Evaluation of Sorption Behavior of Heavy Metals by Contaminated Soil near a Municipal Waste Dumpsite

G Venkata Ramaiah, S. Krishnaiah, Kotresha.K, P. V. Sivapullaiah

Assistant Professor, Department Of Civil Engineering, Govt. Engineering College, Ramanagara-562159 Karnataka, India, Registrar, J.N.T.U-Anantapur- 515002, Andhra Pradesh, India

SRF, Department Of Chemistry, H.K.B.K College Of Engineering Bangalore, India, Pro Vice Chancellor, Gitam University, Bengaluru Campus, Nagadenahalli-562163, Doddaballapur Tq., Bengaluru Rural District (Former Professor, Department Of Civil Engineering, Indian Institute Of Science, Bangalore-560012)

Abstract: In this study an attempt has been made to understand the sorption behavior of Nickel and Lead ions by contaminated soil amended with different proportions of bentonite and 10% of fly ash with a perspective of using them as barrier materials. Batch equilibrium tests have been carried out at different conditions to understand the adsorption capacities of Mavallipura dump site soil with bentonite and flyash mixtures. Two heavy metals lead and nickel have been used as contaminants; it has been observed that the addition of additives has improved their retention capacity under different conditions like varying dilution ratio, different initial concentration and at different pH's. bentonite was better additives to retain lead than flyash. The retention was of the order 6% bentonite >10% fly ash> 4% bentonite >2% bentonite > soil alone, for soil with flyash was found to be a better material to retain nickel than bentonite; the reason being flyash contains Al and Fe which act as good adsorbents for nickel

Keywords: Adsorption, Heavy metal, Containment, Batch adsorption, Contaminated soil, Fly ash, Bentonite

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I. INTRODUCTION

Toxic heavy metals which are discharged from various industries, such as electroplating, mining, metal finishing and storage batteries, printing, painting, dying, insect controls etc., on the ground and subsequently to the ground water [1, 2]. Heavy metal toxicity is dangerous to human health and to entire ecosystem even at very low concentration leading to serious environmental problems. [3-5]. Heavy metals, such as Lead, Iron, Nickel, Zinc, Copper and Chromium are more commonly seen in numerous kinds of industrial and municipal waste and later in landfill leachates. Leachate characteristics are highly variable from acidic to alkaline in nature and the adsorption of the metals present in the leachate on to soil can be considerably vary further with type of soil as well as any amendment made to soil [6]. In order to assess the long-term accumulation of metal ions which are present in leachate by any soil which are susceptible for contamination by the landfill leachate such as those present near landfill sites. It is necessary to establish the adsorption characteristics of different metal ions with respect to initial concentration of the metal and soil leachate ratio [7, 8]. Generally batch tests are conducted to establish the adsorption characteristics. Further the assessment of adsorption capacities of soils is useful to identify appropriate type of soil for selection of soil liners for barrier construction for landfills [9, 10]. Generally most natural soils cannot meet the requirements of barrier material and amended most commonly with bentonite or with waste materials such as fly ash [3, 11]. An attempt is made in this paper to assessment of adsorption characteristics of local soil near a municipal dumpsite as they are prone for contamination and by soil amended with varying amounts of bentonite or fly ash. Particular attention is made to assess their adsorption capacities with respect to Lead and Nickel ions which are more common in both industrial and domestic solid wastes. The role of different components of barrier materials is summarized below:

Soil used

II. MATERIALS AND METHODS

The soil used in this work has been collected from Mavallipura Dumpsite soil (MPS) near Bangalore, India by open excavation at a depth of 1 meter from the natural ground level. The soil was dried and passed through IS 425-micron sieve to carry out different tests.

Stock solutions of Lead and Nickel

Metals salt solutions were prepared by dissolving a known quantity of lead nitrate in distilled water to represent lead; similarly nickel nitrate crystals were dissolved in distilled water to represent nickel. pH alterations were allowed using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH).

Adsorption Studies

The sorption of Nickel and Lead on to soil bentonite and soil fly ash mixtures were determined by conducting batch equilibrium tests at three different operating conditions, i) at different soil to liquid ratio and ii) at varying initial concentration of metal solution. iii) at varying pH

About 5 grams (oven-dried basis) of the weighed air-dried sample was placed into the appropriate container. The samples were weighed to an accuracy of a milligram. Samples with S/L ratios of 1:5, 1:10, 1:15, 1:20, 1:25, 1:50, 1:75, and 1:100 were prepared with distilled water and then placed on shaker. It was agitated continuously for 24 ± 0.5 h at 29 ± 2 r/min at room temperature ($22 \pm 5^{\circ}$ C), and then stock solution of Lead or Nickel was added proportionally to all samples so that the final S/L ratios obtained are 1:10, 1:20, 1:30, 1:40, 1:50, 1:100, 1:150, and 1:200 with same concentration of 100 mg/l and in all the containers and again shaken for 24 hours. The samples were then removed, filtered. After a clear solution has been obtained, an aliquot was placed in an appropriate container, and analyzed or stored in a refrigerator at $4 \pm 2^{\circ}$ C until the analysis. For different initial concentration and for different pH tests the procedure will be the same but maintaining a constant S/L ratio of 1:20 in all the containers [13].

III. RESULTS AND DISCUSSION

Adsorption of metal ions of Nickel or Lead at Different Dilution Ratios:

It can be observed from the fig 1. The highest sorption coefficient was obtained for a mixture of soil with 6% bentonite. It varied from 1.0mg/g to 5.5mg/g of soil. At very low dilution ratio of 1:20 the sorption coefficient was 5.5mg/g which was highest and with a dilution ratio of 1:150, the sorption coefficient was lowest at 1.0 mg/g. This shows that dilution ratio and sorption coefficient were inversely related. At very low dilution ratio the competition for adsorption sites between different cations was low hence maximum sorption took place.

It can also be observed that the adsorption behavior of all the mixtures was uniform with respect to concentration, although the degree of adsorption differs from material to material. Ni^{2+} exhibited good adsorption with soil fly ash mixture, adsorption and precipitation behavior of Ni^{2+} in soils is controlled by a variety of factors like redox potential, oxidation state, pH, soil minerals, competing ions and complexing agents. Soil with 6% bentonite gave maximum adsorption followed by 4% bentonite, 10% fly ash, 2% bentonite and soil alone. Adsorption of nickle normally takes place on Fe and Al oxides.



Fig.1 Sorption behavior of nickel for various mixtures of soil at different dilution:

It can be observed from the fig. 2 the highest sorption coefficient was obtained for a mixture of soil and 6% Bentonite. It varied from 1mg/ g to 7mg/g of soil. At very low dilution ratio of 1:20 the sorption coefficient was highest at 7mg/g and with a dilution ratio of 1:100, the sorption coefficient was lowest at 1.0 mg/g. Pb^{2+} exhibited good adsorption with 6% bentonite undergoes maximum adsorption followed by 10 % fly ash , 4% bentonite and soil alone, followed by 2% bentonite.



Fig. 2 Sorption behavior of Lead for various mixtures of soil at different dilution ratio

It can be seen from Fig.1 and 2 that the the amount of nickel or lead adsorbed by soil amended with bentonite is more than retained by soil with fly ash. This is confirmation that the essential mechanism of retention by fly ash is by precipitation where the main mechanism of retention of soil with bentonite is by physical sorption and /or by cation exchange. The retention of both metal ions by soil increases substantially by inclusion of bentonite in the soil which increases with increase in bentonite content. However increase in the bentonite content beyond 4% is not beneficial. It also known that only minimum amount of bentonite is enough to favorably modify geotechnical properties. In fact increase in the bentonite beyond optimum level may also affect the geotechnical properties adversely.

Adsorption of single metal ion Lead or Nickel at varied initial concentration:

From Fig3 and Fig 4, it can be seen that as the concentration goes on increasing, adsorption also increases. The increase is almost linear with increase in the concentration of metal ion solution. It was also observed that soil bentonite mixtures have given maximum adsorption compared to other mixtures at any given concentration. It can be observed that the retention in almost linear with increase in initial concentrations. It is observed that amount of sorption of Ni or Pb by soil alone is less compared to the amended mixtures and it is about 0.5 mg/g of soil. The sorption of metal ions by all bentonite mixtures with initial concentration of 10 mg/l is almost same. However, beyond 10 mg/l of initial concentration, considerable differences in sorption behavior are seen [14]. Soil with 4% bentonite sorbs higher amount of Nickel and with 6% bentonite sorbs higher amount of Lead. The huge difference in amount of sorption by soil bentonite and soil with fly ash reveals that the sorption of bentonite which is essentially due to higher Cation Exchange Capacity (CEC) value of the bentonite and it has got excellent sorption properties and possesses sorption sites available within its interlayer space, and the sorption of fly ash not by CEC, only by precipitation.



Fig. 3 Sorption behaviour Lead on different mixtures of soil with change in initial concentration



Fig 4 Sorption behavior of different mixtures of soil with change in initial concentration of nickel

pH dependent adsorption characteristics of soil with additives on addition of Lead or Nickel solution

pH dependent adsorption studies were carried out at a pH range of 4 to 12. In order to maintain the pH 0.1 N HCl and 0.1 N NaOH was used, since fly ash and bentonite were used as additives neutralization reaction was bound to occur between acid and base. In order to prevent this, contaminant solution was prepared and its pH was adjusted to the required value and then the adsorbent was added. This method mimics the field condition as the leachate which flows on liner will be having a certain pH which can be acidic, neutral or basic. It can be observed that soil with bentonite has adsorbed the maximum when compared to other mixtures, followed by fly ash mixtures. It can also be observed that soil with different percentages of flyash had adsorbed less than bentonite. From the fig 5 the max adsorption of lead occurred at higher pH with 6% bentonite.Also from Fig 6 the max adsorption of nickel occured at higher pH with 10% fly Ash .



Fig.5 pH dependent adsorption of lead on soil and its mixtures



Fig. 6 pH dependent adsorption of Nickel on soil and its mixtures

CONCLUSIONS

Based on detailed studies carried on the sorption of Lead and Nickel at different initial concentrationsat varying pH concentration and at different soil to liquid ratios by soil with bentonite and fly ash the following conclusions are drawn.

- 1) Inclusion of fly ash or bentonite enhances the retention capacity of local non swelling soil.
- 2) The increase in the retention capacities by fly ash and bentonite are through different mechanisms.
- 3) The retention of metal ions by soil with fly ash is essentially through precipitation of metal ions with increased pH due to alkaline nature of fly ash.
- 4) The retention of metal ions by soil with bentonite is by physical sorption due to large specific surface of bentonite and by cationic exchange due to its high cationic exchange capacity.
- 5) With both fly ash and bentonite optimum retention is at a solid liquid ratio of about 1:100.
- 6) The retention of both the metal ions studied increases with increase in the concentration of metal ions almost linearly in the ranges of concentrations of metal ions studied.
- 7) At different initial concentrations and at different soil to liquid ratios, soil Fly ash mixture with 10 % Fly ash sorbs the highest amount of nickel and whereas soil bentonite mixture with 4% bentonite sorbs higher amount of Nickel and with 6% bentonite sorbs higher amount of Lead.

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