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A comparative study on Pb^{2+} removal efficiencies of fired clay soils of different particle size distributions

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Batch adsorption studies were carried out to evaluate the Pb^{2+} adsorption capacities of three 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 solution's acidity, initial Pb^{2+} concentration, shaking time and adsorbent dose. Adsorption of Pb^{2+} by the clay soils was observed to increase linearly from pH 1 to 5 and then remained nearly constant at higher pH values. The adsorption of Pb^{2+} was observed to increase sharply with Pb^{2+} for the lower initial concentrations (5 to 10 mg/L), while a modest increase in Pb^{2+} adsorption was found from 10 to about 50 mg/L, a concentration at which maximum removal was attained. The Langmuir and Freundlich adsorption models were applied to the adsorption data and the Langmuir model represented the adsorption process better than the Freundlich model, with correlation coefficients (R^2) ranging from 0.97 to 0.99. The adsorption capacities (qm) calculated from Langmuir for the adsorption of Pb^{2+} by S_{3F} , S_{2F} and S_{1F} were found to be 17.3, 15.9, and 11.2 mg/g, respectively.

Key words: Adsorption, fired clay soils, isotherm, adsorption kinetics, sand, silt, particle size.

INTRODUCTION

Lead is known to be one of the most toxic contaminants, even at very low concentrations. Inorganic lead is a general 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 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, and oxide-

tion 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 Pb^{2+} ions from waste water (Bulut and Baysal, 2006; Malakootian et al., 2009; Li et al., 2007; Qaiser et al., 2009). Clays are among the various locally available materials that are used for the removal of Pb^{2+} and other various heavy metals from aqueous solutions (Njoku et al., 2011; Talaat et al., 2011; Mbadcam et al., 2011; Inglezakis et al., 2007; Sar et al., 2007; Nasseem and Tahir, 2001; Shi et al., 2009; Eba et al., 2010). In the

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Abbreviations: S_1 , Clay soil 1; S_2 , clay soil 2; S_3 , clay soil 3; S_{1F} , fired clay soil 1; S_{2F} , fired clay soil 2; S_{3F} , fired clay soil 3.

soil, the variation in size of the particles and the proportionate amounts of fine and coarse materials, that is, the relative proportions of sand, silt and clay, known as the soil texture, determine to a large extent both its physical and chemical properties (McBride, 1994).

Clayey soils are mainly composed of the fine textured fractions, clay and silt, and are used for the production of bricks by firing the aforementioned to temperatures ranging from 900 to 1200°C (Ahmad et al., 2008). 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 underfired 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; Moges et al., 1996; McKay et al., 1985; Priyantha and Bandaranayaka, 2010; Priyantha et al., 2009; Renu et al., 2008; Bina et al., 2012). Bricks, however, are produced from clay soils that may differ widely in their mineral composition and hence textural classification. The variation in the textural composition of soils which the bricks are produced from may result in a difference in their heavy metal removal efficiencies and predicting the efficiency of a soil to adsorptively remove a heavy metal without taking its textural composition into account may be a misguided generalization.

Therefore, the main objective of this study was to evaluate and compare the ability of fired clay chips prepared in the laboratory from clay soils of different textural compositions to remove Pb^{2+} ion from aqueous solutions. In this work, the influence of clay soil firing temperature, adsorbent dosage, solution pH and shaking time on the adsorption of Pb^{2+} ions from aqueous solution by the fired clay soils were investigated. The well-known Langmuir and Freundlich isotherm models were also used to examine fit with the equilibrium data. The pseudo-first-order, pseudo-second-order and the intra-particle diffusion kinetic models were also applied to evaluate the nature of the sorption process.

MATERIALS AND METHODS

Clay soil collection and characterization

Clay soils were collected from ten different small scale brick production sites around Jimma town (South West Ethiopia). The particle size distributions of the clay soils were determined using the standard method developed by Sheldrick and Wang (1993). Three clay soils (S_1 , S_2 and S_3) with wider difference in clay content were selected among the ten for further adsorption study. The proportion of clay was higher than those of silt and sand in the order: $S_3 > S_2 > S_1$.

The cation exchange capacity (CEC) and specific surface area (SSA) of the fired clay soils were determined by using the ammonium acetate (Priyantha et al., 2009) and the Sear's methods (Sears, 1956), respectively. The pH point of zero charge (pHpzc) of

each of the adsorbents was measured by the potentiometric titration method using NaCl as the supporting electrolyte (Chapman, 1965).

Clay soil firing

For each of the three clay soil samples the firing temperature that produces a fired clay soil with the highest adsorption efficiency was determined by transferring about 200 g of each of S_1 , S_2 or S_3 into separate crucibles and firing in a muffle furnace (3 h) at one of six different temperatures: 200, 300, 400, 500, 600, 700°C. Thus, one sample from each soil type was fired at each of the six firing temperatures and, a total of 18 samples were fired. The fired clay soils were then ground using a mortar and pestle and allowed to pass through a 0.5 mm sieve. Then, the Pb^{2+} adsorption efficiency of each of the fired clay soil samples was tested using the fraction ≤ 0.5 mm. The adsorption efficiency studies revealed that, the Pb^{2+} removal efficiencies of fired S_1 and S_2 increased with firing temperature between 200 and 400°C and decreased at higher firing temperatures. Fired S_3 samples, on the other hand, showed an increase in Pb^{2+} removal efficiency with firing temperature between 200 and 500°C and a decline at firing temperatures higher than 500°C. Based on these findings the samples fired at 400°C for S_1 and S_2 , and the sample fired at 500°C for S_3 , were used for subsequent batch adsorption studies.

For the batch adsorption experiments, 100 mL of 50 mg/L Pb^{2+} solution was transferred into a 250 mL conical flask and pH of the solution was adjusted to a desired value depending on the parameter to be studied. The required quantity of fired clay adsorbent was added and shaken on a thermostatic shaker for a predetermined contact time. The solutions were filtered before the measurement of residual Pb^{2+} concentration. For each parameter measured adsorption experiments were carried out in triplicates and averages of the results obtained from the triplicate experiments were reported.

Effect of pH

To study the pH effect on the adsorption of Pb^{2+} by each of the fired clay soils (S_{1F} , S_{2F} and S_{3F}), 100 mL of 50 mg/L Pb^{2+} solution was transferred into 250 mL Erlenmeyer flask containing four grams of the adsorbent. The pH of the solution was adjusted at the desired value by using 0.1 M NaOH or HCl and the mixture was shaken for 2 h on a mechanical shaker at 298 ± 2 K. The pH meter was calibrated with buffer solutions (pH 4.01 and 7.01) before each measurement. Finally, the solution was centrifuged, filtered and the residual metal ion concentration was determined by FAAS.

Effect of contact time

Contact time is one of the vital parameters for the successful application of adsorbents for the removal of metal ions. To study the effect of contact time, 100 mL, 50 mg/L of Pb^{2+} solution was transferred into a 250 mL volumetric flask containing four grams of the adsorbent. pH of the solution was adjusted to 5 using 0.1 M NaOH and HCl and the mixtures was shaken at 200 rpm for 2 h. The supernatant solution was collected in 30 min interval and the Pb^{2+} content of the solution was determined by FAAS.

Effect of adsorbent dose

To study adsorbent dose effect 100 mL, 50 mg/L of Pb^{2+} solution was transferred into each of seven 250 mL volumetric flasks containing one to seven grams of either adsorbent, in one gram

Table 1. Textural composition, CEC, SSA and pHpzc values.

Property	Mean \pm SD		
	S ₁	S ₂	S ₃
Clay (%)	39.98 \pm 0.02	58.20 \pm 0.12	82.01 \pm 0.31
Silt (%)	50.26 \pm 0.04	32.98 \pm 0.33	13.92 \pm 0.26
Sand (%)	9.84 \pm 0.11	8.82 \pm 0.29	4.11 \pm 0.03
CEC (meq/100 g)	29.9 \pm 0.58	51.7 \pm 0.47	69.61 \pm 0.61
	S _{1F}	S _{2F}	S _{3F}
SSA (m ² /g)	39 \pm 3.2	51.8 \pm 5.64	71 \pm 5.85
pHpzc	3.0 \pm 0.12	2.4 \pm 0.10	1.9 \pm 0.11

S₁, S₂ and S₃ = untreated soils; S_{1F}, S_{2F} and S_{3F} = fired clay soils.

interval. The pH of each solution was adjusted at 5 by using 0.1 M NaOH and HCl and the mixtures were shaken at 200 rpm for 2 h at 298 \pm 2 K. Finally, the solutions were centrifuged, filtered and the residual metal ion concentrations determined by FAAS.

Effect of initial concentration

To study the effect of initial concentrations of Pb²⁺, each of the seven 100 mL Pb²⁺ solutions having concentrations of: 5, 10, 20, 30, 40, 50 and 100 mg/L were transferred into seven separate 250 mL Erlenmeyer flasks each containing four grams of either of the three fired clay soil adsorbents. The pH of each solution was adjusted at 5 by using 0.1 M NaOH and HCl and, the mixtures were shaken at 200 rpm for 2 h at 298 \pm 2 K. Finally, the solutions were centrifuged, filtered and the residual metal ion concentrations determined by FAAS.

Reagents and solutions

All chemicals used in this study were analytical grade. Deionized water was used for the preparation of stock standard solution of lead and all subsequent dilutions. A stock standard solution of Pb²⁺ (500 mg/L) was prepared by dissolving 0.80 g of Pb(NO₃)₂ (FINKEM) in 1000 mL deionized water. Calibration standards of the desired concentrations were prepared by serial dilution of the stock solution. Hydrochloric acid (Reideal Dehaen 37%) and/or sodium hydroxide (Fischer Scientific) solutions (0.1 N) were used throughout the experiments to adjust the pH of solutions.

Instrumentation

A NovAA 300 flame atomic absorption spectrometry (FAAS) with deuterium background signal corrector was used for the analyses of the metal ions in sample and standard solutions. An air/acetylene flame was used as an energy source for the atomization step. Before carrying out the actual analysis, the FAAS operating parameters were optimized by measuring the absorption signals of Pb²⁺ standard solutions and all parameters were adjusted at the optimum value during analysis. Ammonium chloride solution (20%) was used to minimize chemical interference.

RESULTS

Clay soil characterization

The particle size distributions and some physico-chemical

Table 2. SSAs of the clay soils fired at different temperatures.

Firing temperature (°C)	SSA (m ² /g)		
	S _{1F}	S _{2F}	S _{3F}
200	24 \pm 2.7	31 \pm 2.4	49 \pm 3.2
300	31 \pm 4.1	38 \pm 4.4	55 \pm 4.2
400	39 \pm 3.2	51.8 \pm 5.6	66 \pm 5.5
500	36 \pm 4.9	45.6 \pm 5.3	71 \pm 5.9
600	33 \pm 3.5	41 \pm 3.2	59 \pm 3.2

properties of the selected clay soils were determined (Table 1). The clay content of S₃ was 1.41 and 2.06 times higher than those of S₂ and S₁, respectively. That of the S₂, on the other hand, was 1.46 times higher in clay content than that of S₁. The CEC and SSAs of the untreated soils follow the same order as their clay contents while their pHpzc was observed to decrease with an increase in clay content. Table 2 depicts the surface areas of the clay soils fired at different temperatures.

From the table, we can clearly observe that the surface areas of fired S₁ and S₂ increase in the temperature range of 200 to 400°C and decrease at temperatures higher than 400°C. On the other hand, the surface area of fired S₃ was found to increase in the temperature range of 200 to 500°C and decrease at temperatures higher than 500°C. The surface areas of the fired clay soils, although very low relative to those of activated carbon adsorbents (500 to 1400 m²/g) which are used for various adsorption purposes, are fairly high relative to other adsorbents such as wheat bran (8.65 m²/g) (Bulut and Baysal, 2006), natural clay (26.90 m²/g) (Njoku et al., 2011) and vanadium mine tailing (42.39 m²/g) (Shi et al., 2009), and cottonseed hull charred at 350 (4.7 m²/g) and 650°C (34 m²/g) (Uchimiya et al., 2011).

Effect of clay soil firing temperature on adsorption

The increase in the adsorption efficiencies of the fired clay soils with temperature in the range 200 to 400/500°C and the subsequent decline can be explained in terms of surface area (Table 2). With an increase in firing temperature more and more water molecules that are adsorbed in the clay matrix will be driven out, leaving porous structures in their place. This results in an increase in the surface areas of the fired clay soils. Temperatures above a certain optimum, however, destroy the clay structure and cause a decrease in surface area (Mortland, 1954). The surface area data in Table 2 confirms this fact. The reason for the higher optimum firing temperature of S₃ relative to those of S₂ and S₁ can be explained in terms of the higher water holding capacity of S₃. Due to the higher clay content of S₃ than S₂ and S₁ it may contain more water molecules

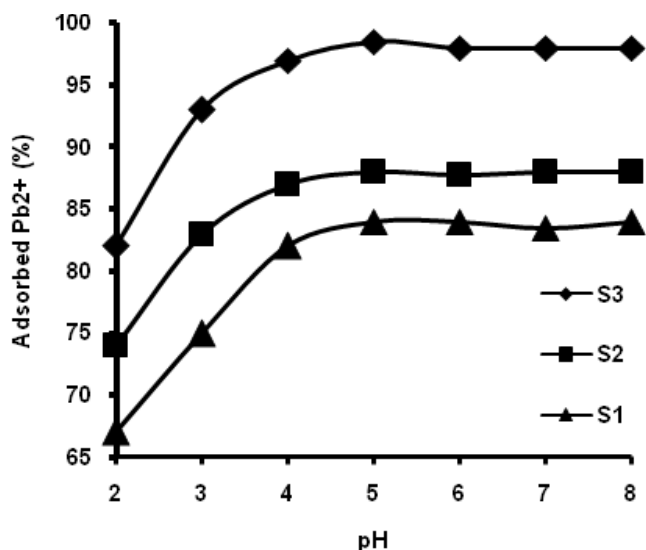


Figure 1. Adsorption of Pb^{2+} ions onto the fired clay soils at different solution pH ($C_o = 50$ mg/L, volume = 100 mL, adsorbent dose = 4 g, shaking time = 120 min, $T = 298 \pm 2$ K).

that are strongly bound in its matrix. As a result, driving out the water molecules in S_3 may require higher temperature than those in S_2 and S_1 .

Effect of pH

The effect of pH on the adsorption efficiency of Pb^{2+} was studied in the pH range of 2 to 10 (Figure 1). Not surprising, the results indicated that adsorption of Pb^{2+} was influenced by the pH of the solution. The adsorption of Pb^{2+} by all the clay-based soils in this study was observed to increase linearly from pH 2 to 4. At pH 5, adsorption increased slightly and remained nearly constant from then until pH 10. This phenomenon is known to be true for metal ions such as Pb^{2+} that have a strong tendency of undergoing hydrolysis (McBride, 1994).

Figure 1 clearly shows that, the Pb^{2+} adsorption efficiency of S_{3F} was higher than both S_{2F} and S_{1F} at all pH values studied. In turn, the adsorption efficiency of S_{2F} was higher than that of S_{1F} . The minimum adsorption efficiency for all the three clay soils was recorded at pH 2 and the maximum at pH 5. The minimum percent Pb^{2+} adsorbed by S_{3F} , S_{2F} and S_{1F} were, 82, 74 and 66%, respectively; while the maximum were 99, 89 and 83%.

Effect of contact time

The influence of contact time for the adsorption of Pb^{2+} on the clay soils was investigated by successively increasing the contact time from 30 to 180 min in 30 min intervals (Figure 2). The quantity of Pb^{2+} adsorbed onto

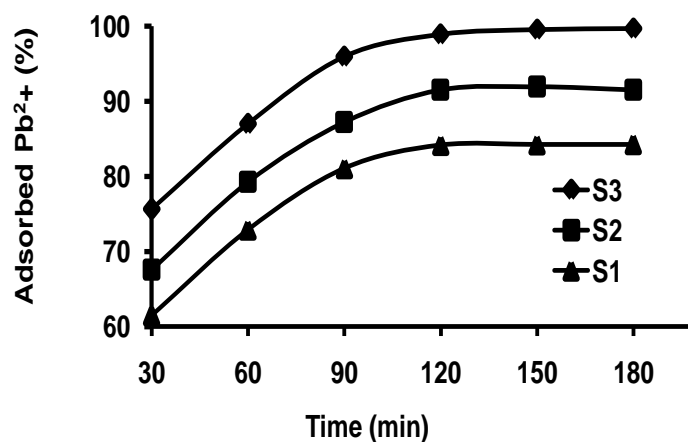


Figure 2. Removal of Pb^{2+} ions by the fired clay soils at different contact time ($C_o = 50$ mg/L, volume = 100 mL, pH = 5, adsorbent dose = 4 g, $T = 298 \pm 2$ K).

the clay soils was found to increase steadily with time and equilibrium was attained at about 120 min in all the clay soils.

The increase in adsorption was rapid between 30 to 90 min and relatively slower until it appeared to reach constant state after 120 min of shaking time. After equilibrium, the adsorption rate was observed to remain nearly constant. The apparently high rate of adsorption in the first 90 min could be attributed to the fact that the available adsorption sites were sufficient when compared with the density of Pb^{2+} adsorbed at the beginning. With further increase in time, the adsorption sites become saturated gradually and the uptake rate will be controlled by the rate at which the adsorbate (Pb^{2+}) is transported from the exterior to the interior sites of the adsorbent particles, so the adsorption became much slower (Talaat et al., 2011). Finally, all possible adsorption sites will be occupied and from then on, a dynamic equilibrium in which Pb^{2+} ions adsorbed onto the clay surfaces are balanced by Pb^{2+} ions leaving the clay surfaces. As a result, no change shall be observed in the level of Pb^{2+} adsorption.

Effect of adsorbent dose

The percent removal of Pb^{2+} was studied by varying the adsorbent dose in the range of 1 to 6 g (Figure 3). It is clearly shown in Figure 3 that the adsorption of Pb^{2+} increased with an increase in the quantity of the clay adsorbent from 1 to 4 g and remained nearly constant at adsorbent quantities higher than 4g. As a result, an adsorbent dose of 4 g in 100 mL of adsorbate solution was used for the study of other parameters.

The maximum adsorptions for S_{1F} , S_{2F} and S_{3F} were found to be 83, 89 and 99%, respectively. The adsorption capacity of S_{3F} , the soil with the highest clay content, was

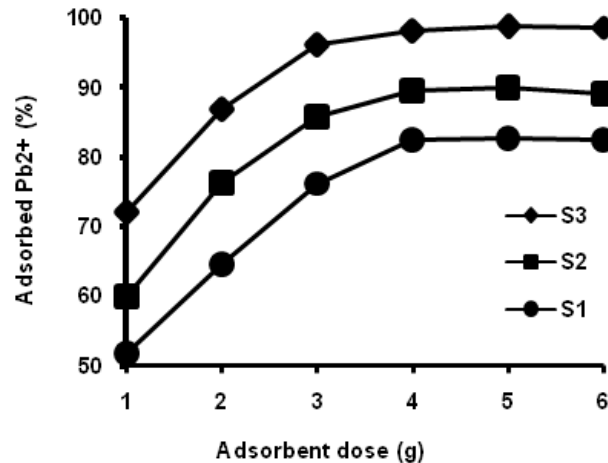


Figure 3. Adsorption of Pb^{2+} as a function of adsorbent dose ($T = 298 \pm 2$ K, $C_o = 50$ mg/L, volume = 100 mL, pH = 5, shaking time = 120 min).

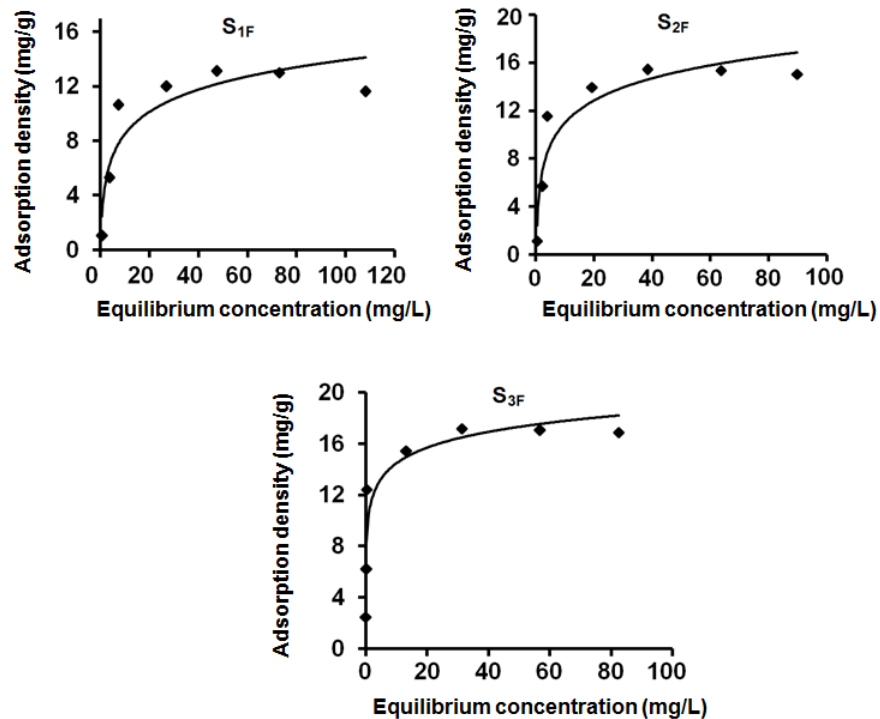


Figure 4. Adsorption isotherms of Pb^{2+} in S_{1F} , S_{2F} and S_{3F} at various equilibrium concentrations (adsorbent dose = 4 g, shaking time = 120 min, pH = 5 and $T = 298 \pm 2$ K).

observed to be about 10 and 20% higher than those of S_{2F} and S_{1F} , respectively. S_{2F} , whose clay content was 1.46 times greater than that of S_{1F} had an adsorption capacity about 6% higher than S_{1F} .

Effect of initial metal ion concentration

The results obtained for the effect of adsorbate concen-

tration on the adsorption efficiencies of the fired clay soils are plotted as adsorption density (q_e) versus bulk equilibrium concentration (C_e) (Figure 4). The isotherms indicate a sharp rise in the adsorption of Pb^{2+} for the lower (5 to 10 mg/L) Pb^{2+} concentrations followed by a slower increase of up to about 50 mg/L. From this concentration onwards, the adsorption density was observed to remain constant.

Adsorption isotherms of the types shown in Figure 4 are extreme cases of the L-type (Langmuir) isotherm and are categorized under H-type (McBride, 1994). Such isotherms are indicative of a very strong adsorbate-adsorbent interaction (chemisorptions).

Adsorption isotherms

The equilibrium equation, commonly known as adsorption isotherm, is a basic requirement for the design of an adsorption system. Such an isotherm provides information on the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the operating conditions. Freundlich and Langmuir equations were early adsorption models and are still frequently used.

The two models differ from each other in their assumption concerning the existence of a finite adsorption capacity. The Langmuir equation includes a term for the maximum amount of metal that can be adsorbed; hence, it predicts a decrease in incremental adsorption, that is, in the $\Delta q_e/\Delta C_e$ ratio at sufficiently high q_e (Payne et al., 1998). The adsorption equilibrium data in the current study was applied to the Langmuir model using the linearized form of the isotherm expressed by equation (1) (Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (1)$$

Where, the term C_e is equilibrium concentration of the metal (mg/L) in solution and q_e is the amount of the metal adsorbed per unit mass of clay soil (mg/g). q_m and K_L are Langmuir constants related to adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively and were evaluated from the slope and intercept of the regression equation for the C_e/q_e versus C_e plots, respectively.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter, R_L , which is defined by Equation 2.

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

Where, C_0 = the initial concentration of Pb^{2+} ; $R_L = 0$ indicates an irreversible adsorption; $0 < R_L < 1$ favourable; $R_L = 1$ linear and, $R_L > 1$ unfavourable.

The plots of C_e/q_e versus C_e for the adsorption of Pb^{2+} on the three clay soils (figures not shown) were found to be linear with R^2 values ranging from 0.971 to 0.999. This shows that adsorption of Pb^{2+} on the fired clay soils conforms to the linear form of the Langmuir model in the concentration range considered in this study. Adsorbents of this type that exhibit the Langmuir isotherm behavior

are supposed to contain fixed individual sites, each of which equally adsorbs only one molecule, thus forming a monolayer (McKinley and Jenne, 1991). The Langmuir adsorption maxima, q_m , and the equilibrium constant, K_L , were found to be high for S_{3F} , 17.27 and 3.05 mg/g, respectively; followed by values of 15.86 and 1.99 mg/g for S_{2F} and 11.63 and 0.68 mg/g for S_{1F} . The orders of both q_m and K_L for the three clay soils were in accordance with the order of their clay contents, that is, the higher the clay content of a soil, the higher were its q_m and K_L values. The higher q_m and K_L values associated with soils of higher clay content indicate that the maximum quantity of Pb^{2+} that can be adsorbed, the affinity of the binding sites and the energy of adsorption of soils of high clay content for Pb^{2+} was high relative to soils of low clay content. The calculated R_L values in all cases were found to be less than 1, indicating a favourable adsorption condition.

Using the q_m and SSA values of each of the clay soils, the maximum adsorption density of Pb^{2+} ions on the clay soils were calculated in terms of number of Pb^{2+} ions adsorbed per unit area of soil. Accordingly, adsorption densities of 2.91, 1.17, and 0.87 Pb^{2+} ions per nm^2 area were obtained for S_{3F} , S_{2F} and S_{1F} , respectively. This reveals that the soil with the highest clay content, S_{3F} , did not only possess a higher surface area than S_{2F} and S_{1F} , but was also able to bind more Pb^{2+} per unit area. This can be attributed to the existence of a higher number of sites on the surface of S_{3F} that are preferred by Pb^{2+} ions for adsorption.

The equilibrium data in the current study were applied to the logarithmic form of the Freundlich model given by Equation 3 (Freundlich, 1906).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where, q_e (mg/g) is the solid-phase concentration of Pb^{2+} which is in equilibrium with the liquid-phase concentration C_e (mg/L), K_F (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. K_F and $1/n$ were determined from the plot of $\log q_e$ versus $\log C_e$, $\log K_F$ being the intercept and $1/n$ the slope of the isotherm. The equation obviously does not predict an adsorption maximum; that is, q_e would be expected to increase as long as C_e increases.

The adsorption pattern of Pb^{2+} on the clay soils were found to fit well with the Freundlich model with R^2 values of 0.968, 0.966 and 0.969 for S_{3F} , S_{2F} and S_{1F} , respectively (figures not shown). Adsorbents that follow the Freundlich isotherm equation are assumed to have a heterogeneous surface consisting of sites with different adsorption potentials, and each type of site is assumed to adsorb molecules, as in the Langmuir equation. The Freundlich adsorption capacities, K_F , for S_{3F} , S_{2F} and S_{1F} , were found to be 1.92, 1.42 and 1.34 mg/g, respectively, indicating that the adsorption capacity of the soil was

Table 3. Rate constants and coefficient R^2 of models of pseudo first and pseudo second order rate equations used to describe adsorption of Pb^{2+} on the studied fired clay soils.

Adsorbent	Pseudo 1 st order			Pseudo 2 nd order		
	q_e	k_1	R^2	q_e	k_2	R^2
S _{1F}	1.206	0.015	0.937	1.909	0.0898	0.999
S _{2F}	1.328	0.021	0.925	1.913	0.102	0.998
S _{3F}	1.418	0.031	0.923	1.948	0.157	0.998

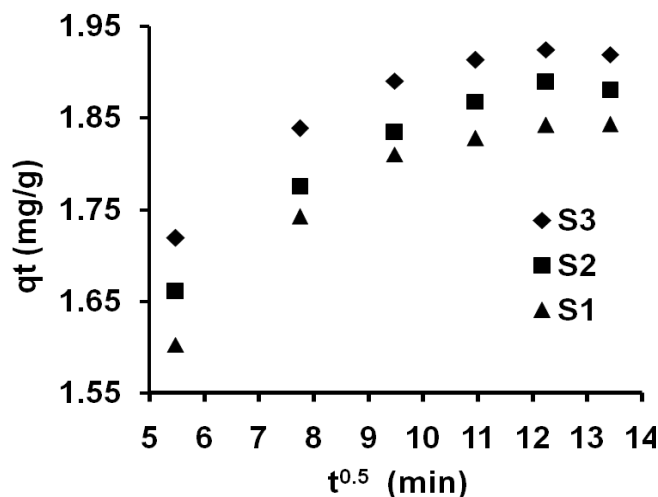


Figure 5. Intra-particle diffusion curve for the adsorption of Pb^{2+} ions on S_{3F}, S_{2F} and S_{1F}.

directly correlated with its clay content. Moreover, the Freundlich coefficients ($1/n$) were found to be below 1 (0.77, 0.71 and 0.53 for S_{3F}, S_{2F} and S_{1F}, respectively) indicating that the adsorptive removal of Pb^{2+} on the clay soils under the studied conditions was feasible.

Adsorption kinetics

Adsorption kinetics describes the solute uptake rate, which in turn governs the residence time of adsorption reaction and is one of the important characteristics in defining the efficiency of adsorption. In order to investigate the kinetics of adsorption of Pb^{2+} by the clay soils and the potential rate-controlling steps, Lagergren-first-order (Lagergren, 1898) and pseudo-second-order kinetic models (Ho and McKay, 1999) given by Equations 4 and 5, respectively, were used.

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (5)$$

where q_e and q_t are the solid-phase concentration at equilibrium and at time t , respectively.

Correlation coefficients and agreement between experimental adsorption data (q_{exp}) and model predicted values of the amounts of Pb^{2+} ions adsorbed (q_e) were used to support the validity of the kinetic models. A satisfactory model shows good linearity of plots, expressed by a high R^2 value, and small deviation between q_e and q_{exp} . The pseudo-first-order rate constant, k_1 (min^{-1}), pseudo-second-order rate constant, k_2 (g/mg/min) and, the adsorption capacity, q_e , were computed from the slopes and intercepts of the plots (Table 3).

The R^2 values of the pseudo-second-order model were higher than those of the Lagergren-first-order model, indicating that the pseudo-second-order model was a comparatively better-fit to describe the adsorption process of Pb^{2+} onto the clay soils. The agreement between q_e and q_{exp} values for the pseudo-second-order and pseudo-first-order models were found to be significant at $p < 0.01$. This result also supports the fact that the pseudo-second-order kinetic model was a better fit. The pseudo-second-order rate constant of S_{3F} ($0.157 \text{ g min}^{-1} \text{ mg}^{-1}$) was found to be higher than those of S_{2F} (0.102) and S_{1F} (0.0898). This could be an indication of the relatively faster rate at which equilibrium in S_{3F} is attained relative to S_{2F} or S_{1F}.

The amount of Pb^{2+} adsorbed per unit mass of adsorbent at time t , q_t , as a function of the square root of time, $t^{0.5}$, was plotted using the Intra-particle Diffusion Model which is based on the theory proposed by Weber and Morris (1963) and given by Equation 6 (Figure 5).

$$q_t = k_p t^{0.5} \quad (6)$$

where, k_p ($\text{mg g}^{-1} \text{ min}^{0.5}$) is the intra-particle diffusion rate constant.

The plot should be linear if the intra-particle diffusion is involved in the adsorption process. If the lines pass through the origin then the intra-particle diffusion is the rate-controlling step; if not, it is indicative of some degree of boundary layer control and this further shows that the intra-particle diffusion is not the only rate-limiting step, but that other kinetic models may also control the rate of adsorption, all of which may be operating simultaneously (Yazid and Maachi, 2008).

The plots in Figure 5 show an initial rising portion which rises linearly and then a plateau at higher $t^{0.5}$ values, which arises due to a difference between the initial and final stages of mass transfer (Panday et al., 1986). All three plots had non-zero intercepts indicating the existence of some degree of boundary layer control. Therefore, intra-particle diffusion was not a suitable mechanism to fully explain and predict the adsorption of the Pb^{2+} ion in this study. Similar results were reported by other researchers (Panday et al., 1986; Weber and Morris, 1963; Gok et al., 2008).

DISCUSSION

Adsorption efficiencies of S_1 and S_2 fired at 400°C were higher than those fired at lower or higher temperatures. While for S_3 , firing temperature of 500°C was the optimum. The observed increase in adsorption efficiency up to 400/500°C and the subsequent decline can be explained in terms of surface area. With an increase in firing temperature more and more water molecules that are adsorbed in the clay matrix will be driven out, leaving porous structures in their place. This results in an increase in the surface areas of the fired clay soils. Temperatures above a certain optimum, however, destroy the clay structure and cause a decrease in surface area (Mortland, 1954). The surface area data in Table 2 confirms this fact. The reason for the higher optimum firing temperature of S_3 relative to those of S_2 and S_1 can be explained in terms of the higher water holding capacity of S_3 . Due to the higher clay content of S_3 than S_2 and S_1 it may contain more water molecules that are strongly bound in its matrix. As a result, driving out the water molecules in S_3 may require higher temperature than those in S_2 and S_1 .

Adsorption of Pb^{2+} 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 H_3O^+ ions in the solution, a competition exists between the positively charged H_3O^+ and Pb^{2+} ions for the available sites on the negatively charged clay surface (Eba et al., 2010). Meanwhile, the positive H_3O^+ ions that have already occupied the negative charges on the clay surface will inhibit the approach of Pb^{2+} ions to the clay surface and reduce or minimize further adsorption of Pb^{2+} ions. As a result, the level of Pb^{2+} adsorption could be predicted to be low. At higher pH values ($pH > PZC$), the clay surfaces become negatively charged due to deprotonation of functional groups, favouring Pb^{2+} 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 Pb^{2+} ion adsorption was observed. Similar observations were reported by other researchers (Chantawong et al., 2001; Kaya and Oren, 2005).

With an increase in adsorbent dose, a corresponding increase in the removal of Pb^{2+} was observed until an optimum dose was reached. The initial increase in adsorption could be explained by an increase in the available active sites for the binding of Pb^{2+} . An increase in the number of active sites after equilibrium was reached, however, had no apparent effect on further increasing the removal of Pb^{2+} .

The amount of Pb^{2+} adsorbed was found to decrease with an increase in the equilibrium Pb^{2+} 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 Pb^{2+} 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. As a result, incremental adsorption is expected to be independent of adsorption density. With an increase in the equilibrium Pb^{2+} 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. Similar results were reported in other studies (Bulut and Baysal, 2006; Li et al., 2007; Qaiser et al., 2009; Njoku et al., 2011; Inglezakis et al., 2007; Sar et al., 2007).

Conclusion

In this study, the relative ability of fired clay soils to remove Pb^{2+} from aqueous solution was investigated. The fired clay soils showed removal efficiencies ranging from 83 to 99% where the highest removal efficiency was recorded for the soil with the highest clay content. In general, an average of 0.4% increase in adsorption capacity was achieved for a 1% increase in clay content. This may be attributable to the higher SSA and CEC possessed by the soil with higher clay content relative to the one with lower clay content. The affinity for Pb^{2+} ion, confirmed by the qm values determined from the Langmuir adsorption isotherm, was highest for the high-clay soil, S_{3F} (17.27 mg/g) followed by the two lower clay-content samples, S_{2F} (15.68 mg/g) and S_{1F} (11.63 mg/g). The isotherms can be better described by the Langmuir model (R^2 0.971 to 0.999) than by the Freundlich model (R^2 0.966 to 0.969). 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. Fired clay soils/bricks prepared from raw clay soil of higher clay : silt : sand ratio can remove Pb^{2+} better than those which were prepared from a lower ratio. Therefore, the selection of clay soils with the highest clay content relative to its silt and sand contents before firing for the purpose of adsorptive removal of Pb^{2+} will be necessary for efficient use of the fired clay soil adsorbents.

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