

Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent

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Abstract

Fly ash is one of the most abundant waste materials; its major components make it a potential agent for the adsorption of heavy metal contaminants in water and wastewaters. The objective of this study was to measure the changes in toxicity of and heavy metals in a municipal (Salisbury, MD) wastewater treatment plant (SWTP) effluent on treatment with fly ash. The effluent from SWTP after treatment with fly ash for 4 h showed a significant reduction in toxicity, Cu and Pb, and PO_4^{3-} and NO_3^- contents. Toxicity of the effluent was measured using the marine luminescent microorganisms—*Vibrio fischeri* ('Microtox' test). Heavy metals (Cu, Pb and Zn) were measured using Atomic Absorption Spectrophotometry. Fly ash removed Cu and Pb from the effluent (through adsorption), and the removal of these toxic heavy metals resulted in the reduction of toxicity. © 1998 Elsevier Science B.V.

Keywords: Wastewater treatment plant; Effluent; Fly ash; Toxicity; Heavy metals

1. Introduction

Increases in population and industrialization have resulted in increased heavy metals content of many municipal wastewater treatment plant effluents. The Salisbury Wastewater Treatment Plant (SWTP, City of Salisbury, on the Eastern Shore of Maryland) discharges 1.6×10^7 Ld of effluents in to the Wicomico River, a tributary of the Chesapeake Bay. The treatment plant receives mostly residential wastewaters, along with a small amount of industrial effluents. The major contributors of metals to the

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Table 1
Metal concentrations ($\mu\text{g}/\text{l}$) in SWTP^a

| Metal | Influent | Effluent | Acute criteria ^b (chronic) | Metal toxicity ^c |
|-------|----------|----------|---------------------------------------|-----------------------------|
| Cu | 65 | 25 | 18 (12) | 800 |
| Pb | 20 | 8 | 82 (3.2) | 600 |
| Zn | 190 | 50 | 120 (110) | 1000 |

^aLudy, 1996 [1]; ^bMaryland Register, 1995 [3]; ^cChou and Hee, 1994 [4].

SWTP include the following facilities: food processing, hospitals, printers, plastics and rubber, schools and universities, water treatment, metal fabrication, metal plating, photography shops and X-ray laboratories. The SWTP effluent has been found to contain high concentrations of Cu, Pb and Zn [1]; all three heavy metals are listed as priority pollutants by the US Environmental Protection Agency [2]. The average concentrations (October–December 1995) of these metals in the influent and effluent of SWTP, along with the acute criteria concentrations for surface waters, are listed in Table 1 [3,4].

The toxic nature of some of the heavy metals, even at low concentrations, poses a problem [5]. Chronic Cu intake is related to hemochromatosis [6]; Cd adversely affects several important enzymes and can cause kidney damage [7]; whereas Pb has a number of toxic effects, including damage to central and peripheral nervous systems [7]. Various methods for the removal of metals from wastewaters include chemical precipitation, membrane filtration, ion exchange and adsorption [5]. The adsorbents commonly recommended are alumina, silica, ferric oxide and activated carbon [5,8]. Fly ash, a coal combustion by-product, is made up of alumina, silica, ferric oxide and calcium oxides [8]. Over 5.5×10^{10} kg of fly ash are generated each year in USA [9]. There are a few reports on the use of fly ash for removal of Cd and Cu from industrial wastewaters [6,10,11]. The objective of this research was to measure the changes in toxicity of and heavy metals in a municipal wastewater treatment plant effluent after treatment with fly ash.

2. Methods and materials

2.1. Sample collection:

Fly ash from the Indian River Power Plant, Millsboro, DE was sieved ($< 125 \mu\text{m}$) and used for the adsorption of pollutants from the SWTP effluent. The chemical composition of this ash is given in Table 2. The SWTP effluent samples were collected on Wednesdays in May and June, 1996 around 2:00 P.M. (EST) at least 3 days after a rainfall event and stored in plastic containers thoroughly washed with 10% (v/v) H_2SO_4 and deionized water to avoid any metal contamination [12].

Table 2
Composition of fly ash^a

| Component | Percentage |
|--------------------------------|------------|
| SiO ₂ | 40.34 |
| Al ₂ O ₃ | 27.59 |
| Fe ₂ O ₃ | 9.75 |
| CaO | 2.49 |
| MgO | 0.42 |
| Na ₂ O | 0.62 |
| K ₂ O | 2.36 |
| TiO ₂ | 2.60 |

^aDalare Assoc., Report No. 713-B, 1994. Prepared for Delmarva Power and Light, Wilmington, DE.

2.2. Fly ash treatment:

The surface area of the fly ash was measured (BET: Brunauer–Emmett–Teller method) using nitrogen gas and the Micromeritics Accelerated Surface and Porosimetry System [13]. The effluent (150 ml) was mixed, using an orbital shaker at 200 rpm, with 0, 1, 3 or 6 g of ash in 250 ml flasks for 4 h at $22 \pm 1^\circ\text{C}$ and then filtered using $0.45 \mu\text{m}$ membrane filters. A 4 h reaction time has been reported to be adequate for equilibrium adsorption of Cd and Zn by fly ash [8]. Part of the filtrate was acidified with HNO₃ to pH < 2.0 to preserve the soluble metals [12]. One fourth of the flasks and filters used were treated with HNO₃ (pH 2) after the experiment to check for metal adsorption on the surfaces.

2.3. Analyses

The filtrate (without acidification) was analyzed [12] for pH, reactive phosphorus, nitrate and ammonia; metals (Cu, Pb and Zn) in the acidified filtrate were analyzed using the Perkin Elmer Atomic Absorption Spectrophotometer (Model 1100-B) with a HGA-700 graphite furnace and auto sampler (detection limits for Cu and Pb were 0.02 and 0.05 $\mu\text{g}/\text{l}$) or flame ionization for Zn (detection limit 0.1 $\mu\text{g}/\text{l}$). Toxicity of the effluent samples before and after fly ash treatment was measured using the marine luminescent micro-organism—*Vibrio fischeri*—the ‘Microtox’ test with the Beckman Toxicity Analyzer—Model 2055 [14]. This test has been used in several toxicity studies and is highly reproducible [15,16].

2.4. Desorption test

The fly ash retained on the membrane filter was washed once with deionized water (15 ml) and then mixed with 150 ml of deionized water in a flask as in the treatment step above. The mixture was filtered ($0.45 \mu\text{m}$) and the filtrate was analyzed as above to measure the release (desorption) of pollutants from the ash.

2.5. Statistical analyses

Means of six samples with three replicates each were used for statistical analyses—ANOVA and Duncan’s Multiple Range Test [17].

3. Results and discussion

After treatment with fly ash, the SWTP effluent showed a significant increase in pH, a significant reduction in phosphate (by 88%), Cu (42%) and Pb (85%) (Table 3); nitrate content of the effluent was also reduced by 18%, but ammonia and Zn did not show any change. Fly ash is alkaline in nature; the pH of 100 ml water + 10 g ash was 8.8. Solubility of Cd, Pb and Zn is reduced as the pH becomes more alkaline [7]. The maximum removal of Cu from aqueous solutions by fly ash has also been reported to be pH dependent [5,6]. On treatment of 10–100 mg/l of chloride solutions of various metals, including Cu, Pb and Zn, with fly ash the removal of metals was attributed to adsorption and precipitation [18]. Because of the low concentrations ($\mu\text{g}/\text{l}$ range) of these metals in the SWTP effluent no precipitation was noticed; turbidity measurements also did not show any change. In the acid leachates of the flasks or filters no metal was detected.

The surface area controls the adsorption capacity of solid particles [19]; BET surface area of the fly ash used was $7.97 \text{ m}^2/\text{g}$, which is in the same range as that of Al_2O_3 . The fly ash used in this experiment is rich in silica, alumina and iron oxides (Table 2). Increasing the amount of fly ash (from 3 to 6 g) did not significantly change the adsorption of the pollutants in the wastewater.

Treatment of the SWTP effluent with fly ash (6 g) resulted in almost complete removal of toxicity (Table 4); over 60% reduction in toxicity was observed with only 1 g fly ash. The major reason for this high reduction in toxicity is the removal of Pb from the SWTP effluent; Pb is more toxic than Cu and Zn (Table 1), and almost double the amount of Pb, compared to Cu, was removed.

Table 3
Effect of fly ash treatment on SWTP effluent

| Fly ash (g) | Phosphate (mg/l) | Nitrate (mg/l) | Ammonia (mg/l) | pH | Cu ($\mu\text{g}/\text{l}$) | Pb ($\mu\text{g}/\text{l}$) | Zn ($\mu\text{g}/\text{l}$) |
|-------------|--------------------|------------------|-------------------|-------------------|-------------------------------|-------------------------------|-------------------------------|
| 0 | 4.7 ^a | 4.5 ^d | 19.4 ^g | 7.98 ^h | 20.3 ^k | 13.3 ⁿ | 27.0 ^q |
| 1 | 1.4 ^b | 4.3 ^d | 18.0 ^g | 8.23 ⁱ | 13.0 ^l | 5.0 ^o | 30.0 ^q |
| 3 | 0.97 ^{bc} | 4.0 ^e | 18.4 ^g | 8.33 ^j | 11.7 ^m | 2.0 ^p | 28.7 ^q |
| 6 | 0.57 ^c | 3.7 ^f | 18.9 ^g | 8.37 ^j | 11.7 ^m | 2.0 ^p | 29.0 ^q |

^a Columnwise comparisons; means with the same letter are not significantly different ($p \leq 0.05$).

Table 4
Effluent toxicity changes after fly ash treatment

| Fly ash (g) | Toxicity (EC_{50} %) |
|-------------|--------------------------------|
| 0 | 54.4 ^a |
| 1 | 87.1 ^b |
| 3 | 95.6 ^c |
| 6 | 99.9 ^c |

^a Means with the same letter are not significantly different ($p \leq 0.05$).

Table 5
Desorption of metals from fly ash (treated with effluent) on leaching with water

| Fly ash (g) | Cu ($\mu\text{g}/\text{l}$) | Pb ($\mu\text{g}/\text{l}$) | Zn ($\mu\text{g}/\text{l}$) |
|-------------|-------------------------------|-------------------------------|-------------------------------|
| 1 | 12.0 ^{* a} | 0.5 ^b | 24.7 ^c |
| 6 | 14.0 ^a | 5 ^c | 22.3 ^c |

* Columnwise comparisons; means with the same letter are not significantly different ($p \leq 0.05$).

Leaching of the treated fly ash resulted in some desorption of the heavy metals removed from the SWTP effluent (Table 5). Increasing the amount of fly ash did not result in increasing desorption of Cu and Zn; however desorption of Pb was significantly increased with increasing fly ash concentration. Fly ash, from the same power plant as in this study, has been used for soil amendment [20]; boron and other soluble salts leached rapidly from the amended soil, but only trace amounts of Cd, Cu, Ni, Pb and Zn were detected in the leachate. The absence of toxicity (Table 4) of the SWTP effluent treated with 3 or 6 g ash suggests that little toxic metals (or other compounds) were released from the ash during this treatment.

4. Conclusions

1. The treatment of SWTP effluent with fly ash significantly reduced the amounts of phosphate, nitrate, Cu and Pb.
2. The toxicity of the SWTP effluent is removed on treatment with fly ash.
3. The treatment of the effluent with fly ash did not result in the release of any toxic materials from the ash.

References

- [1] E. Ludy, personal communication, The City of Salisbury Wastewater Treatment Plant, MD, 1996.
- [2] USEPA (US Environmental Protection Agency), Maximum permissible concentrations of various metals in natural waters for the protection of human health, Fed. Register 56(110), 1987, 26460–26564.
- [3] Maryland Register, Annapolis, MD, Nov. 25, 1995.
- [4] C.C. Chou, S.S.Q. Hee, Bioassay driven analysis of chewing tobacco extracts, Environ. Toxicol. Chem. 13 (7) (1994) 1177–1186.
- [5] M.O. Corapcioglu, C.P. Huang, The adsorption of heavy metals onto hydrous activated carbon, Water Res. 21 (9) (1987) 1031–1044.
- [6] K.E. Panday, G. Prasad, V.N. Singh, Copper removal from aqueous solutions by fly ash, Water Res. 9 (7) (1985) 869–873.
- [7] S.E. Manahan, Environmental Chemistry, 6th edn., CRC Press, Boca Raton, FL, 1994.
- [8] C.H. Weng, C.P. Huang, Treatment of metal industrial wastewaters by fly ash and cement fixation, J. Environ. Eng. 120 (6) (1994) 1470–1487.
- [9] R.F. Keefer, K.S. Sajwan, Trace Elements in Coal and Coal Combustion Residues, Lewis Publ., Boca Raton, FL, 1993.
- [10] K.P. Yadava, B.S. Tyagi, V.N. Singh, Fly ash for the treatment of water enriched in lead, J. Environ. Sci. Health A24 (7) (1989) 783–808.
- [11] T. Viraraghavan, G.A.K. Rao, Adsorption of cadmium and chromium from wastewaters by fly ash, J. Environ. Sci. Health A26 (5) (1991) 721–753.

- [12] American Public Health Association, *Standard Methods for Water and Wastewater Analyses*, 18th edn., Washington, DC, 1995.
- [13] ASAP 2010. *Accelerated Surface Area and Porosimetry Systems*, 1994, Operator's Manual, Norcross, GA.
- [14] A.A. Bulich, *Toxicity Screening Procedures Using Bacterial Systems*, Marcel Dekker, New York, NY, 1984.
- [15] R.A. Hoke, J.P. Geisy, R.A. Kreis, Toxicity of sediments and sediment porewaters from Grand Calumet River, IN, *Ecotoxicol. Environ. Safety* 26 (1993) 86–112.
- [16] M.W. Toussaint, T.R. Shedd, W.H. Schalic, G.R. Leather, A comparison of standard acute toxicity tests with rapid screening toxicity tests, *Environ. Toxicol. Chem.* 14 (5) (1995) 907–915.
- [17] SAS Statistics, *Users Guide*, 1985, SAS Institute, Cary, NC.
- [18] N. Gangoli, D.C. Markey, G. Thodos, Removal of heavy metal ions from aqueous solutions with fly ash, 1975, Proc. 2nd Natl. Conf. Complete Water Reuse, Chicago, IL.
- [19] M.R. Schure, P.A. Soltys, D.F. Natusch, T. Mauney, Surface area and porosity of coal fly ash, *Environ. Sci. Technol.* 19 (1985) 82–86.
- [20] M. Ghodarti, J.T. Sims, B.L. Vasilas, Evaluation of fly ash as a soil amendment for the Atlantic Coastal plain, *Water, Air Soil Pollut.* 81 (1994) 349–361.