption conformed to Freundlich model (32). They found that the equilibrium time for adsorption was three hours and that the optimum pH range was 3.5 to 4.5. Fly ash was found to be a good adsorbent for the removal of lead; an equilibrium time of two hours and a pH of 5.0 was found to be most effective for the removal of lead (33).

USE OF FLY ASH IN SLUDGE MANAGEMENT

Eye and Basu concluded, based on their investigation, that fly ash could be a useful agent in conditioning sludge prior to vacuum filtration (12). Helm *et al.* concluded that mixtures up to 10% wastewater sludge with fly ash appeared suitable for use in highway embankments and other structural fills (34). Kincannon *et al.* showed that an admix of municipal wastewater sludge with fly ash could produce a dry, deodorized and sterile product with a potential for use as a soil conditioner (35).

RESEARCH AT THE UNIVERSITY OF REGINA

Batch studies were conducted to evaluate the use of fly ash in the removal of cadmium, chromium, copper, nickel, zinc, mercury and phenol from municipal wastewater. The fly ash used in the study was obtained from unit #2 of the Poplar River Power Station of the Saskatchewan Power Corporation. The fly ash generated from the combustion of lignite was collected from the first bunker of the power station's electrostatic precipitators. The wastewater used in the study was collected from the City of Regina Municipal Wastewater

Treatment Plant, before the wastewater enters the primary sedimentation tanks. The first study related to cadmium and chromium, the second study was conducted with copper, nickel and zinc; the third study was on mercury removal and the fourth related to phenol. For the studies, the wastewater was spiked with the respective heavy metals to raise their concentrations to approximately 1 mg/L. Batch (kinetic and adsorption isotherm) studies were conducted using a Jar Test Apparatus. Adsorption studies were conducted at various pH values and the best pH for maximum adsorption was chosen. Isotherm studies were conducted at 5°C, 10°C, 15°C and 21°C for heavy metal removal. Methods outlined in "Standard Methods" (36) were followed for the analysis. Batch studies showed that fly ash removed 93% of the cadmium in the wastewater in the pH range 7 to 8, and 44% of the chromium in the wastewater in the pH range 2 to 3 in an equilibrium time of 3 hours (37). The adsorption of cadmium and chromium on fly ash was found to be exothermic. Isotherm analysis of the data showed that the adsorption of cadmium on fly ash was described by the Langmuir isotherm at 5°C, 10°C, 15°C, and 21°C whereas the adsorption of chromium on fly ash followed the Freundlich isotherm at 5°C, 10°C and 15°C and Langmuir isotherm at 21°C. Removals of copper, zinc and nickel attained equilibrium in two hours (38). Removals of the three metals were found to reach maximum values in the pH range 3 to 3.5. It was found that the adsorption capacity of fly ash with respect to these three heavy metals generally decreased with an increase in temperature. Removals of copper, nickel and zinc were approximately 73%, 33% and 59% respectively at 21°C at a pH of 3.0 to 3.5. The adsorption of the three metals on fly ash generally followed the Langmuir isotherm. It was found that a contact time of two hours was necessary for the adsorption of mercury from wastewater to reach equilibrium (39). The optimum pH was found to be between 5.0 and 5.5. The adsorption isotherm data were described adequately by both the Langmuir and the Freundlich models. In the case of the adsorption of phenol from wastewater by fly ash, it was found that the removal of phenol was optimum at a pH of 5.0 in an equilibrium time of five hours. The adsorption data was adequately described by the Langmuir isotherm.

ACKNOWLEDGMENTS

The author would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for funds provided to the project by way of an operating grant to the author.

REFERENCES

1. R.C. Ballance, J.P. Capp and J.C. Burchinal. Fly Ash as a Coagulant Aid in Water Treatment. Report of Investigation 6869. Washington, DC: U.S. Department of the Interior, Bureau of Mines, 1966.
2. S. Torrey. Coal Ash Utilization: Fly Ash, Bottom Ash and Slag. Park Ridge, NJ: Noyes Data Corporation, 1978, p. 62.
3. C.R. Schriener. Use of Bottom Ash as a Medium for the Construction of a Septic Tank Effluent Disposal System. Morgantown, WV: Department of Civil Engineering, West Virginia, 1979.
4. N. Oshkoohi. Use of Bottom Ash as Media for the Construction of a Septic Tank Effluent Disposal System. Morgantown, WV: Department of Civil Engineering, West Virginia, 1979.
5. S.P. Dix, M. Usmen and A.W. Babcock. "Bottom Ash Analysis for Effluent Treatment." Orlando, FL: Proceedings of the Seventh International Ash Utilization Symposium, 1985, pp. 517-529.
6. D.J. Ralph, D.H. Vanderholm and W.D. Lembke. "Recirculating Sand Filters for Onsite Sewage Treatment in Areas with Soils Unsuitable for Seepage Fields." New Orleans, LA: Paper presented at the 1979 Winter Meeting of the American Society of Agricultural Engineers, 1979.
7. D.L. Hill. Evaluation of Bottom Ash from Southern Illinois Power Company for Use as

- Filter Media. Marion, IL: Memorandum, Illinois Environmental Protection Agency, June 1983.
8. M.A. Usmen and S.A. Dix. "Use of Bottom Ash as Filter Aggregate for Septic Tank Wastewater Treatments." Istanbul, Turkey: Proceedings of the Third Symposium on Environmental Management for Developing Countries, 1986.
 9. G.E. Johnson, L.M. Kanka and J.H. Field. "Use of Coal and Fly Ash as Adsorbents for Removing Organic Contaminants from Secondary Municipal Effluents." Industrial and Engineering Chemistry - Process Design and Development, Vol. 4, No. 3, July 1965, pp. 323-327.
 10. P.K. Deb, A.J. Rubin, A.W. Launder and K.H. Mancy. "Removal of COD from Wastewater by Fly Ash." W. Lafayette, IN: Engineering Bulletin, Purdue University Extension Series 121, 1966.
 11. M.D. Nelson and C.F. Guarino. "The Use of Fly Ash in Municipal Waste Treatment." Journal of Water Pollution Control Federation, Vol. 41, No. 11, Part 1, November 1969, pp. 1905-1911.
 12. J.D. Eye and T.K. Basu. "The Use of Fly Ash in Wastewater Treatment and Sludge Conditioning." Journal of Water Pollution Control Federation, Vol. 42, No. 5, Part 2, May 1970, pp. R125-R135.
 13. G.S. Gupta, G. Prasad and V.N. Singh. "Removal of Color from Wastewater by Sorption for Water Reuse." Journal of Environmental Science and Health, A. Vol. 23, No. 3, 1988, pp. 205-217.
 14. G.S. Gupta, G. Prasad and V.N. Singh. "Removal of Chrome Dye from Aqueous Solutions by Mixed Adsorbents: Fly Ash and Coal." Water Research, Vol. 24, No. 1, 1990, pp. 45-50.
 15. K. Lorenz. "Secondary Treatment of Power-Plant Phenol Waste with Fly Ash and Cinders." Gesundb. Ing. Vol. 75, 1954, p. 189.
 16. V. Solin and M. Kustka. "The Treatment of Wastewaters Containing TNT by Sprinkling on Ashes." Scientific Papers from Institute of Chemical Technology, Prague, Vol. 2, 1958, p. 247.
 17. R. Bhargava, R.P. Mathur and P. Khanna. "Removal of Detergent from Wastewater by Adsorption on Fly Ash." Indian Journal of Environmental Health, Vol. 16, No. 2, April 1974, pp. 109-120.
 18. K.H. Mancy, W.E. Gates, J.D. Eye and P.K. Deb. "The Adsorption Kinetics of ABS on Fly Ash." Lafayette, IN: Proceedings of the 19th Industrial Waste Conference, Purdue University, 1965, pp. 146-160.
 19. P. Khanna and S.K. Malhotra. "Kinetics and Mechanism of Phenol Adsorption on Fly Ash." Indian Journal of Environment Health, Vol. 19, No. 3, July 1977, pp. 224-237.
 20. K.K. Jain, G. Prasad and V.N. Singh. "Application of Langmuir Isotherm for Oxalic Acid Adsorption by Fly Ash and Activated Carbon." Indian Journal of Chemistry, Vol. 19A, No. 2, February 1980, pp. 154-156.
 21. K. Banerjee, P.Y. Horng, P.N. Cheremisinoff, M.S. Sheih and S.L. Cheng. "Sorption of Selected Organic Pollutants by Fly Ash." West Lafayette, IN: Proceedings of 43rd Industrial Waste Conference, Purdue University, 1988, pp. 397-406.
 22. N. Gangoli, D.C. Markey and G. Thodos. "Removal of Heavy Metal Ions from Aqueous Solution with Fly Ash." Chicago, IL: Proceedings of the Second National Conference on Complete Water Reuse, May 1975, pp. 270-275.
 23. M. Grover and M.S. Narayanaswamy. "Removal of Hexavalent Chromium by Adsorption on Fly Ash." Journal of the Institution of Engineers (India), Vol. 63, Part EN 1, October 1982, pp. 36-39.
 24. K.P. Yadava, B.S. Tyagi, K.K. Panday and V.N. Singh. "Fly Ash for the Treatment of Cd (II) Rich Effluents." Environmental Technology Letters, Vol. 8, 1987, pp. 225-234.
 25. K.K. Panday, G. Prasad and V.N. Singh. "Removal of Cr (VI) from Aqueous Solutions by Adsorption on Fly Ash-Woolastonite." Journal of Chemical Technology and Biotechnology, Vol. 34A, 1984, pp. 367-374.

26. T.J. Cha, G.R. Steiner and C.L. McEntyre. "Removal of Complex Copper-Ammonia Ions from Aqueous Wastes with Fly Ash." Journal of Water Pollution Control Federation, Vol. 5, No. 9, 1978, pp. 2157-2174.
27. K.K. Panday, G. Prasad and V.N. Singh. "Copper (II) Removal from Aqueous Solutions by Fly Ash." Water Research, Vol. 19, No. 7, 1985, pp. 869-873.
28. P.V.S.S. Prabhu, M.S. Narayanaswamy and T.S.S. Narasa Raju. "Adsorption of Zinc from Aqueous Solutions by Fly Ash." IAWPC Technical Annual, Vol. 8, 1981, pp. 46-52.
29. S.T. Gashi, N.M. Daci, X.M. Ahmeti, T.J. Selimi and E.M. Hoxha. "Removal of Heavy Metals from Industrial Wastewaters." In: Chemistry for Protection of the Environment 1987 (ed. L. Pawlowski et al.). Amsterdam: Elsevier Publishers, 1988.
30. A. Mathur, S.K. Khare and D.C. Rupainwar. "Removal of Heavy Metals from Main Sewer-Water of Varnasi City by Adsorption on Fly Ash and Blast Furnace Slag." Journal of Industrial Pollution Control (India), Vol. 5, No. 2, 1989, pp. 52-57.
31. C.H. Weng and C.P. Huang. "Removal of Trace Heavy Metals by Adsorption and Fly Ash." Arlington, VA: Proceedings of the 1990 ASCE Environmental Engineering Specialty Conference, 1990, pp. 923-924.
32. A.K. Sen and A.K. De. "Adsorption of Mercury (II) by Coal Fly Ash." Water Research, Vol. 21, No. 8, 1987, pp. 885-888.
33. A. Mathur and D.C. Rupainwar. "Removal of Lead from Polluted Waters by Adsorption on Fly Ash." Asian Environment, Vol. 10, No. 3, 1988, pp. 19-25.
34. R.B. Helm, G.B. Keefer and W.A. Sack. "Environmental Aspects of Compacted Mixtures of Fly Ash and Wastewater Sludge." Proceedings of the 4th International Ash Utilization Symposium, St. Louis, MO, March 1976, pp. 396-421.
35. D.F. Kincannon, A.F. Gaudy, Jr., W.F. Scriminger and W. Ricketts. "Some Effects of Western Coal Fly Ash on Municipal Sewage Sludge." Proceedings of the Fifth International Ash Utilization Symposium, Atlanta, Georgia, February 1979, pp. 898-903.
36. Standard Methods for the Examination of Water and Wastewater. Washington, DC: American Public Health Association, 1985.
37. G.A.K. Rao. Adsorption of Cadmium and Chromium from Wastewaters by Peat and Fly Ash, M.Sc. Thesis, University of Regina, Regina, Saskatchewan, Canada, 1989.
38. M.M. Dronamraju. Removal of Copper, Nickel and Zinc from Wastewater by Adsorption Using Peat and Fly Ash, M.Sc. Thesis, University of Regina, Regina, Saskatchewan, Canada.
39. A. Kapoor. Adsorption of Mercury from Wastewater by Peat, Fly Ash and Bentonite, M.Sc. Thesis, University of Regina, Regina, Saskatchewan, Canada.