



Full Length Review Article

**PB²⁺ REMOVAL EFFICIENCIES OF FIRE CLAY SOILS THROUGH THE DISTRIBUTION OF
DIFFERENT PARTICLE SIZE: AN OVERVIEW**

¹Pattanayak, B., ²Muduli, S. D. and ²Dhal, N. K.

¹Department of Biotechnology, F.M. University, Balasore, Odisha, India

²Department of Environment and Sustainability, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar-751013, Odisha, India

ARTICLE INFO

Article History:

Received 19th May, 2014
Received in revised form
20th June, 2014
Accepted 18th July, 2014
Published online 31st August, 2014

Key words:

Characterization, Adsorption,
Removal, Langmuir,
Freundlich Intercalation,
Staining, pH.

ABSTRACT

Batch adsorption studies were carried out to evaluate the Pb²⁺ adsorption capacities of different fired clay soils with different particle size distributions. Adsorption efficiency was observed to increase with an increase in clay content. Adsorption efficiencies of the fired clay soils were also influenced by the firing temperature, the solutions acidity, initial Pb²⁺ concentrations, shaking time and adsorbent dose. Adsorption of Pb²⁺ by the clay soils was observed to increase linearly from pH 1 to 5. Many problems from soil research to ceramics require a reliable characterization of clay minerals involved. This can be done using four clay organic reaction such as: i) Staining test and Dye adsorption ii) Intercalation iii) Reaction type of Kaolin and iv) Alkyl ammonium ion exchange. The Langmuir and Freundlich adsorption models were applied for the immobilization of metal ions mutual interactions between the molecules ions sorbed on the surface.

Copyright © 2014 Pattanayak et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

Lead is known to be one of the most toxic contaminants, even at very low concentrations. Inorganic lead is a generally metabolic poison and enzyme inhibitor (like most of the heavy metals). One of the most insidious effects of inorganic lead is its ability to replace calcium in bones and remain there to form a semi-permanent reservoir for long-term release of toxin and long after the initial absorption. Lead contamination exists in aqueous waste streams as a result of industrial processes such as the manufacture of storage batteries, pigments, leaded glass, fuels and photographic materials (Bhattacharyya and Gupta, 2006). Conventionally, lead is removed from waste water by one or more of precipitation, adsorption with activated carbon, ion exchange, membrane separation, oxidation and reduction technologies (Wang et al., 2003). Due to the fact that these waste water purification methods require high capital, high operating costs and often generate chemical sludge, which itself is a disposal problem, the feasibility of using various low-cost locally available adsorbents has been investigated for the removal of Pb²⁺ ions from waste water (Bulut and Baysal,

2006; Malakootian et al., 2009; Li, et al., 2005; Qaiser et al., 2009). The phase composition of raw brick clays and fired bricks are generally complex due to the use of highly heterogeneous soil. The major phases found in the raw soil materials, however, included quartz, calcite, chlorite and albite. In under fired bricks, illite is the most persistent of the clay minerals (Ahmad et al., 2008). The use of fired clay for the removal of non-metallic and metallic pollutants has been reported in the literature (Seneveratne and Priyantha, 2009; Priyantha and Bandaranayaka, 2010).

About Fire Clays

Harvey and Chantawong (2001:79-86) investigated the adsorption characteristics of the nitrate form of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II), and Zn(II) ions by ballclay. This included adsorption isotherms of single-metal solutions at 30-60 °C by batch experiments, and studies of ion selectivity in a mixed and binary combination solution. Adsorption of metals from the single-metal solutions were in the order of: Pb > Cr > Cd : Zn > Cu > Ni, where as those in the mixed solution were: Cr > Cd : Cu > Zn : Pb. Adsorption could be described by the Langmuir and Freundlich isotherms, and followed Lewis acid-base principles. Ballclay exhibited relatively hard

***Corresponding author: Pattanayak, B.,**
Department of Biotechnology, F.M. University, Bhubaneswar-751013, Odisha, India

Lewis base adsorption sites. Except for Cu and Zn, the adsorptions were endothermic reactions.

Optimized Condition of Fire Clay

Adsorption of lead and nickel were severely suppressed by the presence of other metals. The decrease of lead occurred because of ion competition, particularly by Pb whilst a decrease of nickel was mainly dependent on the pH of the solution. Orumwense (1996:363-369) studied the removal of lead from water by adsorption on a kaolinitic clay. Many investigations have shown that the adsorption capacity of clay for the removal of lead increases with an increase in temperature of the solution, that is, the equilibrium amount of lead decreases with an increase in temperature. The high lead adsorption capacity (6.457 mg g⁻¹) by the clay at high temperature (50 °C) suggests an endothermic reaction; the adsorption process does exhibit a Langmuir type behaviour, which is affected by temperature. Lead adsorption decreases from 93% to 82% with an increase in the pH of the solution. It was found that the presence of a negative charge on the silica surface sites of the adsorbent is responsible for the adsorption of lead. This study indicated that lead removal is favoured by low concentration of the metal ion, high temperature and acidic pH. Kaolinitic clay was found to be a good adsorbing medium for lead ions.

Heavy Metal Adsorption Efficiencies

Co²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ single and multicomponent heavy-metal solutions were percolated through fixed beds of Mg-enriched sepiolite to study both the dynamic interactions between the mineral and heavy-metal cations and the ion-sorption kinetics. The metal concentrations in the eluates were determined by atomic absorption and/or inductively-coupled plasma and kinetics by the classical kinetic approach, using isothermal experiments at room temperature. It was found that heavy-metal ion-sorption by sepiolite is fast at the beginning and then proceeds slowly, mostly for cations with a cation-water coordination sphere similar to that of Mg²⁺. Therefore, the ability of sepiolite to remove Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ is virtually independent of the competitive cation interactions, whereas its affinity for Co²⁺ is lower when other metals coexist in the solution.

Justification of the review

History

Clay has been used in bricks and pottery for millennia. Sun-dried brick were used from possibly over 10,000 years ago and kiln-fired bricks were used in the construction of a temple in the Euphrates region, considered to more than 5000 years old. Sumerian and Babylonian builders constructed ziggurats, palaces, and city walls of sun-dried bricks and covered them with more durable kiln-baked bricks, often brilliantly glazed and arranged in decorative pictorial friezes (Christie *et al.*, 2000:26). The oldest porcelain, a translucent, originated in China during the T'ang dynasty (618-907 AD), but the porcelain best known in the West (where it is called chinaware) was not produced until the Yuan dynasty (1278-1368 AD).

Formation, Mining and Processing

Clays are present in soils and sediments derived from soils. They may be formed in soils during soil development through the weathering of various minerals, or they can be found essentially without change in the parent material from which the soils were formed. Parent material, climate, topography, and vegetation determine the kinds of clays that are found. Hydrothermal alteration may also lead to clay formation. As erosion acts on the landscape, clay may be suspended in water and carried until they are deposited by sedimentation. Most sedimentary rocks contain more or less clay as, for example, shales (almost exclusively clay), lime stones, and sandstones. Clays are generally mined by highly selective open pit methods using hydraulic excavators, front-end loaders, or draglines. The clay is processed using either a dry (air flotation) or a wet process (water washing). The wet process produces a higher cost and higher quality product than the dry process. The dry process involves crushing, drying, pulverising, and air flotation, to remove the grit particles (mostly quartz and feldspar). In the wet process, the first step is to remove the non-clay minerals, usually by extracting the grit from clay slurry in drag boxes, classifiers, and/or hydrocyclones.

Clay particles and their interactions

Considerable knowledge exists regarding the surface chemistry and adsorptive properties of clays, and thus, with information on the nature of the solute, it is possible to have some idea of their interaction. Clays could act as vehicles for transport of toxic compounds through adsorption in one environment, followed by release of the toxic material when the clay enters a different environment. The interactions of metal cations with clays include adsorption by ion-exchange, precipitation as hydroxides or hydrous oxides on clay surfaces, and adsorption as complex species. Obviously, pH and Eh are critical factors in determining the nature of interactions between clays and some transition and heavy metal ions (Drinking Water and Health). Clays remove metals in a variety of ways (Smith, 2000) –

- Cation-exchange capacity (CEC), where metal ions present on the clay are exchanged for other metals in the surrounding medium.
- Clays have a very high surface area due to their small particle size. This allows them to bind to a large number of metal ions.
- Clays often contain organic matter which can form complexes with metals.

Physical and chemical properties of clay

Some physical and chemical properties of clay are listed below

Physical properties – structurally complex

- Colloidal – sub-microscopic and held in suspension in solution.
- When wet – viscous and gelatinous, sticky; when dry – hard, packed and cohesive.
- Composed of micelles = flat, sheet-like plates laminated into stacks.

- Very large internal and external surface area.
- Very small internal and external pores.

Chemical – very complex; negatively charged

- Very high cation exchange capacity (CEC): 10-100 meq/100g.
- Charge allows flocculation or de-flocculation.

Application of Clay Materials

Clay raw materials are used in industry and other areas of human activity. The most extensive applications are naturally in industrial branches. Many applications, however, include the area called the “formation and protection of the environment”. It is enough to be aware of the fact that industrial products utilizing clay raw materials, such as porcelain, various ceramic goods, plastics, rubber goods, innumerable sorts of paper and other products influence the environment of mankind. In the formation of modern human environment, all ceramic products have a substantial significance. The building ceramic parts, manufactured bricks and roofing tiles, sanitary ceramics, easily washable tiles for exteriors and interiors in subways, airports and railway stations, shopping centers, private flats, all of them are mainly manufactured from clay raw materials (Konta, 1995:283). Certain clay minerals are noted for their specific adsorption properties. Kaolinite is e.g. suitable for the sorption of fluoride ions from water. Radioactive alkaline metals are most effectively sorbed by mica clay minerals, while chlorite is suitable for divalent radio nuclides. Clay minerals in rivers, both in suspension and settled in muds, are important adsorbents of toxic substances in solution. The stirring properties of clay in water (including adsorption) have been known since the days of ancient Greece and Rome (Konta, 1995:283). The role of clay minerals is also fundamental in agriculture, fruit growing and forestry.

The clay minerals in soils are important sources of nutrients and water. As negatively charged colloidal bridges, they encourage a long-term proton exchange from plant roots for necessary cations released from weathering primary minerals. Clay minerals are the most common carriers of pesticides, insecticides and herbicides and sometimes also special fertilizers (Konta, 1995:284). In the building industries, the numerous manufacturers of structural materials and the knowledge of ground soils are closely connected with clay science. A simple but important fact underscoring the significance of clay science in the building industries is that most of the building is “from” clays or loams and “on” clays or loams. Clay minerals are the essential constituents of clays, loams and along with calcite, also of cement raw metal mixture. Thermally expanded clay raw materials are used as lightweight granules whose use in the lightweight concrete, plasters and suspensions in the modern building industries continually rises. Exfoliated vermiculite has a similar application (Konta, 1995:286). In archeology, clay minerals can serve as “archaeological thermometers” in the investigation of ancient ceramics. The investigation of clay minerals and argillaceous rocks in geological sciences today is an extensive region of theoretical and applied research. Clay minerals and argillaceous sediments play an important role in the oil geology and oil industry. They are of use partly as

adsorbents of unwanted compounds, and partly as catalysts for cracking (Konta, 1995:288).

Lead Bioavailability

Lead from ammunition may contribute to soil in any of three forms: metallic lead, Pb^{+2} (dissolved from the crust of the ammunition), and as a variety of oxidized compounds (largely hydroxycarbonates, carbonates, and sulphates). Ingestion of fragments of lead ammunition may be the cause of children exhibiting pica behaviour, although metallic lead is largely insoluble. Lead speciation within the soil matrix, soil type, mineralogy, and soil particle size have been shown to affect soil-lead bioavailability. Bioavailability of metallic lead has been shown to decrease with increasing particle size (Bartrop & Meek, 1975,1979). There also is evidence to suggest that smaller soil particles (e.g., <100 – 250 μm) are more likely to be incidentally ingested than larger particles because the particles adhere more readily to the skin (Duggan, *et al.*, 1985). The Adult Lead Model relates soil-lead concentrations to blood-lead concentrations in the developing fetus of an adult woman who has potential exposure to the site and can be used to determine target cleanup levels at non-residential (i.e., commercial and industrial) sites. The default estimate of bioavailability of lead in the Adult Lead Model is 12%, based on an absorption factor for soluble lead in adults of 20% and the relative bioavailability of lead in soil compared to soluble lead of 60%. Potential Bioavailability of Various Lead Minerals has shown in table no.1

Table 1. Potential Bioavailability of Various Lead Minerals

Potentially Lowered Bioavailability (RBA<25%)	Intermediate Bioavailability (RBA=25-75%)	Potentially Higher Bioavailability (RBA>75%)
Galena(PbS)		
Anglesite(PbSO ₄)	Pb Oxide	
Pb(M)Oxide	Pb Fe (M) Oxide	Cerrusite = PbcO ₃
Pb Fe(M)	Pb Phosphate	Pm Mn (M) Oxide
Sulphates	Slags	
Native Pb		

Four Reactions for Characterizing Fire Clay Minerals

Adsorption of dyes and staining tests

Various organic substances change colour on interaction with clays. Frequently the colour varies depending on the identity of the clay minerals. Identifying the clay mineral components of clay materials by staining tests is rapid and simple, but their applicability is restricted because of the mutual interference of the common components of clay materials. Many colour reactions are redox processes and the colour is determined by other factors, e.g. pH. Typical dyes used are benzidine, safranine, malachite green or fluorescent dyes (Grim, 1968; Fahn & Gennrich, 1955). Brindley & Thompson (1970) showed that methylene blue adsorption can be used for the measurement of both surface areas and exchange capacities of clay minerals. The exchange capacities are determined from the plateaux of the adsorption isotherms. CECs of montmorillonites are obtained correctly only when the Na form is used. In the presence of Na salts sorption of methylene blue is considerably increased. This is explained by additional

adsorption of methylene blue hydroxide molecules due to the alkaline reactions of most Na salts. K^+ ions retard the sorption of methylene blue and K salts do not increase the methylene blue adsorption above the CEC (Hofmann & Dammler, 1969; Brindley & Thompson, 1970). In industry, methylene blue adsorption is used as a simple and rapid method for estimating the smectite content of bentonites.

Glycerol adsorption method

Glycerol adsorption is a standard method for investigating interstratified minerals with smectitic interlayer spaces. The proportion of expanding layers in randomly interstratified smectite-illite can be estimated by the method of Wier *et al.*, 1975, based on the measurement of the shape of first order basal reflections. An alternative method is to match the X-ray pattern against a set of computer simulated traces from models composed of varying proportion of smectite layers. Glycerol adsorption can also be used for a rough estimation of the proportion of smectites in clays. For this purpose the application of polymeric molecules may be of advantages. Lavy and Francis recommended the quantitative determination smectites in soils from the intensity of the basal spacings after adsorption of polyvinylpyrrolidone.

Reaction types of Kaolins

Some organic molecules can be intercalated as “guest molecules” between the layers of kaolin. The reaction provides a simple method for distinguishing between halloysite, dehydrated halloysite and kaolin. Weiss and co-workers concluded that kaolin in general are mixture of different types of kaolinites with different chemical reactivity. Using di-methyl sulphoxide and Urea as guest molecules, three types were distinguished.

1. A highly reactive type, which react with a large number of guest molecules.
2. Other type with low, but detectable reactivity.
3. Another type which unable to form intercalation compounds.

Alkyl ammonium Ion exchange

Quantitative exchange of the interlayer cations of smectites by alkyl-ammonium ions provides the best methods for characterization of smectites and determination of their layer charge. The different types can easily be detected by their basal spacings. The basal spacing of alkyl ammonium smectites increase in steps with the alkyl chain length. It has the application in Investigation of bentonites.

Chemical Extraction

As with any treatment technology, soil parameters play a significant role in the success of the technology. For chemical treatment, these include but are not limited to the following:

Feed soil pH and buffering capacity determine the volume of chemical addition to reach the pH required for efficient leaching.

Cation exchange capacity (CEC) indicates the ability of the soil to bind lead in an exchangeable form. Generally, CEC is proportional to the clay content of the soil, making sandier soils easier to treat.

Total organic carbon indicates the volume of organic material (humates) present in the soil on a weight-to-weight basis. Dissolved metals complexed with humates are difficult to remove and may require a separate humate-removal step prior to chemical leaching.

Iron and manganese levels indicate the presence of iron and manganese oxides that can absorb lead. These materials tend to bind lead very strongly and may leach out with other metals, increasing overall chemical consumption during leaching and precipitation steps.

These parameters provide some indication of difficulties that may be encountered during leaching. The leachant selection and optimization process can be further focused, if required, by determining heavy-metal speciation and binding mechanisms in the soil. Heavy-metals speciation indicates the types of chemical compounds the metals are present as. Any leaching steps should be performed only after the particulate lead has been removed using physical separation techniques. Lead oxides and lead sulphate are other lead compounds that may occur under certain conditions and are very difficult to leach. Soil containing a high percentage of these compounds may be more amenable to stabilization than chemical leaching. All of these parameters should be evaluated in a thorough treatability study prior to field mobilization.

Commencement

- While metals that are mixed and bound with organic contaminants can be extracted, the residuals may be restrictive of future land use.
- The toxicity of the solvent is an important consideration as traces may remain in the treated soil.
- After acid extraction, any residual acid in treated soil needs to be neutralized.
- In solvent extraction, impermeable membrane liners and covers should be used to reduce solvent evaporation and to protect against rain.

Adsorption Kinetics

Adsorption (or sorption) is a process that involves the contact of a free aqueous phase with a rigid particulate phase that has the ability to selectively remove or store one or more solutes (e.g., metal species) present in the solution (waste streams). Usually, the sorbent has a fixed total uptake, where by one solute is exchanged for another (as in ion exchange processes). When a quantity of adsorbent is contacted with a given volume of a liquid containing an absorbable solute, adsorption occurs until equilibrium is achieved. The equilibrium state is characterized by a certain solute concentration on the adsorbent (q_e) and an associated final solute concentration in the liquid phase (C_e). Depending on the volume of liquid involved, the initial solute concentration in the liquid, and the amount of adsorbent employed, a wide range of q_e vs. C_e values may be obtained. Two of the more common mathematical formulations used in establishing adsorption isotherms are the Freundlich and Langmuir equations.

The Langmuir Isotherm

One particular mathematical form of an isotherm which is often found to fit experimental data is the so-called Langmuir isotherm, (Cooney, 1999) which was derived in 1916 by Irving Langmuir (Laidler and Meiser, 1999:3rd edition). The Langmuir equation applicable to adsorption is described as (Demirba, *et al.*, 2002:291):

$$(C_e / q_e) = \{1 / (Q_0 \times b)\} + (C_e / Q_0)$$

Where,

C_e = the equilibrium concentration of the adsorbate (mg/L) in solution.

q_e = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

Q_0 and b = Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. When C_e/q_e is plotted versus C_e , the slope is equal to $1/Q_0$ and the intercept is equal to $1/Q_0b$ (Bayat, 2002:262).

The Freundlich Isotherm

Non-ideal systems can sometimes be fitted to an empirical adsorption isotherm developed by the German physical chemist Herbert Max Finlay Freundlich (1880-1941) (Laidler and Meiser, 1999:852). The Freundlich equation applicable to adsorption is described as (Dakiky *et al.*, 2002:534)

$$\text{Log}(q_e) = \text{log}(K_f) + \{1/(n \times \text{log}C_e)\}$$

Where

C_e = the equilibrium concentration of the adsorbate (mg/L) in solution.

q_e = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

K_f and n = constants incorporating all factors affecting the adsorption such as adsorption capacity and intensity, respectively. Values of K_f and n may be calculated by plotting $\text{log}(q_e)$ versus $\text{log}(C_e)$. The slope is equal to $1/n$ and the intercept is equal to $\text{log}(K_f)$ (Bayat, 2002:262). Both of these are "two-parameter" equations. That is, other than the variables q_e and C_e , there appear only two parameters in the equations. The two parameters are evaluated by "fitting" the data to the equations. These two equations are used more than 99% of the time to describe the equilibrium adsorption of solutes onto solid particles. The reason is simple: in almost every case, one of these two equations fits the data quite well. Thus, there is no need for more elaborate isotherm equations, particularly those involving three or more parameters (Cooney, 1999:42).

The Langmuir model assumes the surface of the sorbent to be homogeneous and the sorption energies to be equivalent for each sorption site. Immobilisation of metal ions occurs without mutual interactions between the molecules ions sorbed on the surface. The Freundlich model is based on an exponential distribution of sorption sites and energies. Moreover, molecules adsorbed on the surface can interact (Curkovic *et al.*, 2001:3437). Adsorption of heavy metals is an attractive option due to the proven efficiency of this process in the

treatment of wastewater and removal of a large number of different contaminants (Townsend and Zhu, 2001:1). It is a cost competitive operation that can contribute effectively to the removal of pollutants remaining in solution (Potgieter, 1990:393).

CONCLUSIONS AND DISCUSSION

Various study successfully proved that Pb(II) can be adsorbed from aqueous solution in significant amounts by palygorskite. In batch mode adsorption studies, removal of the metal ions increased with an increase in contact time, amount of adsorbent and pH. The increase in initial metal ion concentration increased the amount of metal uptake per unit weight of the sorbent (mg/g). The equilibrium data could be described by the Langmuir and Freundlich isotherm equations. However, the Langmuir model better represented the sorption process in comparison to the Freundlich model. This study provided a basis for the batch equilibrium studies, which have an important contribution to the understanding of the capacity of clay. Adsorption efficiencies at 400°C were higher than those fired at lower or higher temperatures. Temperatures above a certain optimum, however, destroy the clay structure and cause a decrease in surface area (Mortland, 1954). Adsorption of Pb²⁺ by the clay soils was observed to increase from pH 2 to 5 and then levelling off after that.

This could be explained as follows: at lower pH values (pH < PZC), where there are excess H³O⁺ ions in the solution, a competition exists between the positively charged H³O⁺ and Pb²⁺ ions for the available sites on the negatively charged clay surface (Eba, *et al.*, 2010). Meanwhile, the positive H³O⁺ ions that have already occupied the negative charges on the clay surface will inhibit the approach of Pb²⁺ ions to the clay surface and reduce or minimize further adsorption of Pb²⁺ ions. Various investigations revealed that the level of Pb²⁺ adsorption could be predicted to be low. At higher pH values (pH > PZC), the clay surfaces become negatively charged due to de-protonation of functional groups, favouring Pb²⁺ uptake by the clay soils. Due to this, adsorption goes on increasing with an increase in pH. At about pH 5, the limited adsorption sites will be fully occupied and no further increase in Pb²⁺ ion adsorption was observed. Similar observations were reported by other researchers (Chantawong *et al.*, 2001; Kaya and Oren, 2005). The initial increase in adsorption could be explained by an increase in the available active sites for the binding of Pb²⁺. An increase in the number of active sites after equilibrium was reached, however, had no apparent effect on further increasing the removal of Pb²⁺.

The amount of Pb²⁺ adsorbed was found to decrease with an increase in the equilibrium Pb²⁺ ion concentration in solution after an initial nearly-linear increase. This could be related to the well known "loading effect", which is conventionally interpreted as - the number of sites highly preferred by a given metal ion are a small portion of the total number of sites (Jenne, 1998; Payne, *et al.*, 1998). The initial sharp rise observed in adsorption followed by the relatively slow increase may be explained as follows: at lower equilibrium Pb²⁺ ion concentrations, surface coverage could be low and the availability of sites that are not occupied by the metal adsorbate may not be a limiting factor. With an increase in the equilibrium Pb²⁺ ion concentration, the linearity of the

increase in adsorption density with the equilibrium Pb^{2+} ion decreases due to an increase in the surface coverage. The ratio of adsorbed Pb^{2+} to that of equilibrium concentration, however, generally decreases as the equilibrium concentration increases after only a small percentage of the adsorption capacity has been utilized. This could be due to the fact that only fractions of the total number of sites have high specificity for the adsorbate. In this study, the relative ability of fired clay the relative ability of fired clay soils to remove Pb^{2+} from aqueous solution was investigated. The kinetic studies conducted using the Weber and Morris equation showed that the adsorption mechanism involves intra-particle diffusion but it was not the fully operative mechanism in the adsorption of Pb^{2+} by the three clay soils. The pseudo-second-order kinetic model was found to be a better fit for the adsorption of Pb^{2+} by the clay soils. The findings of the current study in general revealed that the Pb^{2+} (and possibly other metal ions) removal efficiencies of fired clay soils/bricks differ depending on the textural compositions of the clay soils from which the fired clays/bricks were prepared.

Recommendation

The relevant study suggested that the different clay soil may also be reused by following lead reclamation. Current situation may be handled to establish safe clean-up levels, use industrial exposure as a basis. Many of the clay-mining sites have become more dispersed reactional areas that have been deeded restriction prohibiting development. The exposure pathways for dispersed reaction are much different and exposure rates are lower than for residential or industrial exposure seasons. Establishing physical and chemical treatment operation within confines of the fireclay mines, long term effectiveness has not been demonstrated for many contaminants. Depth of this contaminant may limit this process. Future use of these clay soils and environmental condition may erode the materials used to encapsulated contaminants, thus affecting materials capacity to immobilize. Hazardous waste materials may interfere with stabilization process, it may included inorganic acids that will decrease durability of the emulsion and chlorinated organic that may increase and decrease durability of the emulsion, if the concentration is too high. Certain condition such as pH, temperature and other variables may lead to a reversal of the filtration process for metals. So, during this operation, wildlife may be adversely affected by the presence of metals that have accumulated in plants and sediment.

REFERENCES

- Ahmad, S., Iqbal, Y. and Ghani, F. 2008. Phase and Microstructure of Brick-Clay Soil and Fired Clay-Bricks from Some Areas in Peshawar Pakistan. *journal of the Pakistan Material Society.*, 2 : 33-39.
- Bayat, B. 2002. Comparative Study of Adsorption Properties of Turkish Fly Ashes: I. The Case of Nickel(II), Copper(II) and Zinc(II). *Journal of Hazardous Materials.*, B 95: 251-273.
- Bhattacharyya, K.G. and Gupta, S.S. 2006. Adsorption of chromium(VI) from water by clays', *Industrial and Engineering Chemistry Research.*, 45: 7232-7240.
- Brindley, G.W. and Thompson, T.D. 1970. Methylene blue adsorption by montmorillonite determination of surface areas and exchange capacities with different initial cation saturations. *ijrael journal chemical society.*, 8: 409-415.
- Bulut, Y. and Baysal, Z. 2006. Removal of Pb(II) from wastewater using wheat bran. *Journal of Environmental Management.*, 78: 107-113.
- Bartrop, D. and Meek, F. 1975. Absorption of different lead compounds. *Postgrad. Med. J.*, 51:805-809.
- Bartrop, D. and Meek, F. 1979. Effect of particle size on lead absorption from the gut. *Arch. Environ. Health* 34:280-285.
- Chantawong, V., Harvey, N. and Bashkin, V.N. 2001. Adsorption of lead nitrate on Thai kaolin and ball clay. *Asian journal of Energy and Environment.*, 2:33-48.
- Cooney, D.O. 1999. *Adsorption Design for Wastewater Treatment*. Boca Raton: Lewis Publishers.
- Christie, A.B., Thompson, B.N. and Brathwaite, R.L. 2000. Mineral Commodity Report 20 – Clays. *New Zealand Mining*, 27: 26-43.
- Curkovic, F., Cerjan-stefanovic, D. and Rastovean-mioe, A. 2001. Batch Pb^{2+} and Cu^{2+} Removal by Electric Furnace Slag. *Water Research*. 31: 1379-1382.
- Dakiky, M., Khamis, M., Manassra, A. and Mer'eb, M. 2002. Selective Adsorption of Chromium (VI) in Industrial Wastewater Using Low-cost Abundantly Available Adsorbents. *Advances in Environmental Research.*, 6 (4): 533-540.
- Demirba, E., kobyra, M., Öncel, S. & Sencan, S. 2002. Removal of Ni(II) from Aqueous Solution by Adsorption onto Hazelnut Shell Activated Carbon: Equilibrium Studies. *Bioresource Technology.*, 84(3):291-293.
- Duggan, M.J. and Inskip, M.J. 1985. Childhood exposure to lead in surface dust. *Public Health Review.*, 13: 2-54.
- Eba, F., Gueu, S., A-Mvongbote, A.E., Ondo, J.A., Yao, B.K., Ndong Nlo, J. and Biboutou, R.K. 2010. Evaluation of the absorption capacity of the natural clay from Bikougou (Gabon) to remove Mn (II) from aqueous solution. *Int. J. Eng. Sci. Technol.*, 2:5001-5016.
- Furukawa, T. and Brindley, G.W. 1973. Adsorption and oxidation of Benzidine and Aniline by montmorillonite and hectorite. *clays clay miner.*, 21: 279-288.
- Fahn R. & Gennrich M. 1955. Staining of clay minerals with fluorescent dyes. *Tonind. Zig. Keram. Rundschau.* ,79:233-236.
- Grim R.E. 1968. *Clay Mineralogy*. McGraw-Hill Book Company, New York.
- Harvey, N.W. and Chantawong, V. Adsorption of Heavy Metals by Ballclay: their Competition and Selectivity. *Journal of Tokyo University of Information Sciences Aug 2001*; 78.
- Hofmann, U. and Dammler, J. 1969. Dimethylen blauadsorption an Montmorillonit. *chimia.* , 23: 476-480.
- Jenne, E.A. 1998. Adsorption of metals by geomeia: data analysis, modeling, controlling factors, and related issues. In: *Adsorption of Metals by Geomeia* (E.A. Jenne, editor)'. *Academic Press*: San Diego. pp. 1-73.
- Kaya, A. and Oren ,A.H. 2005. Adsorption of zinc from aqueous solutions to bentonite'. *Journal of Hazardous Material.*, 125:183-189.
- Konta, J. 1995. Clay and Man: Clay Raw Materials in the Service of Man. *Applied Clay Science.* , 10: 275-335.
- Laidler, K.J. & meiser, J.H. 1999. *Physical Chemistry*. 3rd edition. Boston: Houghton Mifflin Company.

- Li, Y., Di, Z., Ding, J., Wu, D., Laun, Z. and Zhu, Y. 2005. Adsorption thermodynamic, kinetic and desorption studies of Pb²⁺ on carbon nanotubes. *Water Research.*, 39 :605–609.
- Malakootian, M., Nouri, J. and Hossaini, H. 2009. Removal of heavy metals from paint industry's wastewater using Leca as an available adsorbent. *International Journal Environment Science and Technology.*, 6: 183-190.
- Mbadcam, J.K., Anagho, S.G., Ndinsami, J. and Kammegne, A.M. 2011. Kinetic and equilibrium studies of the adsorption of lead (II) ions from aqueous solution onto two Cameroon clays: Kaolinite and smectite. *J. Environ. Chem. Ecotoxic.*, 11:290-297.
- Mortland, M.M. 1954. Specific Surface Area and its Relationship to Some Physical and Chemical Properties of Soil. *Soil Science.*, 78: 343-347.
- Nassem, R. and Tahir, S.S. 2001. Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent. *Water Research.*, 35(16):3982-3986.
- Njoku, V.O., Oguzie, E.E., Obi, C., Bello, O.S. and Ayuk, A.A. 2011. Adsorption of Copper (II) and Lead (II) from Aqueous Solutions onto a Nigerian Natural Clay. *Aust. J. Basic Appl. Sci.*, 5:346-353.
- Orumwens, E. 1996. Removal of Lead from Water by Adsorption on a Kaolinitic Clay. *Journal of Chemical Technology and Biotechnology.*, 65: 363-369.
- Priyantha, N. S. and Bandaranayaka, A. 2010. Optimization of parameters for effective removal of Cr(VI) species by burnt brick clay. *J. Natl. Sci. Foundat. Sri Lanka.* 38:107-112.
- Potgieter, J.H. 1990. An Experimental Study of the Adsorption Behaviour of Methylene Blue on Activated Carbon. *Colloids and Surfaces.*, 50:393-399.
- Payne, T.E., Lumpkin, G.R. and Waite, T.D. 1998. Uranium(VI) adsorption on model minerals: controlling factors and surface complexation modelling. In: *Adsorption of Metals by Geomedia: Variables, Mechanisms and Model Applications* (E.A. Jenne, editor). Academic Press, San Diego. pp. 75-97
- Qaiser, S., Saleemi, A.R. and Umar, M. 2009. Biosorption of lead(II) and chromium(VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study. *Electronic Journal of Biotechnology.*, 12: 1-17.
- Seneveratne, C. and Priyantha, N. 2009. Correlation between firing temperature and defluoridation capacity of brick clay. *International Journal of Global Environment.*, 9: 239-248.
- Smith, P.R.J. 2000. Use of a Glauconitic Clay to Remove Copper from Effluents Produced during Manufacture of Printed Circuit Boards', [Online]. Available at: <<http://www.aecuk.com/PCB.html>>. Accessed: 05/03/2004. *Surfaces* 50: 393-399.
- Theng B.K.G., Greenland, D.J. and Quirk, J.P. 1967. Adsorption of alkylammonium cations by montmorillonite., *clay miner.*, 7:1-17.
- Townsend, W. and Zhu, H.Y. 2001. Adsorption of Metal Cations by Anion Clay Hydrotalcite. *Individual Inquiry* [Online]. May:1-34. Available at: <<http://www.cheque.uq.edu.au/ugrad/theses/2001/Pdf/W.Townsend.PDF>>. Accessed: 10/07/2003.
- Wang, Y.H., Lin, S.H. and Juang, R.S. 2003. Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents. *Journal of Hazardous Materials.*, 102: 291-302.
- Wier, A.H., Ormerod, E.C. and Mansi, I.M.I. 1975. clay mineralogy of the sediments at western Nile delta. *clay mines.*, 10: 376-379.
