Influence of lead and copper on behavioural changes of compacted bentonite

Saswati Rayi), Anil K. Mishraii), and Ajay S. Kalamdhadiii)

i) Research Scholar, Department of Civil Engineering, Indian Institute of Technology, Guwahati - 781039, India
ii) Associate Professor, Department of Civil Engineering, Indian Institute of Technology, Guwahati - 781039, India
iii) Professor, Department of Civil Engineering, Indian Institute of Technology, Guwahati - 781039, India

ABSTRACT

In the garbage disposal site, a liner is installed to prevent contaminant migration and reducing the groundwater and surrounding environment getting polluted. Due to chemical stability, high swelling capacity, high specific surface area, low hydraulic conductivity, and high cation exchange capacity, bentonite clay is utilized as a liner material in the disposal site to stop the contamination of the surrounding environment. However, chemicals present inside the landfills may affect the liner properties. This investigation was carried out to determine the influence of heavy metal solution on the change in properties of compacted bentonite. In this study, the sorption and hydraulic conductivity of lead (Pb$^{2+}$) and copper (Cu$^{2+}$) were studied on the bentonite clay at an initial concentration of 100 and 1000 mg/L. Test parameter like pH, initial metal concentration, contact time, and agitation speed was examined. The results showed that the sorption capacity of the bentonite increased with a rise in the initial concentration of heavy metals. For an initial concentration of 1000 mg/L, the removal percentage for Pb$^{2+}$ and Cu$^{2+}$ was found to be 90.68 and 72.178, respectively. The outcome also reveals that the hydraulic conductivity value of the bentonite raised with the rise in Pb$^{2+}$ and Cu$^{2+}$ concentration.

Keywords: bentonite; liner material; heavy metal; sorption; hydraulic conductivity

1. INTRODUCTION

Due to the rapid growth in population, waste generation surges to many folds. Waste generated from various industries like mining, petrochemical, paint, smelting electroplating, etc. comprises a large quantity of heavy metals. Heavy metals are potentially toxic and non-biodegradable and can have a severe impact on human health and the ecosystem. As per WHO standard, for drinking water, 2 mg/L and 0.05mg/L are considered as permissible limits for Pb$^{2+}$ and Cu$^{2+}$, respectively (Baylan and Meriçboyu, 2016).

The method adopted for the disposal of waste by various countries is landfilling. At the bottom of the landfill, a liner is placed to prevent the migration of pollutants. The significant role of the bentonite clay as a liner material has been illustrated in numerous studies by various researchers (Ray et al., 2021a; Ray et al., 2021b; Ray et al., 2019). Bentonite Clay is low-cost and effective adsorbent and has high potential because of its high chemical stability, high montmorillonite mineral content, low permeability, high specific surface area, and excellent sorption capacity (Kul and Koyuncu, 2010, Ray et al., 2020).

Numerous studies related to adsorption and hydraulic conductivity on various clay minerals are reported in the literature. Li (2003) examined the adsorption tendency of lead, copper, and cadmium ions and their combination on kaolinite clay and concluded that binary and ternary ion solution showed lower sorption capacity compared to single ion solution on to the kaolinite clay. A study reported by Lo et al. (2004) on the migration of Pb, Zn, Cd ions in the saturated sand, and bentonite soil admixture concluded that hydraulic conductivity raised to six orders of magnitude greater for compacted saturated sand as compared to bentonite soil admixture. Thammathiwat and Chimoye (2010) studied the impact of monovalent, divalent, and trivalent salt solutions on hydraulic behaviour and swelling of geosynthetic clay liners (GCL) and reported that for similar concentration, divalent and trivalent cation solutions show less swelling and higher hydraulic conductivity value as compared to monovalent cations. Xue et al. (2012) investigated the influence of KCl, NaCl, MgCl$_2$, and CaCl$_2$ on the hydraulic behaviour of GCL materials. They concluded that the hydraulic conductivity value of the liner material increased two orders of magnitude when saturated with salt solutions in comparison with water.

Similarly, much work has been done on the removal of lead (Baylan and Meriçboyu, 2016; Deka and Sekharan, 2017), copper (Pawar et al., 2016; Freitas et al., 2017) zinc (Araujo et al., 2013; Olu-Owolabi and Unuabonah, 2010) nickel (Liu and Zhou, 2010; Taha et
al., 2017) by bentonite. However, a combined study of adsorption along with hydraulic conductivity is limited. Adsorption and the hydraulic conductivity are the vital parameters of bentonite clay for its practicality as a liner material in landfill. This investigation aimed to determine the adsorption and alteration of hydraulic conductivity of bentonite in the presence of Pb2+ and Cu2+ at various concentrations. The test results showed that various factors such as pH of the mixture, contact time, agitation speed, type of heavy metal, and various concentration effects the adsorption capacity and hydraulic conductivity of bentonite.

2. MATERIALS AND METHODS

2.1. Characterization of bentonite

Bentonite clay used in this investigation is obtained from Rajasthan, India. The characterization of bentonite used in the present investigation is tabulated in Table 1. The cation exchange capacity of bentonite was determined by following the Ammonium acetate method given by Chapman (1965) and Pratt (1965). The specific surface area (SSA) was found to be 396.3 m²/g by adopting the method given by Cerato and Lutenegger (2002). By following ASTM D4318 (ASTM, 2010), liquid and the plastic limit were determined for the soil. By following ASTM D698 (ASTM, 2012), optimum moisture content, as well as maximum dry density, was analyzed. The specific gravity of the soil was obtained by using Pycnometer as per ASTM D854 (ASTM, 1996). Bentonite and DI were mixed together at the optimum moisture content (OMC). The mixture was then placed inside a desiccator in moisture grade.

| Properties                      | Bentonite |
|---------------------------------|-----------|
| CEC (meq/100 gm)                | 40.2      |
| Na+                             | 20.9      |
| Ca²⁺                            | 15.2      |
| K⁺                              | 2.2       |
| Mg²⁺                            | 1.9       |
| Specific surface area (SSA) (m²/g) | 396.3  |
| Free Swelling (mL/2g)           | 32.5      |
| pH                              | 8.9       |
| Montmorillonite content (%)     | 72        |
| Liquid limit (%)                | 480.0     |
| Plastic limit (%)               | 40        |
| Plasticity index                | 440       |
| Specific gravity                | 2.73      |
| Optimum moisture content (OMC) (%) | 33      |
| Maximum dry density (MDD) g/cm³ | 1.31      |

2.2. Chemicals and solutions

Table 1. Properties of Bentonites.

Stock solution of Pb²⁺ and Cu²⁺ was prepared by dissolving required amount of lead nitrate [Pb(NO₃)₂] and copper nitrate [Cu(NO₃)₂·3H₂O] in deionized (DI) water. From the stock solutions the required concentration of both the metals were prepared. Reagents used in the present study were of analytical grade.

| Major and minor element oxides | Bentonite |
|--------------------------------|-----------|
| SiO₂                           | 48.79     |
| Al₂O₃                          | 18.17     |
| Fe₂O₃                          | 16.16     |
| MnO                            | 0.454     |
| MgO                            | 0.94      |
| CaO                            | 1.20      |
| Na₂O                           | 4.67      |
| K₂O                            | 1.45      |
| TiO₂                           | 2.00      |
| P₂O₅                           | 0.18      |

2.3. Equilibrium batch experiments

The equilibrium batch experiment was carried out as per ASTM (2008). 5 g of bentonite soil was added to 100 mL of various concentration (ranges from 100 - 500 mg/L) of Pb²⁺ and Cu²⁺ solution in a stoppered conical flask of 250 mL. The mixtures were agitated over 24 h at room temperature at pH 5 ± 0.1. pH of the mixture was adjusted by using 0.1 M NaOH and 0.1M HNO₃. To isolate the solid and liquid part, the mixtures were centrifuged at 3000 rpm for 10 minutes. The mixtures were then filtered by using Whatman 42 filter paper and supernatants obtained were analyzed in atomic absorption spectroscopy (AAS). The removal percentage (PR) and adsorption capacity of Cu²⁺ and Pb²⁺ on the bentonite were calculated using the following equations.

\[ q_e = \frac{(C_i - C) V}{m} \]  \hspace{1cm} (1)

\[ PR = \frac{C_i - C}{C_i} \times 100\% \]  \hspace{1cm} (2)

Where, \( q_e \) is the equilibrium capacity of metals adsorbed on the bentonite soil (mg/g), \( C_i \) is the initial concentration of metals (mg/L), \( C \) is the concentration of metals in equilibrium solution (mg/L), \( m \) the mass of bentonite (g), and \( V \) the volume of metal solution (L). All the tests were conducted in triplicate.

2.4. Hydraulic conductivity study

Hydraulic conductivity of the bentonite was estimated by performing consolidation test as per ASTM D2435 (ASTM, 1996). Bentonite and DI were mixed together at the optimum moisture content (OMC). The mixture was then placed inside a desiccator in moisture-
controlled condition for a period of 24 hours so as to obtain uniformly distributed moisture through equilibrium. The sample was furthermore, subjected to compaction, to its maximum dry density (MDD) for post attainment of the equilibrium condition. The compaction was carried out in a consolidation ring of specimen dimensions, 6 cm in diameter and 1.5 cm in height. The whole setup was then placed inside a consolidation frame, submerged in DI water and respective Pb\(^{2+}\) and Cu\(^{2+}\) concentration. Thereafter, a seating pressure of 4.9 kPa was applied to the sample and the sample was allowed to swelling. Once the swelling was completed, progressive pressure, up to a maximum limit of 784 kPa, was applied for consolidating the sample. The reduction in the height and void ratio, as well as the coefficient of volume change \(m_v\) was determined for each pressure increment. The time-settlement curve provided the time required for 90% consolidation \(t_{90}\) and eventually the coefficient of consolidation \(c_v\) (Taylor, 1948). The hydraulic conductivity values \(k\) was determined by using various consolidation parameters. Ray et al. (2019) give a detailed procedure for determination of the parameters.

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH

Figure 1 shows the removal of 1000 mg/L of Cu\(^{2+}\) and Pb\(^{2+}\) at pH ranges from 2-8, with a maximum error of ±0.1. Any deviation in the pH of the mixture was adjusted by using either 0.1 M NaOH or 0.1M HNO\(_3\), depending on whether the pH is deviating to the positive or negative side, respectively, thereby keeping the pH constant during the entire process. The pH greatly influences the adsorption of metals on bentonite. At pH 2, the removal percentage of both the metal was low (Pb\(^{2+}\)- 67.8 %, Cu\(^{2+}\)- 33.7%).

At lower pH, excess metal amount of H\(^+\) ions are present, which competes with metal ions for adsorption site, and consequently, removal percentage of both the metals reduced. With the rise in pH from 3 to 5, the removal percentage of Cu\(^{2+}\) and Pb\(^{2+}\) gradually reaches from 78.8 to 90.5% and 45.7 to 71.4%. pH ranges from 3-5 the mechanism which governs the process is ion exchange. Beyond pH 5, the removal of Cu\(^{2+}\) and Pb\(^{2+}\) was abruptly increased. The removal percentage reached 98.7 % and 99.0 % at pH 8 for Pb\(^{2+}\) and Cu\(^{2+}\) due to the formation of a hydroxyl compound (Barbier et al., 2000). To avoid precipitation of metal ion, pH 5 was chosen for further study.

3.2. Effect of initial concentration

Figure 2 shows the relationship between percentage removal of metal ions (Pb\(^{2+}\) and Cu\(^{2+}\)) and the initial concentration of metals. It shows that the removal of Pb\(^{2+}\) and Cu\(^{2+}\) reduced with the increase in the concentration of the metal ion. With an increase in metal concentration from 100 to 1000 mg/L, the removal percentage of Pb\(^{2+}\) and Cu\(^{2+}\) reduced from 97.5 to 90.68 % and 93.44 to 72.47 %, respectively. At a lower concentration, a huge number of sorption sites are available for adsorption. As the initial metal concentration increases, the more amount of metal ions gets adsorbed at the sorption site and consequently, the removal percentage decreases.

Fig. 2. Effect of initial concentration on bentonite in presence of Pb\(^{2+}\) and Cu\(^{2+}\).

Figure 3 shows the amount of Cu\(^{2+}\) and Pb\(^{2+}\) ion adsorbed on bentonite.

Fig. 3. Amount of Cu\(^{2+}\) and Pb\(^{2+}\) ion adsorbed on bentonite.
Figure 3 illustrates the plot between the amount of Cu\(^{2+}\) and Pb\(^{2+}\) ion adsorbed on bentonite and initial metal concentration. It shows that the adsorption capacity of the bentonite rises with a rise in concentration. With the rise in concentration from 100 to 1000 mg/L, the adsorption capacity rises from 1.94 to 18.07 mg/g and 1.86 to 14.43 mg/g for Pb\(^{2+}\) and Cu\(^{2+}\), respectively. Adsorption of Pb\(^{2+}\) was higher as compared to Cu\(^{2+}\). As the hydrated ionic radius of Cu\(^{2+}\) (4.19 Å) is higher than Pb\(^{2+}\) (4.01 Å), the Pb\(^{2+}\) adsorbed by the bentonite soil is greater as compared Cu\(^{2+}\) (Baylan and Meriçboyu, 2016).

3.3. Effect of contact time

Adsorption Kinetic study was conducted on bentonite at room temperature in the presence of Cu\(^{2+}\) and Pb\(^{2+}\) solution for a time duration ranges from 5 to 200 minutes. In 100 ml of 500 mg/L of metal solutions, 5 g of bentonite was added, and pH was adjusted to 5. Figure 4 shows that with the increase in shaking time, the removal percentage of both the metals increased. Initially, the uptake of both the metal was very fast because a large number of active sites were available in the initial phase. The percentage removal achieved by Cu\(^{2+}\) was 67.52 % within 5 min; however, for Pb\(^{2+}\), it was 83.14 %. The graph also shows that Pb\(^{2+}\) and Cu\(^{2+}\) reach equilibrium within 40 and 120 min.

3.4. Effect of agitation speed

The plot in Fig. 5 shows the relation between agitation speed (0, 50, 150, and 300 rpm) and the removal of metal ions by bentonite at pH 5. It shows that the removal of both the metal upsurges with the rise in agitation speed. The highest removal achieved was 96.24 % for Pb\(^{2+}\) and 84.31 % for Cu\(^{2+}\) at 300 rpm; however, 61.43 and 57.25 % removal were obtained achieved at 0 rpm (without agitation).

3.5. Effect of hydraulic conductivity

The hydraulic conductivity of the bentonite was determined in the presence of Pb\(^{2+}\) and Cu\(^{2+}\). Figure 6 reveals that with the rise in the concentration of Pb\(^{2+}\) and Cu\(^{2+}\), the value of hydraulic conductivity rises. When the metal solutions come in contact with soil, the thickness of the diffuse double layer reduced.
mg/L, the hydraulic conductivity rises. Pb$^{2+}$ and Cu$^{2+}$ show 1.18 and 1.62 times increase in hydraulic conductivity value when the level of concentration rises from 0 to 100 mg/L. However, 4.55 and 9.94 times of rise in concentration was observed with the increase in concentration level to 1000 mg/L for Pb$^{2+}$ and Cu$^{2+}$ respectively.

| Concentration (mg/L) | Hydraulic conductivity (cm/sec) |
|----------------------|---------------------------------|
| DI Water             | 3.10×10^{-10}                  |
| Pb 100               | 3.66×10^{-10}                  |
| Pb 1000              | 1.41×10^{-09}                  |
| Cu 100               | 5.03×10^{-10}                  |
| Cu 1000              | 3.08×10^{-09}                  |

### 4. CONCLUSION

The present work was carried out to determine the impact of Pb$^{2+}$ and Cu$^{2+}$ on various concentrations of bentonite. pH 5 was found to be effective for removal of Pb$^{2+}$ and Cu$^{2+}$. Adsorption capacity of the bentonite was found to be 18.07 and 14.43 mg/g in the presence of 1000 mg/L of Pb$^{2+}$ and Cu$^{2+}$ solution. Pb$^{2+}$ shows higher removal as compared to Cu$^{2+}$. The kinetic study revealed that the equilibrium achieved by 120 and 10 minutes for adsorption of Pb$^{2+}$ and Cu$^{2+}$ on bentonite. Agitation speed influences the removal of Pb$^{2+}$ and Cu$^{2+}$ on bentonite. The result showed that with the rise in the concentration level of metals, the value of hydraulic conductivity increased. The change in hydraulic conductivity of bentonite was more prominent at higher concentrations.

### REFERENCES

1) Araujo, A. L. P. D., Gimenes, M. L., Barros, M. A. S. D. D., & Silva, M. G. C. D. (2013): A kinetic and equilibrium study of zinc removal by Brazilian bentonite clay. Materials Research, 16(1), 128-136.

2) ASTM. (1994): Standard test method for specific gravity of soils, ASTM D854-92, West Conshohocken, PA: ASTM.

3) ASTM. (1996): Standard test method for one-dimensional consolidation properties of soils, D 2435, American Society for Testing and Materials, Philadelphia.

4) ASTM. (2008): Standard test method for 24-h batch-type measurement of contaminant sorption by soils and sediments, ASTM D4646, West Conshohocken, PA: ASTM.

5) ASTM. (2010): Standard test methods for liquid limit, plastic limit, and plasticity index of soils, ASTM D4318, West Conshohocken, PA: ASTM.

6) ASTM. (2012): Standard test methods for laboratory compaction characteristics of soil using standard effort, D 698, American Society for Testing and Materials, Philadelphia.

7) ASTM. (2006): Standard test method for swell index of clay mineral component of geosynthetic clay liners, ASTM D5890-06, West Conshohocken, PA: ASTM.

8) ASTM. (2001): Standard test method for specific gravity of soils, ASTM D1557-96, West Conshohocken, PA: ASTM.

9) Barbier, F., Duc, G. and Petit-Ramal, M. (2000): ‘Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface’, Colloids and Surfaces A, Physicochemical and Engineering Aspects, 166(1-3), 153-159.

10) Baylan, N., and Mericboyu, A. E. (2016): ‘Adsorption of lead and copper on bentonite andgraphed activated carbon in single-and binary-ion systems’, Separation Science and Technology, 51(14), 2360-2368. https://doi.org/10.1080/01496395.2016.1212888.

11) Cerato, A. B., and Lutenegger, A. I. (2002): ‘Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method’, Geotechnical Testing Journal, 25(3), 315-321.

12) Chapman, H. D. (1965): ‘Cation-exchange capacity I. Methods of soil analysis, Part 2, Chemical and microbiological properties’, (methodsofsoilana), 891-901.

13) Deka, A., & Sekharan, S. (2017): ‘Contaminant retention characteristics of fly ash–bentonite mixes’, Waste Management & Research, 35(1), 40-46.

14) Freitas, E. D., Carmo, A. C. R., Neto, A. A., & Vieira, M. G. A. (2017): ‘Binary adsorption of silver and copper on Verde-lodo bentonite: Kinetic and equilibrium study’, Applied Clay Science, 137, 69-76.

15) Inglezakis, V. J., Stylianou, M. A., Gkanztou, D., & Loizidou, M. D. (2007): ‘Removal of Pb (II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents’, Desalination, 210(1), 248-256.

16) Kul, A. R., & Koyuncu, H. (2010): ‘Adsorption of Pb (II) ions from aqueous solution by native and activated bentonite: kinetic, equilibrium and thermodynamic study’, Journal of Hazardous Materials, 179(1-3), 332-339.

17) Li, L. Y. (2003): ‘Multi-component of heavy metal contaminants adsorpvtivity and compatibility onto variable charge clay mineral’, Clay Science, 12(2), 73-80. https://doi.org/10.11362/jcsscylayscience1960.12.73.

18) Liu, Z. R., & Zhou, S. Q. (2010): ‘Adsorption of copper and nickel on Na-bentonite’, Process safety and environmental protection, 88(1), 62-66.

19) Lo I, Luk A, Yang X (2004): ‘Migration of heavy metals in saturated sand and bentonite/soil admixture’, J Environ Eng 130, Special Issue: Waste Containment Barrier Materials, pp 906-909.

20) Olu-Owolabi, B. L., & Unuabonah, E. I. (2010): ‘Kinetic and thermodynamics of the removal of Zn2+ and Cu2+ from aqueous solution by sulphate and phosphate-modified Bentonite clay’, Journal of hazardous materials, 184(1-3), 731-738.

21) Pawar, R. R., Bajaj, H. C., & Lee, S. M. (2016): ‘Activated bentonite as a low-cost adsorbent for the removal of Cu (II) and Pb (II) from aqueous solutions: Batch and column studies’, Journal of Industrial and Engineering Chemistry, 34, 213-223.

22) Pratt, P. F. (1965): ‘Sodium. Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties’, (methodsofsoilana), 1031-1034.

23) Ray, S., Mishra, A. K., & Kalamdhad, A. S. (2021b): ‘Influence of real and synthetic municipal solid waste leachates on consolidation and shear strength behaviour of bentonites’, Environmental Science and Pollution Research, 1-11.

24) Ray, S., Mishra, A. K., & Kalamdhad, A. S. (2021): ‘Adsorption and Hydraulic Conductivity Studies on Bentonite in Presence of Copper Solution’, Journal of Hazardous, Toxic, and Radioactive Waste, 25(2), 06020007.

25) Ray, S., Kalamdhad, A. S., & Mishra, A. K. (2020): ‘Bentonites as a Copper Adsorbent: Equilibrium, pH, Agitation, Dose, and Kinetic Effect Studies’, Journal of Hazardous, Toxic, and Radioactive Waste, 24(1), 04019027.
26) Ray, S., Mishra, A. K., & Kalamhdad, A. (2019): Influence of various concentration of lead on consolidation parameters of bentonite, International Journal of Geotechnical Engineering, 1-7.

27) Taha, A. A., Ahmed, A. M., Abdel Rahman, H. H., Abouzeid, F. M., & Abdel Maksoud, M. O. (2017): Removal of nickel ions by adsorption on nano-bentonite: Equilibrium, kinetics, and thermodynamics, Journal of Dispersion Science and Technology, 38(5), 757-767.

28) Taylor, D.W. (1948): Fundamentals of soil mechanics, Wiley, New York.

29) Thammathiwat, A., and Chimoye, W. (2010): Effect of permeant liquid on the swell volume and permeability of geosynthetic clay liners, Electron. J. Geotech. Eng., 15, 1183–1197.

30) Xue, Q., Zhang, Q., and Liu, L. (2012): Impact of high concentration solutions on hydraulic properties of geosynthetic clay liner materials, Materials, 5, 2326–2341.