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Technical Note

Heavy Metal Retention Behaviour of Fly Ashes

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Introduction

Effective waste management requires the protection of ground water resources against potential contamination from the leachates generated by land disposed wastes. In general, waste disposal facilities are lined with impermeable barriers to protect against the migration of leachates into natural water bodies. Clayey soils, due to their easy availability and economic viability, are normally preferred as liner materials for the construction of impermeable liners. It is also known that the clayey soils retain the heavy metal ions due to their surface characteristics (Cherry, 1987; Fetter, 1990 and Kays, 1977). But these soils are not stable when the electrochemical environment changes; for example their permeability will change considerably when exposed to chemical contaminants (Rajasekhar, 1996). Low liquid limit soils have low cation exchange capacity. Hence their permeability does not get affected when exposed to chemical contaminants. Thus, even though low liquid limit soils may serve as good liner materials from permeability criteria, they have the inherent limitation of low retention capacity for heavy metal cations. Hence there is a necessity to increase their retention capacity.

Gray et al. (1988) used bio-mass boiler ash (wood ash) to pre-treat the landfill leachate and observed that the concentration of some of the heavy metals like lead and zinc in the outflow reduced substantially. The ability of wood ash to act as a filter material for lead and zinc ions is the consequence of chemical reactions between wood ash and heavy metal ions (Gray et al.,

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1988). Although, wood ash can be an effective pre-filter material for the retention of heavy metals, it is not available in large quantities as required. Hence, there is a need to find a material, which can retain the heavy metal ions as well as abundantly available. In this study it is proposed to explore the possibility of using fly ash as a pre-filter material for the retention of heavy metal ions. Further, disposal of fly ash itself is a problem in thermal power stations. Hence, if fly ash can be used as pre-filter material for the retention of contaminant cations, to some extent its disposal problem is also solved.

Materials Used

In this study, two fly ashes were examined for possible use as pre-filter materials. These were obtained from Neyveli thermal power plant, Tamilnadu, henceforth called as Neyveli fly ash or as fly ash (N), and from Vijayawada thermal power plant, Andhra Pradesh henceforth called Vijayawada Fly Ash or Fly ash (V). The physical properties of the fly ashes tested are presented in Table 1 and their chemical compositions are given in Table 2 (Pandian and Balasubramonian, 1999, 2000a and 2000b).

TABLE 1 : Physical Properties

Property	Fly Ash (N)	Fly Ash (V)
Atterberg Limits		
Liquid limit (%)*	44	48
Plastic limit (%)	NP	NP
Shrinkage limit	40	42
Specific Gravity	2.67	2.03
Particle size distribution		
Fine sand size fraction	27	4
Silt size fraction	67	89
Clay size fraction	6	7
Compaction Characteristics		
Optimum moisture content (%)	40.0	41.9
Maximum dry density (g/cm3)	1.22	1.00
Surface Area (sqm/g)		
BET method	9.7	0.14
Desiccator method	15	1.5

* By cone penetration method NP: Non Plastic

TABLE 2 : Chemical Compositions of Fly Ashes

Constituents	Fly Ash (N) (% by weight)	Fly Ash (V) (% by weight)
SiO_2	50.97	58.88
Al_2O_3	18.81	29.67
Fe_2O_3	16.61	5.87
TiO_2	0.28	0.27
CaO	9.00	3.03
MgO	1.41	0.24
MnO	0.03	0.02
Na_2O	0.18	0.21
K_20	0.23	0.28
Loss in Ignition	2.48	1.53
Free lime (part of CaO)	(3.92)	(0.22)

Since lead and zinc ions are abundantly present in most of the industrial landfill leachates as well as are very toxic in nature, they are considered as contaminant cations for the present problem. Only analytical grade reagent chemicals were, used for chemical analysis in the present study. AR grade lead chloride was marketed by Fluka Company, Switzerland, and AR grade zinc chloride was marketed by Merck Company, Germany.

Test Procedure

To study the effects of concentration of cation, duration of reaction time and pH of the leachate on the retention characteristics of fly ash, experiments were conducted on both fly ash (N) and fly ash (V) in the presence of lead or zinc ions in solutions using the accelerated process method (Rajasekhar, 1996). Five grams of each fly ash were put into a number of conical flasks and one thousand ml of pH 5.0 lead or zinc solution of various concentrations added to these Samples. These samples were agitated for a minimum of 72 hours to reach the equilibrium conditions. (72 hours equilibration time has been established (Rajasekhar, 1996) as the time required for the reactions to be completed and is explained in the next paragraph). Representative samples of the supernatant solution were taken out periodically and analyzed for the lead or zinc ions. The difference between the initial and the final concentrations of the ion gives the amount of ions retained by the fly ash. The results are expressed as the amount of ions retained as a function of the initial concentration of the solution.

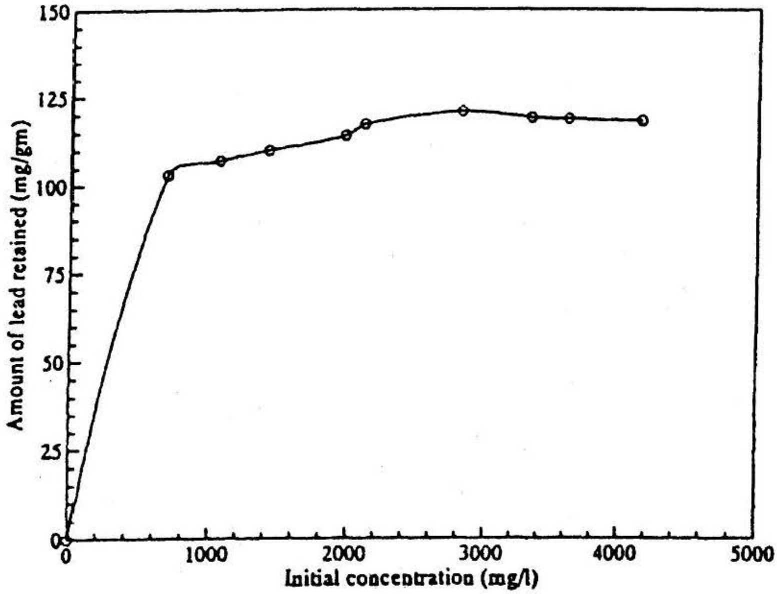

FIGURE 1(a) : Retention of Lead by Fly Ash (N) as Affected by Initial Concentration

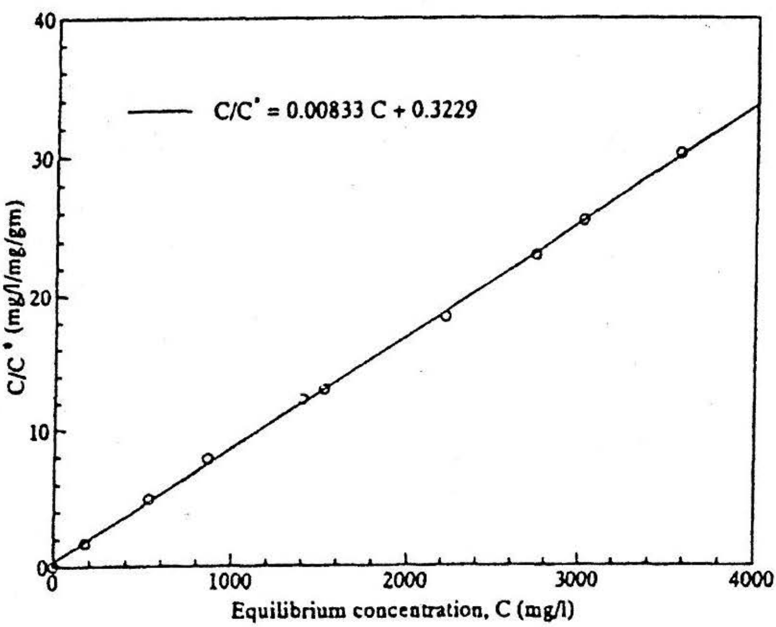

FIGURE 1(b) : Langmuir Adsorption Isotherm for Lead Adsorbed by Fly Ash (N)

To study the effect of the duration of reaction time on the retention characteristics of the fly ash, experiments were conducted on both the fly ashes in the presence of lead and zinc ions at a concentration of 28 meq/l. This is the concentration established (Rajasekhar, 1996) from experiments as the optimum concentration at which fly ash retains the ions to its maximum capacity. A known amount (5 g) of fly ash was taken into a conical flask and one thousand ml of lead or zinc solution at various initial pH conditions added to these samples. These samples were kept on a mechanical shaker for continuous agitation for the reactions to take place. Representative samples of the supernatant solution were taken out periodically and analyzed for lead or zinc. The difference in the initial and the final concentrations of the ion gives the amount of ions retained by the fly ash which is presented as a function of reaction time.

To study the effect of pH of the leachate on the retention characteristics of fly ash, experiments were conducted on both the fly ashes in the presence of lead or zinc solutions at various (initial) levels of pH. Five grams of fly ash was taken into a conical flask. Thousand ml of inorganic cationic solution was added. The samples were placed on a mechanical shaker and agitated for 72 hours for the reactions to be completed. At the end, the pH of the suspension was measured. 'Me samples were filtered through no.41 Whitman filter paper. The filtrate was analyzed for the lead or zinc ions. The amount of metal ion retained by the fly ash is calculated as the difference between the initial and the final concentrations in the solution. The percentage of retention is expressed as a function of pH.

Results and Discussions

Fly Ash

Figure 1a presents the amount of lead retained by the fly ash (N) as a function of the initial concentration of lead. It can be observed from the figure that the amount of lead retained by the fly ash increases to a maximum and remains constant with further increase in the initial concentration of lead. The shape of the curve suggests that the variation of retention of lead by fly ash is similar to Langmuir's adsorption isotherm. The Langmuir adsorption isotherm equation is given by (Gregg, 1961 and Fetter, 1990)

$$C/C^* = 1/ab + C/b$$

where C = equilibrium concentration of the ion (mg/l)

C^* = amount adsorbed per unit weight of fly ash (mg/g)

a = adsorption constant related to the binding energy and

b = maximum adsorption for the fly ash

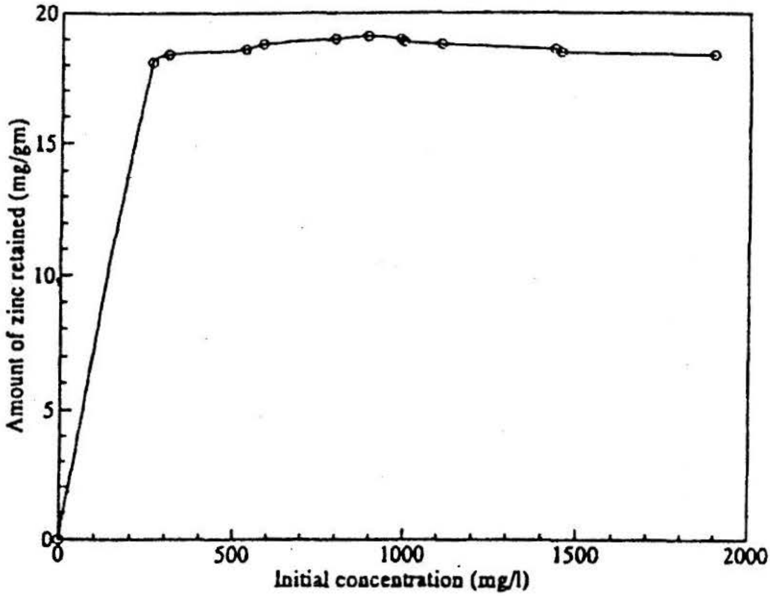

FIGURE 2(a) : Retention of Zinc by Fly Ash (N) as Affected by Initial Concentration

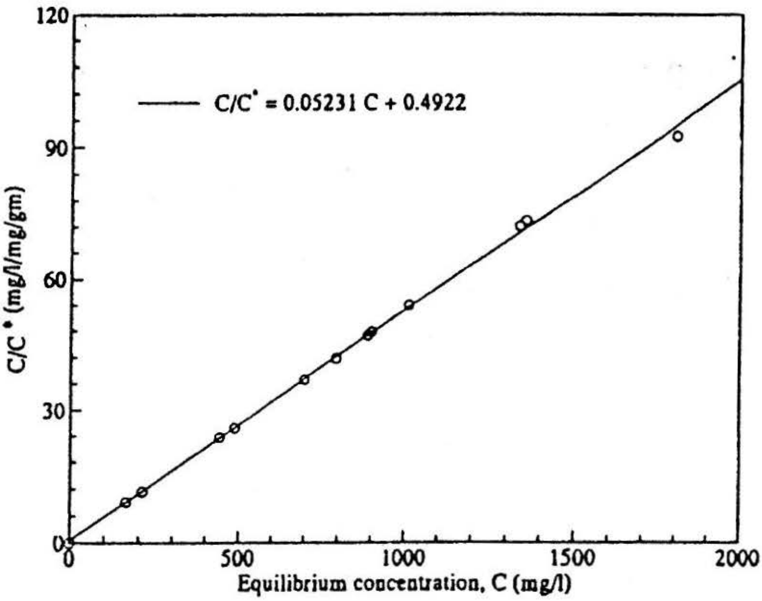

FIGURE 2(b) : Langmuir Adsorption Isotherm for Zinc Adsorbed by Fly Ash (N)

When the adsorption isotherm is plotted according to the Langmuir's adsorption equation (i.e. C/C^* vs. C) (Fetter, 1990), it gave a straight line of slope 0.00833 (Fig.1b). The inverse of the slope (=120) for the isotherm is the parameter 'b' which gives the amount of maximum adsorption of lead by fly ash (N). Corresponding to this maximum adsorption of 120 mg/g, the initial concentration is seen to be 2900 mg/l (Fig.1a).

Similarly, Fig.2a presents the variation of the amount of zinc retained by fly ash (N) as function of the initial concentration of the zinc ions. It can be observed from the figure that the zinc retained by the fly ash increases to a maximum and remains constant with further increase in the initial concentration of the zinc ions. When this data was plotted using the Langmuir equation, it yielded a straight line of slope 0.05231 (Fig.2b). The inverse of the slope gives a value of the maximum adsorption of' zinc by fly ash (N) to be 19.1 mg/g. Using this maximum adsorption, the corresponding value for the initial concentration is obtained from Fig.2a as 920 mg/l.

It can be observed that the values (in mg/l) of initial concentration for the different ions at which their adsorption by the fly ash is maximum are different when these concentrations are expressed in mg/l. Since these two ions are possessing different atomic weights, the concentrations should be expressed in milliequivalents per litre (meq/l) in order to normalize the effect of atomic weight. The normalized minimum initial concentration values for lead and zinc ions, at which maximum adsorption by fly ash occurs are, approximately equal to 28 meq/l and are independent of cation types.

Fly Ash (V)

Figures 3a and 4a present the adsorption isotherms for lead and zinc for fly ash (V). It can be observed from Fig.3a that the shape of the isotherm is similar to that observed for lead adsorption by fly ash (N). The only difference is that the amount of lead adsorbed by fly ash (N) is more compared to fly ash (V). This is because of the low specific surface and low cation exchange capacity of fly ash (V). Figure 3b presents the Langmuir adsorption isotherm for lead adsorption by fly ash (V). The slope of the line is 0.10522. The inverse of the slope gives the value of maximum adsorption of lead by fly ash (V) as 9.5 mg/g. Based on this, the initial concentration required for lead solution corresponding to the maximum adsorption can be seen from Fig.3a to be 2900 mg/l.

Similarly, Fig.4a presents the amount of zinc ions retained by fly ash (V) on variation of concentration of zinc ions applied. This also follows a similar shape observed for fly ash (N). When the data was plotted as per Langmuir adsorption isotherm equation, it yielded a straight line of slope

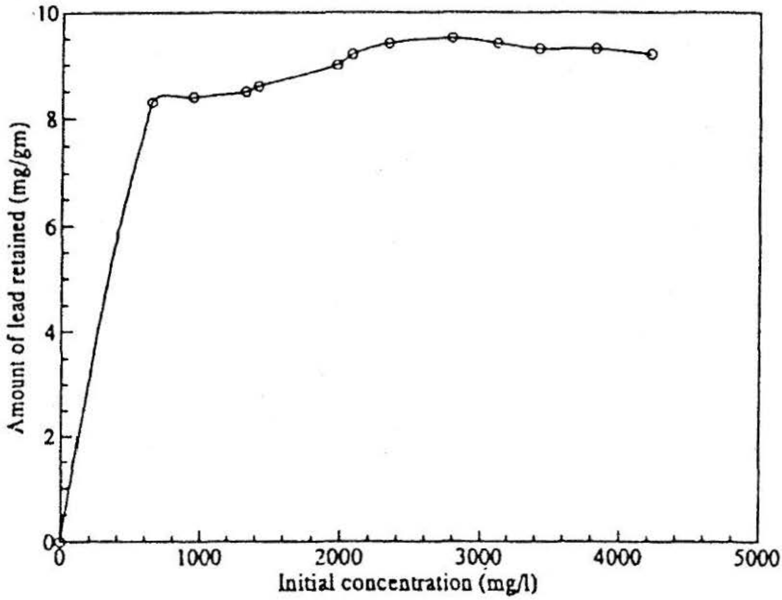

FIGURE 3(a) : Retention of Lead by Fly Ash (V) as Affected by Initial Concentration

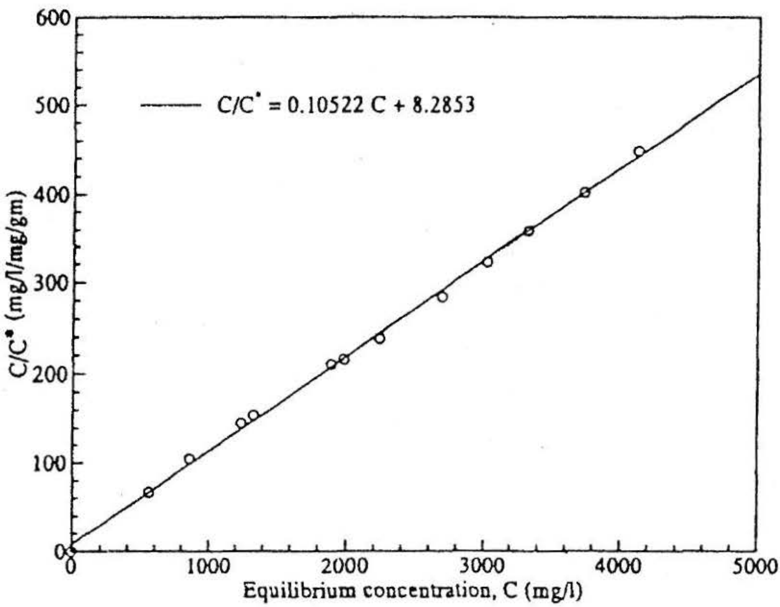

FIGURE 3(b) : Langmuir Adsorption Isotherm for Lead Adsorbed by Fly Ash (N)

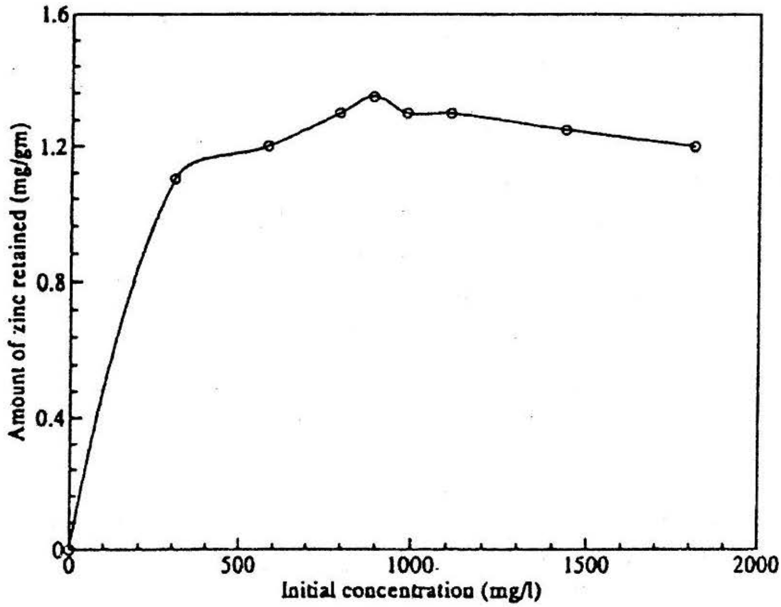

FIGURE 4(a) : Retention of Zinc by Fly Ash (V) as Affected by Initial Concentration

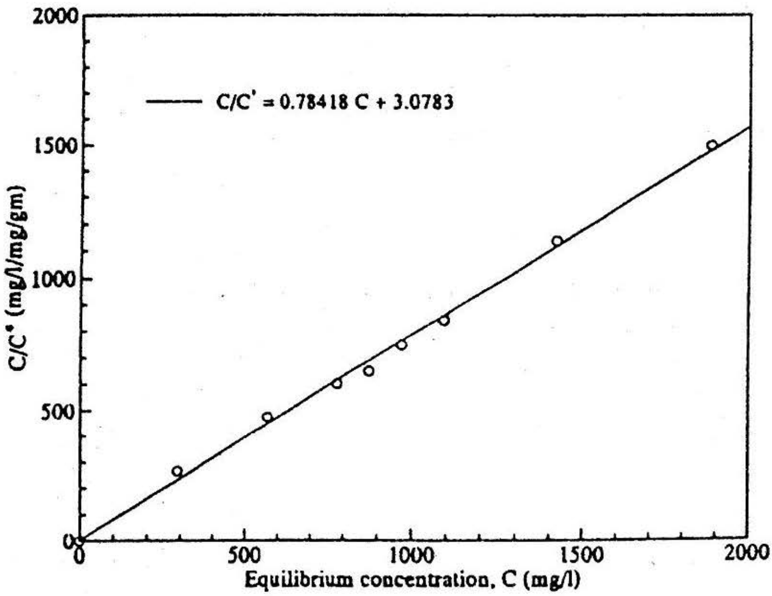

FIGURE 4(b) : Langmuir Adsorption Isotherm for Lead Adsorbed by Fly Ash (V)

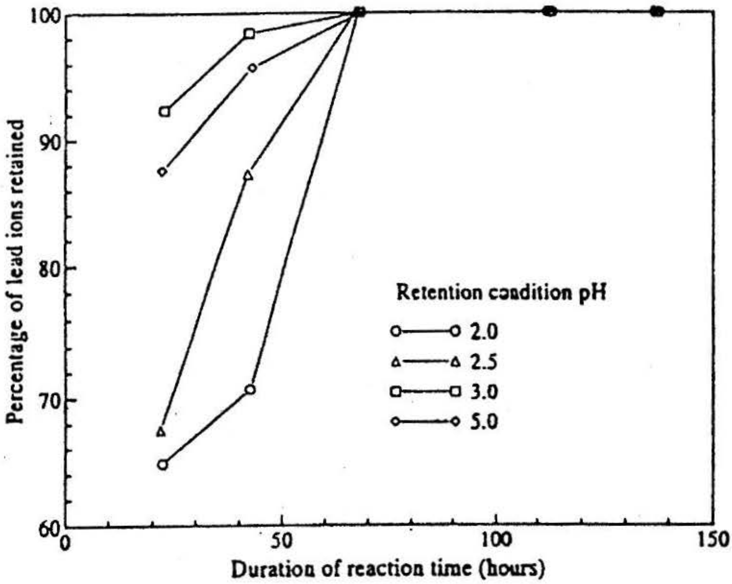

FIGURE 5 : Percentage of Lead Ions Retained by Fly Ash (N) as Affected by Duration of Reaction Time

0.78418. In this case, the initial zinc ion concentration is obtained as 920 mg/l, which corresponds to the maximum adsorption (Fig.4b) of 1.29 mg/g.

From the above results, the minimum initial concentration of lead and zinc ions required for both the fly ashes to retain maximum quantity of lead or zinc ions is estimated to be approximately 28 meq/l, as has been noted earlier for fly ash (N).

Duration of Reaction for Fly Ashes

Time is an important factor that influences the retention capacity of fly ash. Since the adsorption process is not instantaneous, it requires a minimum period of time for the adsorption reactions to be completed. This minimum period of time required to reach equilibrium condition is different for different systems. Hence, the equilibrium time for different systems needs be studied separately.

Figure 5 presents the percentage of lead ions retained by fly ash (N) as a function of the duration of reaction time. The experiments were conducted at various initial pH conditions. It can be ob served from the figure that for all the initial pH conditions studied, the equilibrium condition has been reached or the 100 percent of retention is achieved at around 66 hours. Figure 6 presents the percentage of zinc ions retained by fly ash (N) as a function of time. Here, hundred percent retention occurred only after 70 hours. Figures 7 and 8 present the percentage of lead and zinc ions retained by fly ash (V) as a function of time. It can be observed from these figures that maximum retention occurred only after 70 hours. Thus it can be generalised that the equilibrium condition is reached around 72 hours. This is also in conformity with the findings of earlier researchers (Reed and Arunachalam, 1994). Figures 5, 6, 7 and 8 give the percentage of the metal ions retained by fly ashes at various initial pH conditions. It can be observed from the figures that in all the cases, hundred percent retention for the material was achieved in less than 72 hours. Hence it can be concluded that a duration of 72 hours of reaction time is sufficient to reach the equilibrium conditions.

Summary and Concluding Remarks

The main aim is to study fly ash as a possible pre-filter material to retain the contaminant cations. The capacity of fly ash to retain the contaminant ions is found to depend on the type of fly ash, ion concentration, pH of the ionic solution and duration of the reaction time. This paper also reports the experiments conducted in order to find out the minimum concentration required for maximum retention as well as the duration of reaction time required for the reactions to be complete.

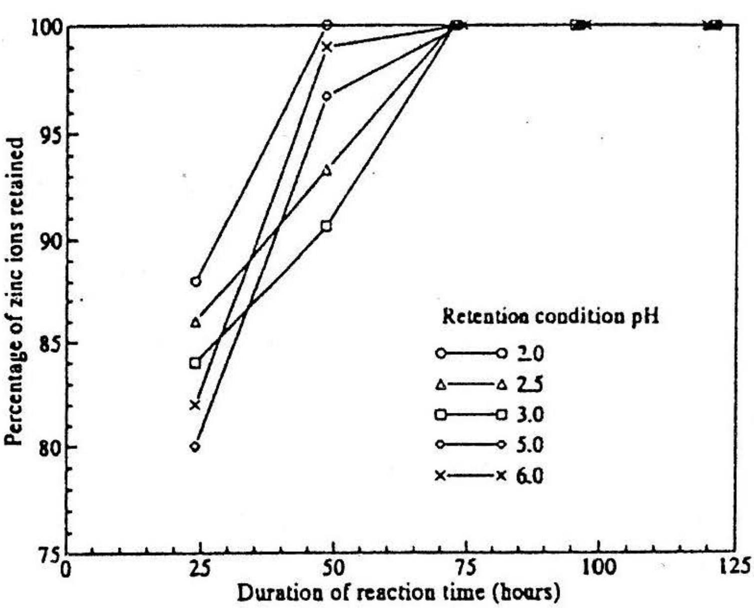

FIGURE 6 : Percentage of Zinc Ions Retained by Fly Ash (N) as Affected by Duration of Reaction Time

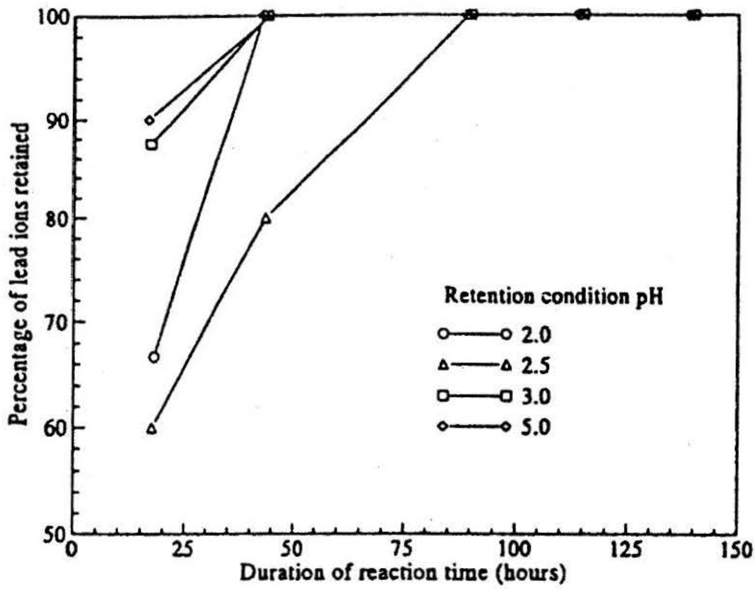

FIGURE 7 : Percentage of Lead Ions Retained by Fly Ash (V) as Affected by Duration of Reaction Time

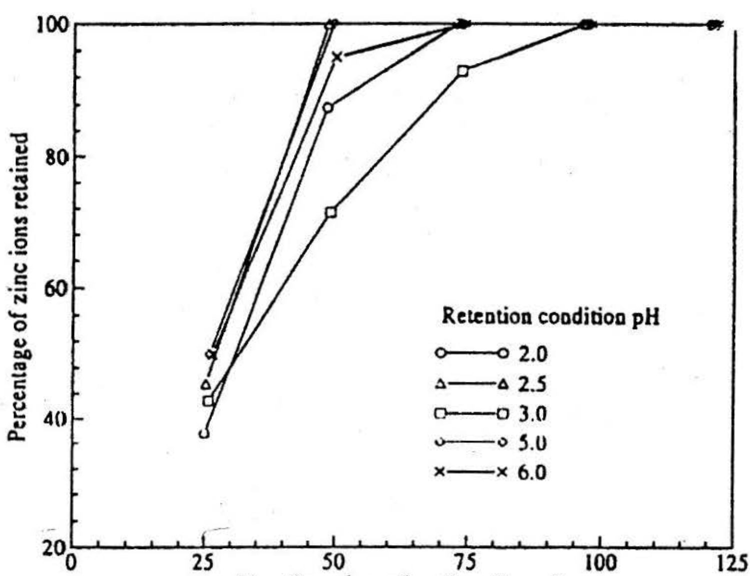

FIGURE 8 : Percentage of Zinc Ions Retained by Fly Ash (V) as Affected by Duration of Reaction Time

The results indicate that the capacity of fly ash to retain ions increases with increase in its initial concentration upto a maximum and remains constant thereafter. This minimum initial concentration of lead or zinc required for maximum retention of the ions by both the fly ashes is found to be 28 meq/l. Hence, the effect of pH of the ionic solution on retention characteristics of fly ash has been and should be studied at this concentration.

Another important aspect, namely the duration of reaction time required for the fly ash to retain metal ions to its maximum capacity (that is, the duration of reaction time required to complete the reaction), is found to be 72 hours.

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