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Full Length Research Paper

Assessment of total coliform removal and leaching of metal ions from sewage sludge-fly ash mixture at different pH and washing conditions

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Effectiveness of fly ash as a stabilising agent for heavy metals leaching was studied for different ratios of sewage sludge (SS)-fly ash (FA) mixtures at different pH and washing conditions. The supernatant liquid was analysed for total coliforms. The results obtained from the microbiological analysis of 1:1, 4:1, 1:4 sewage sludge and fly ash ratios showed that the initial concentration of total coliforms was 2.4 × 10^4 MPN/100ml, 150 MPN/100ml and 120 MPN/100ml which were finally reduced to 28, 4 and 3 with successive washings. The leachate after shaking of the SS:FA mixture were analysed for heavy metals contents and the results showed that the maximum removal of heavy metals was achieved with SS/FA (1:1) mixture, while Co was absent in all the samples. Out of the three pH conditions (5, 6, 7), it was observed that the maximum removal of different heavy metals was achieved at the lower pH (5) conditions.

Key words: Fly ash, sewage sludge stabiliser, leaching, heavy metals, coliforms.

INTRODUCTION

Sewage sludge (SS) is defined as the insoluble residue produced from the municipal wastewater treatment after aerobic and anaerobic digestion processes. It has been reported that disposal of sewage sludge and its management is a major problem throughout the world. At present, land filling process is practised for disposal and management of sewage sludge; however, the process is used only in a small amount in agriculture due to its limitations. Wong et al. (1999) has reviewed that due to the large amounts of sewage sludge produced daily, landfill is a costly option and inappropriate as a long-term alternative because of the substantial scarcity of landfill spaces. Additionally, the main problems associated with application of sewage sludge include increase in the salt content and toxicity level in the plants due to the presence of heavy metal ions in sewage sludge (McGrath et al., 2000). Several methods such as liquid heat, liming, drying, composting are being practised for the disposal of sewage sludge. It has been reported by De et al. (1983) and Inbar et al. (1983) that composting of sewage sludge would be an appropriate method for the disposal of sewage sludge, eradication of pathogens and to stabilize organic matter by using biological stabilization process. But the presence of high heavy metal concentration in the sewage sludge compost is harmful both for the plant growth as well as for the soil microbial activity. Lime treatment, another method for sewage disposal, is used for reducing the concentration of heavy metals and the microbial community. Lime is able to maintain the high pH due to its physical properties, and hence helping in the removal of microbial communities present in sewage sludge. However, lime application in the sewage sludge stabilization depends upon a number of factors including the time of stabilization, dose of the lime supplied and its associated costs.

This paper analyses how fly ash (FA) could be utilized in the sewage sludge mixture for reduction of heavy metal content. It was observed by Adriano et al. (1980) that the use of fly ash in agriculture can be enhanced by

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blending it with potentially acid-forming organic by-products such as sewage sludge, poultry and cattle manure which are significantly rich in nitrogen and phosphorus. Abbott et al. (2001) has explored the application of NFA (neutral fly ash) with LSB (lime stabilized biosolid mixture) to during AMS (acid mine soil) reclamation. It was found that based on the results of simulated weathering, the combined application of large volumes of NFA with LSB proved an appropriate mechanism for the disposal of NFA and LSB as combustion by-product during AMS reclamation. Fly ash in combination with lime increases the particle size and enhances the heavy metal removal capacity from the aqueous medium. The concentrations of chromium, copper, lead and zinc in effluents can be reduced from initial concentration of 100.0 mg/l to 0.08, 0.14, 0.03 and 0.45 mg/l, respectively. Jusoh et al. (2007) and Kang et al. (2008) showed that activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants from the wastewater. It is mainly used because of its large micropore and mesopore volumes and thus resulting in the high surface area and better adsorption capacity similar to fly ash.

It was observed by Helm (1976) that mixtures of fly ash and sewage sludge along with addition of lime when examined for leaching and physical properties shows lesser leaching of hazardous trace elements such as boron. This observation was supported by Reynolds et al. (2002), who had analyzed the leaching effect, when SLASH (Sewage sludge, Lime and Fly ash) mixture is added into the soil. A growth in variety of plants was observed and also leaching level of 2 to 3 order of magnitude was observed, which is below the legal limit set for the leachate of sewage sludge. Decrease in leaching was observed due to addition of fly ash, which acts as an adsorbent of heavy metals. Sajwan et al. (2003) also observed that mixture of sewage sludge and fly ash when used in soil can prevent leaching of metals and found that a lesser leaching of metal ions took place in the 1:1 FA+SS mixture. Kuchar et al. (2006) investigated the use of hydration products prepared from fly ash as adsorbents in the effluent sludge and found that the adsorbent restricts the long-term prevention of organics dissolution from waste water sludge. Hence fly ash proved as a good adsorbent which prevented organic materials from leaching out from the sludge.

Not only this, lime can be substituted with fly ash for sewage sludge grooming and maintenance and being a waste, the huge costs of lime can be avoided. Therefore, fly ash in mixture with sewage sludge has proved to be a feasible and best management option for removal of heavy metal content from sewage sludge. Fly ash and sewage sludge have also solved disposal problem of the two wastes, when used in landfilling process. It has been observed by Adrino et al. (1980) that fly ash can be used for restoring the degraded soil and is able to increase crop productivity depending on the nature of both soil and fly ash. It may improve the physical, chemical and biological properties of problem soils and increase the available macro and micronutrients for plants. It has also been reported by Sen and De, (1987) and Tadesse et al. (1991) that a change in pH can bring about a change in the metal uptake capacity of plants, that is, a decrease in the metal content by the plant parts was observed as a result of increase in pH causing an increase in the fixation of metals by soil. Ozverdi and Erdem (2006) investigated that lower pH (below 3) was observed to be the best for the removal of heavy metals using the chemical precipitation. It was reviewed by Jamali et al. (2009) that the ash prepared from the hazelnut shell was successful in the of removal cadmium ions from the water solution at different conditions of appropriate equilibrium time, amount of adsorbent used, concentration of adsorbate, pH of the solution and particle size of the sorbent using a batch system. It has been investigated by Badriya et al. (2011) that a number of techniques such as nano-filtration technique and absorption process has proved beneficial for the removal of certain heavy metals such as Cu(II), Cd(II), Mn(II), Pb(II) As(III), and As(V) from aqueous medium. Kersch et al. (2004) observed that residues of fly ash and sewage sludge contain large amounts of heavy metals, which are toxic in nature. These toxic heavy metal pollutes the groundwater after coming in contact with water and it was also investigated that increase in the concentration of Sb in the leachates and decrease in the leachate content of certain heavy metals such as Zn, Pb and Mn after the leachability test. Zeid et al. (2009) reported that whatever precipitating agent is used, vacuum filtration is more efficient in water elimination [total solids: 11-73% (w w^{-1})] than in centrifugation [5-11% (w w^{-1})] from sludge. Vacuum filtration is also helpful in the removal of heavy metal ions from the mixture of fly ash, sewage sludge and soil by the precipitation process from the aqueous medium. The lime is also used in the precipitation process and when combined with the fly ash, it can further increase the precipitation process (Chen et al., 2009b). The objective of this current paper was to investigate the stabilising capacity of fly ash in the leaching of heavy metal ions from sewage sludge-fly ash mixtures into the aqueous medium at different washing and pH conditions.

MATERIALS AND METHODS

Collection and preparation of samples

The digested sewage sludge sample was collected from the Wastewater Sewage Treatment Plant Okhla, New Delhi, (India). At the treatment plant, the sewage sludge goes through different treatment processes including primary and secondary treatment and at the end, the sewage sludge is placed on the sludge drying beds. The collected sample was taken from the drying beds and was tested for the heavy metal contents in the laboratory of Thapar University, Patiala (India). At the laboratory, sewage sludge sample was crushed, homogenized by a high speed blender, sieved and dried in oven at 120°C for five hours. Different standard solutions for metals including Pb, Cd, Co, Ni and Cu were prepared by the

Table 1. Physical analysis of fly ash.

Parameter	Value
Specific gravity (OD)	1.705
Specific gravity	1.785 g/cc
Density	1701 Kg/m^3
Percent Absorption	4.712%
Fineness modulus	7.522

Table 2. Chemical composition of fly ash.

Constituent	Weight (%)
SiO_2	55.78
Al_2O_3	26.22
Fe_2O_3	9.65
CaO	3.25
SO_3	0.15
Na_2O	0.39

Table 3. Metal concentration in sewage sludge (mg/Kg of waste, dry basis).

Metal	Sewage sludge
Iron (as Fe), mg/Kg	14283.93
Manganese (as Mn), mg/kg	199.840
Copper (as Cu), mg/Kg	131.54
Zinc (as Zn), mg/Kg	1908.68
Cadmium (as Cd), mg/Kg	2.75
Cobalt (as Co), mg/Kg	ND
Nickel (as Ni), mg/Kg	35.07
Lead (as Pb), mg/Kg	69.84

ND, Not detected.

analytical grade salt to analyse the heavy metal content with the help of atomic absorption spectrophotometer. The complete description of heavy metal concentrations in the digested sample of sewage sludge are shown in Table 3.

The fly ash sample was collected from the Thermal Power Plant, Panipat. (India) and the sample was dried in oven at 120°C for five hours. At the laboratory, the Physical and Chemical analysis of fly ash sample shown in (Tables 1 and 2) was carried out in accordance with ASTM[1] Standard C618, which is one of the most widely and internationally used method for physical and chemical analysis of fly ash.

Sewage sludge (SS) was mixed with Fly ash (FA) in three different ratios of SS/FA mixtures (1:1, 1:4, 4:1). Three ratios were taken in order to check the leachability of heavy metal ions from different sewage sludge and fly ash mixtures in aqueous medium. Earlier, Zhang et al. (2009) has also worked on four different ratios of 3:1 (A), 2:1 (B), 1:1 (C) and 0.5:1 (D) of SS/FA mixtures in order to investigate the leaching of heavy metals from sewage sludge, by using fly ash as a stabilizing agent. Samples of SS/ FA were prepared taking the solid part as 5g/100ml of distilled water at three different pH conditions (5, 6 and 7). The pH of the aqueous medium was adjusted with the help of HNO_3 (1N) acid and the effect of different pH were studied followed by three washings of the solid matter. The samples were aerated with the help of aerators for 10 h and the supernatant liquid was vacuum filtered through 0.45 µm membrane.

Microbiological analysis

The microbiological analysis of the samples was carried out according to the standard method of the American Public Health Association (MPN test 9221-B, APHA 2005) without any pH adjustment. The samples of SS/FA for microbiological analysis were composed of 5 g/100 ml of distilled water and filtered with a sterile membrane filter (0.45/µm). The supernatant liquid was then tested for the total coliforms. The standard test for the coliform group was carried out by the multiple-tube fermentation technique (MTF). The whole process involved preparation of three series. For first series, three tubes (which include three different ratios of SS/FA) marked as double strength (DS) and filled with 10 ml of double strength Maconkey broth. Rest six tubes of the remaining two series (three tubes of each series contain three different ratios of SS/FA), marked as single strength and added 10 ml of single strength Maconkey broth. Upon preparation of three series, media is sterilized at 120°C for 15 min and then inoculated with 10 ml aliquot of water sample in the three tubes labelled as double strength (first series); 1ml aliquot is added in three single strength tubes (second series) and lastly, 0.1ml aliquot is added in the remaining three single strength tubes (third series). In the last step, all tubes were incubated for 48 h at 37°C (MPN test 9221-B, APHA 2005).

Leaching assay

The solid samples of sewage sludge and fly ash mixtures were assessed for their leaching properties. In general, when solid waste comes in contact with water, the water gets contaminated with solutes (heavy metals) and stream out of the solid waste, which is termed as leachate. At the laboratory, a similar procedure was adopted to identify the leachability characteristics of SS/FA mixture. The 5 g mixture of SS/ FA in the ratio of 1:1, 1:4 and 4:1 were taken and were allowed to mix with 100 ml of deionized water. The samples were placed on rotatory shaker at 120rpm for 10 h. The process was carried out at controlled temperature conditions of 26°C. Afterwards, the samples were allowed to settle down and the supernatant liquid was vacuum filtered with the help of 0.45 µm membrane. Metal contents in the supernatant liquid were analysed with the help of atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The effect of pH was studied using different pH 5, 6 and 7 followed by three subsequent washings of the solid material.

RESULTS

Microbiological analysis

The results obtained from the microbiological analysis are shown in Table 4. After one hour, the supernatant was serially diluted and inoculated in Maconkey broth, as given in materials and methods. The results obtained from the microbiological analysis of 1:1, 4:1, 1:4 SS/FA ratios showed that the initial concentration of total coliforms observed was 2.4×10^4 MPN/100 ml, 150

Table 4. Total coliform removal of the microbial community achieved at different sewage sludge (SS)/fly ash (FA) ratios mixed at different washings.

SS/FA (with different washing)	Mixing time (h)	Total coliform removed
1:1(1)	10	$2.4{\times}10^4$
1:1(2)	10	1200
1:1(3)	10	28
4:1(1)	10	150/100ml
4:1(2)	10	11
4:1(3)	10	4
1:4(1)	10	120Cells/100ml
1:4(2)	10	21
1:4(3)	10	3

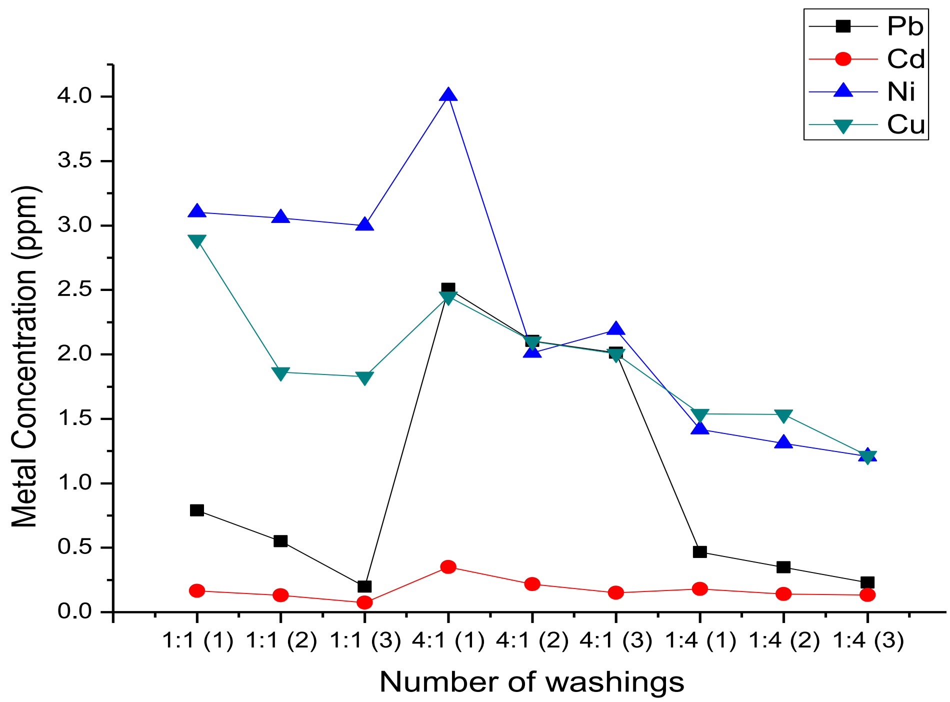

Figure 1. Plots showing metal concentration (ppm) at pH 5 in the leachates to the various SS/FA mixtures at different washings after each mixing for 10 h.

MPN/100 ml and 120 MPN/100 ml, respectively. The concentration of total coliforms gradually decreased in further washings. In second washing, microbial count reduced to 1200MPN/100ml, 11 MPN/100 ml and 21MPN/100 ml while the maximum reduction was observed in third washing which is 28MPN/100ml, 4 MPN/100 ml and 3 MPN /100 ml, respectively. It indicates that MPN count decreases with successive washings.

Leaching of heavy metal ions

The concentration of metal leaching from the various sewage sludge and fly ash mixtures are shown in (Figures 2 and 3). Out of the five selected heavy metals, Co was not detected in any of the mixtures. At pH 5 the maximum removal of lead was observed, that is, 0.790 ppm in 1:1 washing which decreased in second and third wash. A similar trend was observed for cadmium, nickel and copper, whereas, in the case of 4:1 SS/FA ratio, initially the solubility of all the four metals was high as shown in (Figures 1 and 2). In the first wash 2.5 ppm Pb, 4.0 ppm Ni, 2.4 ppm Cu and 0.3 ppm Cd were observed whereas, in second and third washings, a small decrease was observed. Similar trends were observed in the case of 1:4 SS/FA ratio of metal content, except for Cu whose maximum solubility was observed in the first washing. Similar trends were also observed at pH 6 and 7 as

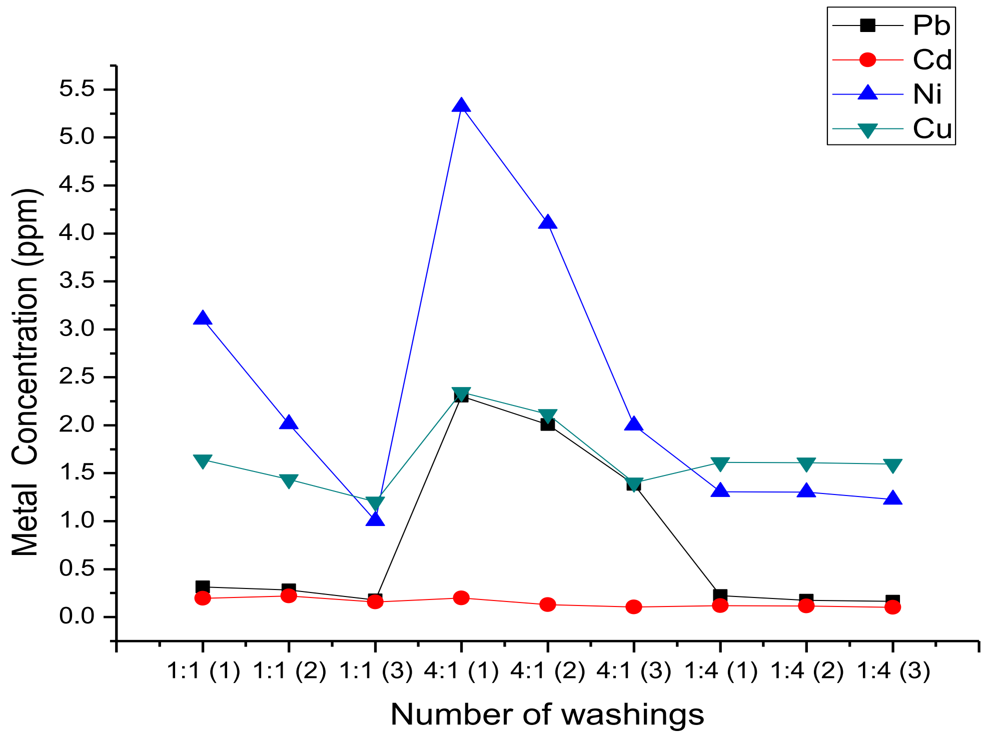

Figure 2. Plots showing metal concentration (ppm) at pH 6 in the leachates to the various SS/FA mixtures at different washings after each mixing for 10 h.

shown in (Figures 2 and 3) where maximum dissolution of Ni, Cu and Pb was observed (1:1) in first washing, whereas in 1:4 ratio of SS/FA comparatively less dissolution was observed. This trend indicated that the metal concentration from leaching decrease with increase in the concentration of fly ash content for a given washing. Hence, it can be concluded that fly ash is able to retain the heavy metals and prevent the leaching of heavy metals from entering the sub-soil water table. Another observation, which can be drawn from the (Figures 1 to 3), is that the tendency to retain heavy metal ions from release into the environment is more effective after third wash of sewage sludge and fly ash mixture. Our results also show that maximum efficiency was observed in 1:1 ratio of sewage sludge mixture and fly ash.

DISCUSSION

The results obtained from the microbiological analysis of SS/FA mixtures in proportions of 1:1, 4:1, 1:4 showed reduction of total coliforms from the initial concentration of 2.4×10^4 to 28 MPN cells/100 ml, 150 to 4 MPN cells/100 ml, 120 to 3 MPN cells/100 ml, respectively in successive washings. No serial dilution of the microbial culture was done. The values of counts of the coliform represent the MPN found in the successive washings of the SS/FA mixture with distilled water taken each time. Similar results were reported for the removal of total coliforms on washing of SS/FA mixtures Papadimitriou et al. (2008). The addition of fly ash to sewage sludge not only reduces the total coliform population present in the sewage sludge but it has also been proved helpful in minimizing the leaching of metal from the sewage sludge (Zhang et al., 2009). Wang and Viraraghavan, (1997) reported that addition of fly ash to the sewage sludge is beneficial in reduction of harmful pathogens up to 93.5%. Wang and Viraraghavan, (1998) has also found that fecal coliforms were reduced up to 100% when fly ash was mixed with dewatered primary sewage sludge in different ratios of 1:1, 1:2 and 1:3 (FA/SS). Incorporation of these two components (Fly ash and sewage sludge) as reported by Wang et al. (2008) increases the efficient environmental friendly management process of these widely produced wastes. Using SS/FA (1:1) mixture the metal removal was achieved in the order Pb (64%), Cd (44%) and Cu (36%). It was found that out of the three different pH conditions (5, 6 and 7) the maximum removal of heavy metals was achieved at the lower pH (5) condition. Eakalak et al. (2009) has also reported that the degree of metal mobility depends on the pH of the

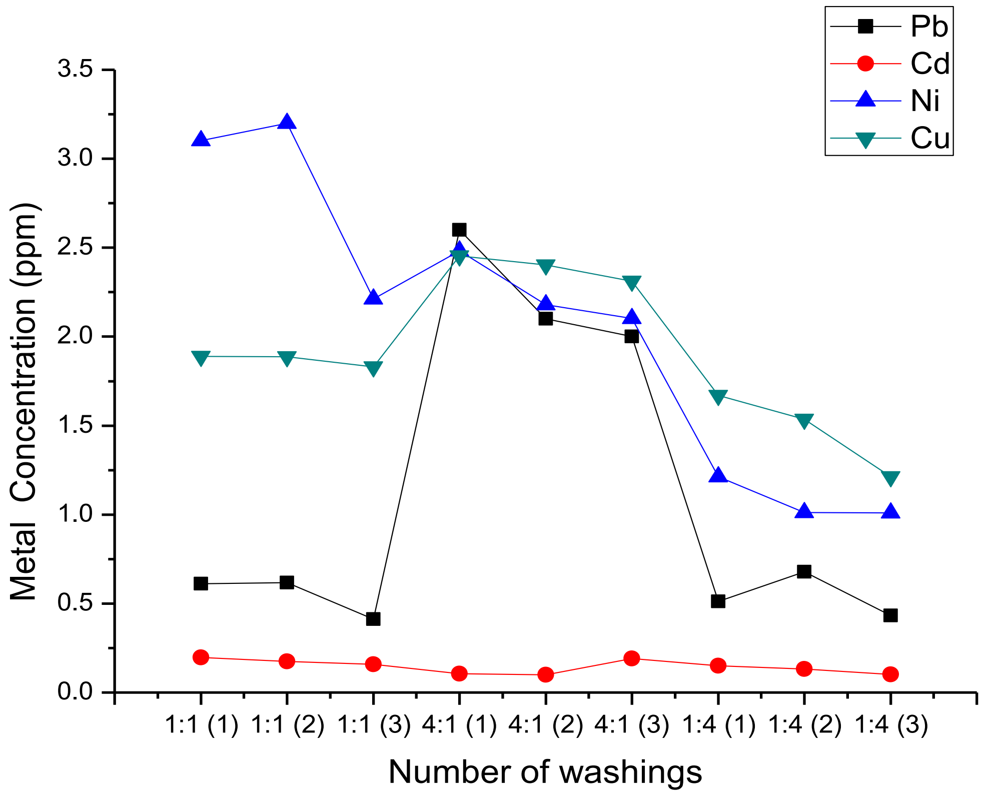

Figure 3. Plots showing metal concentration (ppm) at pH 7 in the leachates to the various SS/FA mixtures at different washings after each mixing for 10 h.

mixture. The above findings of this present study are supported by Alexandre et al. (2008), who had reported better results for the metal adsorption on to chitosan column at pH 5.0 which favoured the use of chitosan in battery wastewater treatment. This result indicated that the solubilization of metals depended on the source of the waste and the pH of the solution. Serpil and Erol (2007) reported that with fly ash and activated carbon, the removal efficiency of Ni and Zn is dependent on pH of the solution and concluded that fly ash was better adsorbent than activated carbon. Maria et al. (2010) reported that advanced removal of metals by fly ash is due to its constituents like silica, alumina, iron oxide and un-burned carbon particles, which increase the heavy metal adsorption efficiency.

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