

Assessment of the Adsorption Capacities of Fired Clay Soils From Jimma (Ethiopia) For the Removal of Cr (VI) from Aqueous Solution

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Abstract:

The abilities of three thermally treated clay soils, S1, S2 and S3, which differed in textural compositions, to remove Cr (VI) from aqueous solutions were evaluated. Removal efficiencies of the clays were found to be influenced by textural composition, pH, initial Cr(VI) concentration, shaking time and adsorbent dose. An increase in the clay content of a clay-based soil by 1 % was found to result in an increase of about 0.5% in Cr(VI) removal. The adsorption of Cr(VI) by the clay-based soils was highest at pH 1 and 2 and, decreased above pH 2. For the lower initial concentrations (5 – 50 mg/L) of Cr(VI), adsorption was observed to increase sharply. A slower increase was observed up to about 75 mg/L and adsorption density remain nearly constant above 75 mg/L. The Cr(VI) adsorption process was better represented by the Langmuir model than by the Freundlich, with correlation coefficients (r^2) ranging 0.97 to 0.99. The adsorption capacities (qm) of S3, S2 and S1 calculated by using the Langmuir model were 8.77 mg/g, 4.81 mg/g, and 4.74 mg/g, respectively. The kinetics of Cr(VI) adsorption followed the pseudo-second-order model as determined by the stronger correlation (r^2 ranging from 0.971 to 0.992) and higher agreement between qe and q_{exp} .

Keywords: adsorption; clay soils; texture; adsorption kinetics; adsorption isotherm.

1.0 Introduction:

Hexavalent chromium is one of the most known toxic contaminants which enter the water streams through various industrial operations such as: metallurgy, electroplating, leather tanning, textile dyeing, paint, ink, and aluminium manufacturing industries (Qaiser *et al.*, 2009; Bhattacharyya and Gupta, 2006). Conventionally, heavy metal pollutants including Cr(VI) are removed from waste water by one or more of precipitation, adsorption with activated carbon, ion exchange, membrane separation, and 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 Cr(VI) ions from waste water (Bhattacharyya and Gupta, 2006; Wang *et al.*, 2003; Ahalya *et al.*, 2010; Khaldoun Al-Sou'od, 2012; Ayeni, 2012; Tasrina, *et al.*, 2012).

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks, and water (Pinnavai

1983) and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. Clays are among the various locally available materials that are used for the removal of Pb^{2+} and various other heavy metals from aqueous solutions (Bhattacharyya and Gupta, 2006; Yuan *et al.*, 2009; Priyantha and Bandaranayaka, 2011; Eba *et al.*, 2010; Njoku *et al.*, 2011;). In the soil, the variation in size of the particles and the proportionate amounts of fine and coarse materials, i.e., 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 brick chips for the removal of various non-metallic and metallic pollutants, including Cr(VI), has been reported in the literature [Priyantha, and Bandaranayaka, 2011; Seneveratne and Priyantha, 2009; Moges *et al.*, 1996]. 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 Cr(VI) 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 Cr(VI) 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.

2.0 Experimental:

2.1 Clay Soil Collection and Characterization:

The clay soils used in clay brick production at ten different brick production sites around Jimma town (South West Ethiopia) were sampled. The textural composition of these was determined by the standard method developed by (Sheldrick and Wang, 1993). Based on the range in soil texture, three of these ten soils, representing the three highest clay contents (S1, S2 and S3) were selected for further analysis. Six replicates, in 150 – 200 g portions, of each of the three selected soils were placed separately in crucibles and fired in a muffle furnace (3 h) at one of six different temperatures: 200, 300, 400, 500, 600, 700 °C respectively. The fired soils were then ground using a mortar and pestle; the fraction with ≤ 0.5 mm size particles was used for the adsorption studies. The adsorption efficiencies of each of the six samples fired at different temperatures from each of the three clay soils were tested and those with the highest Cr(VI) adsorption capacities were chosen for subsequent batch adsorption studies from each clay soil.

The Cation Exchange Capacity (CEC) and specific surface area (SSA) of the 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, 1963).

2.2 Reagents and Solutions

All chemicals used in this study were analytical grade. Deionized water was used for the preparation of stock standard solution of chromium and all subsequent dilutions. A stock standard solution of Cr(VI) (500 mg/L) was prepared by dissolving 1.414 g of $K_2Cr_2O_7$ (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.

2.3 Adsorption Experiments

Adsorption experiments were carried out using the batch method. A sample volume of 100 mL of 30 mg/L Cr(VI) was transferred into a 250 mL conical flask and its pH adjusted to the desired value. Then, the required quantity of the fired clay adsorbent (depending on the parameter to be studied) was added and shaken on a thermostatic shaker for a predetermined period of contact time. The solutions were filtered and the concentrations of residual Cr(VI) ions in the filtrates were analyzed using flame AAS.

2.4 Instrumentation

A NovAA 300 flame AAS with deuterium background signal corrector was used for the analyses of chromium 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 Cr(VI) standard solutions and all parameters were adjusted at the optimum value during analysis. Ammonium chloride solution (20%) was used to minimize chemical interference.

3.0 Results and Discussion:

3.1 Clay Soil Characterizations

The textural compositions and some physico-chemical properties of the selected clay soils were determined (Table 1).

Table 1: Textural composition, CEC, SSA and pH_{pzc} values of S1, S2 and S3.

Property	Clay type		
	S1	S2	S3
% Clay	39.98 ±0.02	58.20 ±0.12	82.01 ±0.31
% Silt	50.26 ±0.04	32.98 ±0.33	13.92 ±0.26
% Sand	9.84 ±0.11	8.82 ±0.29	4.11 ±0.03
CEC (meq/100g)	29.9 ±0.58	51.7 ±0.47	69.61 ±0.61
SSA (m ² /g)	39 ±3.2	51.8 ±5.64	71 ±5.85
pH _{pzc}	3.0 ±12	2.4 ±0.10	1.9 ±0.11

The clay content of S3 was 1.4 and 2.1 times higher than those of S2 and S1 respectively. That of the S2 soil, on the other hand, was 1.5 times higher in clay content than that of soil S1. The CEC and SSAs of the soils follow the same order as their clay contents while their pH_{pzc} was observed to decrease with an increase in clay content. The surface areas of the clay soils (Table 1), although very low relative to those of activated carbon adsorbents (500 – 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 °C (4.7 m²/g) and 650 °C (34 m²/g) (Uchimiya *et al.*, 2011). The CECs of the clay soils on the other hand were found to be higher than a Spanish soil composed of 30% sand, 25% silt and 45% clay, and had a CEC value of 13.2 meq/100 g (Alvarez-Bened *et al.*, 2005) however, they were lower than some pure clay minerals: clinoptilolite (188.40 meq/100 g), bentonite (100.19 meq/100 g) (Inglezakis *et al.*, 2007), kaolinite (7820 meq/100g), smectite (8600 meq/100 g) and vermiculite (123.4 meq/100 g) (Mbadcam *et al.*, 2011). Sawdust, with a reported surface area of 70 meq/100 g (Sumathi *et al.*, 2005) had a higher CEC than S1 and S2 but was comparable with that of S3.

3.2 Effect of Clay Soil Firing Temperature on Adsorption

The adsorption of Cr(VI) by the three clay soils fired at different temperatures were tested at pH 4, with an adsorbent dose of 4 g, a shaking time of 180 minutes and 100 mL of 50 mg/L Cr(VI) ion

solution. The results indicated that the maximum Cr(VI) ion removal varied with the firing temperature. Removal efficiencies of the lower clay soils S1 and S2 were found to increase in the firing temperature range of 200 to 400 °C and decreased at firing temperatures higher than 400°C. The higher clay soil (S3), on the other hand, was observed to increase in removal efficiency up to a firing temperature of 500 °C and exhibited a reduced adsorptive capacity when fired at temperatures exceeding 500 °C. The increase in adsorption efficiencies of the clay soils fired between 200 and 400/500 °C, and the subsequent decrease, can be explained in terms of surface area. With an increase in temperature during thermal treatment process, water molecules in the clay matrix are driven out, leaving porous structures in their place which result in an increase in the surface areas of the clay soils. Temperatures above a certain optimum will destroy the clay structure and cause a decrease in surface area (Mortland 1954). The reason for the higher optimum firing temperature of S3 relative to those of S2 and S1 can be explained in terms of its higher water holding capacity. S3, with higher clay content than S2 and S1, may contain more strongly bound water molecules and therefore would be expected to require a higher firing temperature to remove those water molecules from its structure than from the lower clay adsorbents S2 and S1.

3.3 Effect of pH:

The pH of the aqueous solution is an important parameter that affects the adsorption of metal ions on a clay surface. The effect of pH on the adsorption efficiency of Cr(VI) was studied in the pH range of 1 – 10 (Figure a). Not surprising, the results indicated that adsorption of Cr(VI) was influenced by the pH of the solution. The adsorption of Cr(VI) by all of the clay-based soils in this study was observed to remain the same for pH 1 and 2 then decrease at pH values above 2.

The higher adsorption of Cr(VI) at the strongly acidic solutions of pH 1 and 2 followed by a decrease in adsorption with an increase in pH can be explained as follows. At acidic pH, the predominant species of Cr(VI) are Cr₂O₇²⁻, HCrO₄⁻ and CrO₄²⁻ (Ahalya *et al.*, 2010). Elements like Cr that exist in the anionic form in solution are retained in the soil primarily by selective bonding (chemisorptions) processes at variable-charge mineral surfaces and layer silicate particle edges. The most important minerals in this regard are noncrystalline aluminosilicates; oxides and hydroxides of Fe, Al, and Mn; and layer silicate clays (edge sites only). It is the H₂O or valence-

unsatisfied OH⁻ ligands bound to surface metal ions (usually Fe, Al, or Mn) that are the sites of chemisorptions (McBride, 1994). In general terms, the surface reaction can be given as equations 1 and 2.

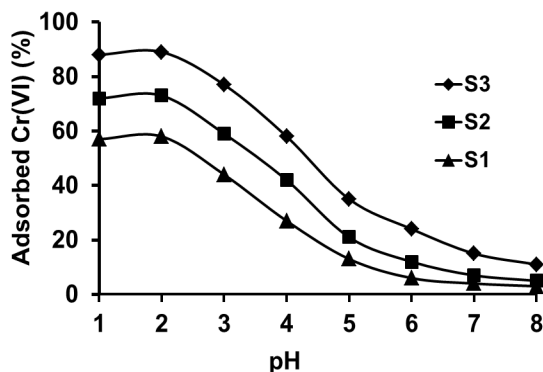
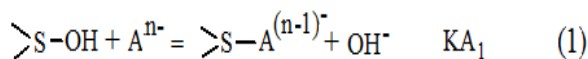
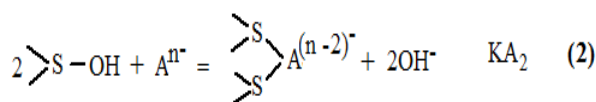


Figure a. Adsorption of Cr(VI) ions onto the clay soils at different solution pH ($C_o = 30$ mg/L, Volume = 100 mL, adsorbent dose = 4 g, shaking time = 150 minutes, $T = 298 \pm 2$ K).



Or, for the binuclear reaction:



Where A^{n-} is an anion (inorganic) of charge $-n$, and >S-OH is a reactive metal hydroxyl group.

These reactions are favoured by low pH, as is evident from the release of OH^- into solution. Low pH causes surface OH^- groups to accept protons, and since H_2O is an easier ligand to displace from metal bonding sites than OH^- , this facilitates the ligand exchange. Therefore, from the point of view of kinetics as well as equilibrium thermodynamics, low pH promotes anion adsorption (Gupta *et al.*, 2001; Zubair *et al.*, 2008).

3.4 Effect of Contact Time:

The influence of contact time for the adsorption of Cr(VI) on the clay soils was investigated by successively increasing the contact time from 30 to 240 minutes in 30 minute intervals (Figure b).

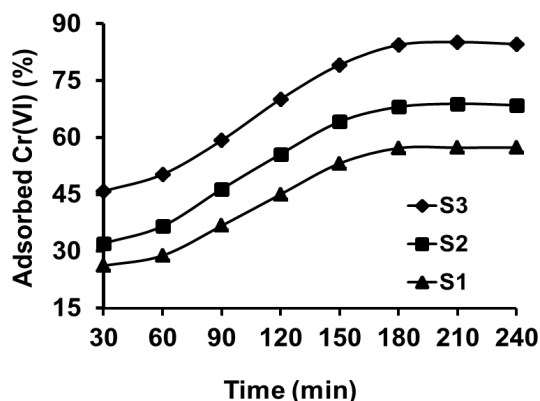


Figure b. Removal of Cr(VI) ions by the clay soils at different contact time ($C_o = 30$ mg/L, Volume = 100 mL, pH=2, adsorbent dose = 4 g, $T = 298 \pm 2$ K)

As shown in Figure b, Cr (VI) uptake rate was rapid within the first 150 min of contact time. This could be due to the large number of vacant spaces on the adsorbent surface and, the initial strong attraction between adsorbent positive sites and the negatively charged chromate species. Above 150 min a relatively slower adsorption was observed until it appeared to reach constant state after 180 minutes of shaking time in all the clay soils. Further increase in contact time did not show an increase in adsorption. The relatively slower adsorption above 150 min until equilibrium can be explained as follows. At about 150 min of shaking time, most of the adsorption sites on the surface of the clays are occupied by adsorbate ions and repulsion between adsorbed chromium species and those approaching to occupy the remaining vacant surface sites from the bulk solution increases. As a result, the rate at which Cr(VI) ions get adsorbed will decrease (Bhattacharyya and Gupta, 2006; Wang *et al.*, 2003; Yuan *et al.*, 2009). The diminishing removal with increasing time may also be due to intraparticle diffusion process dominating over adsorption (Deo and Ali 1992; Dave *et al.*, 2012). Finally, all possible adsorption sites will be occupied and from then on, a dynamic equilibrium in which Cr(VI) ions adsorbed onto the clay surfaces are balanced by Cr(VI) ions leaving the clay surfaces.

3.5 Effect of Adsorbent Dose

Adsorbent dose is another important parameter in adsorption studies because it determines the capacity of an adsorbent for a given initial concentration of the metal ion at the operating conditions. The percent removal of Cr(VI) was studied by varying the adsorbent dose in the range of 1 – 7 g for a constant quantity of Cr(VI) (Figure c).

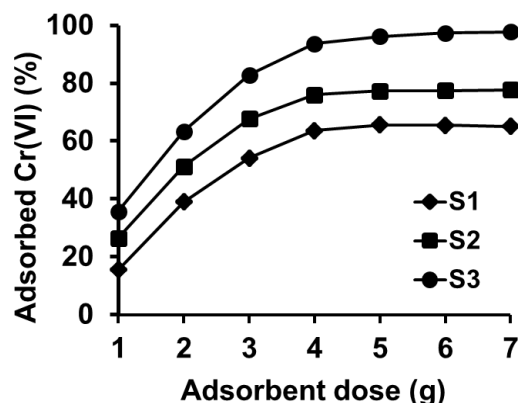


Figure c. Adsorption of Cr(VI) as a function of adsorbent dose ($T = 298 \pm 2$ K, $C_0 = 30$ mg/L, Volume = 100 mL, pH = 2, shaking time = 150 minutes).

It is clearly shown in Figure c that the adsorption of Cr(VI) 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 4 g. The maximum adsorptions of S1, S2 and S3 were found to be 65, 77 and 97% respectively. The adsorption capacity of S3, with the highest clay content, was observed to be about 20 and 32 % higher than those of S2 and S1 respectively. S2, whose clay content was 1.46 times greater than that of S1 had an adsorption capacity about 12% higher than S1. The observed initial increase in the removal of Cr(VI) from the solution with an increase in adsorbent dose could be due to an increase in the available active sites for Cr(VI) binding. Since the quantity of Cr(VI) is constant, an increase in the amount of adsorbent above a quantity that can completely adsorb the available Cr(VI) had no apparent effect on further increasing the removal of Cr(VI). After an adsorbent dosage of 4 g Cr(VI) removal was not observed to increase significantly.

3.6 Effect of Initial Metal Ion Concentration

The effect of initial concentration of Cr(VI) on the adsorption capacities of the clay soils was studied at initial concentrations (C_0) of 5, 25, 50, 75, 100, 125 and 150 mg/L. The results obtained are plotted as the adsorption density (q_e) versus the equilibrium bulk concentration (c_e) (Figure d). Adsorption isotherms of the types shown in Figure d 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 (i.e., chemisorptions).

The isotherms indicate a sharp rise in the adsorption density of Cr(VI) for the lower (5 mg/L – 50 mg/L) initial concentrations followed by a slower increase of up to about 75 mg/L. Above 75 mg/L, the adsorption density was observed to remain nearly constant. The initial sharp rise observed in adsorption followed by the relatively slow increase may be explained as follows: at lower equilibrium Cr(VI) ion concentrations, surface coverage could be low and the availability of sites that are not occupied by Cr(VI) 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 Cr(VI) ion concentration, the linearity of the increase in adsorption density with the equilibrium Cr(VI) ion decreases due to an increase in the surface coverage. The ratio of adsorbed to equilibrium Cr(VI) 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 (Bhattacharyya and Gupta, 2006; Yuan *et al.*, 2009; Priyantha, and Bandaranayaka, 2011).

3.7 Adsorption Isotherms

Adsorption isotherm is a basic requirement for the design of an adsorption system. It 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, i.e., in the $\Delta q_e / \Delta C_e$ ratio at sufficiently high q_e (Payne *et al.*, 1998). The adsorption equilibrium data in this study was applied to the Langmuir model using the linearized form of the isotherm expressed by equation (3) (Langmuir 1918).

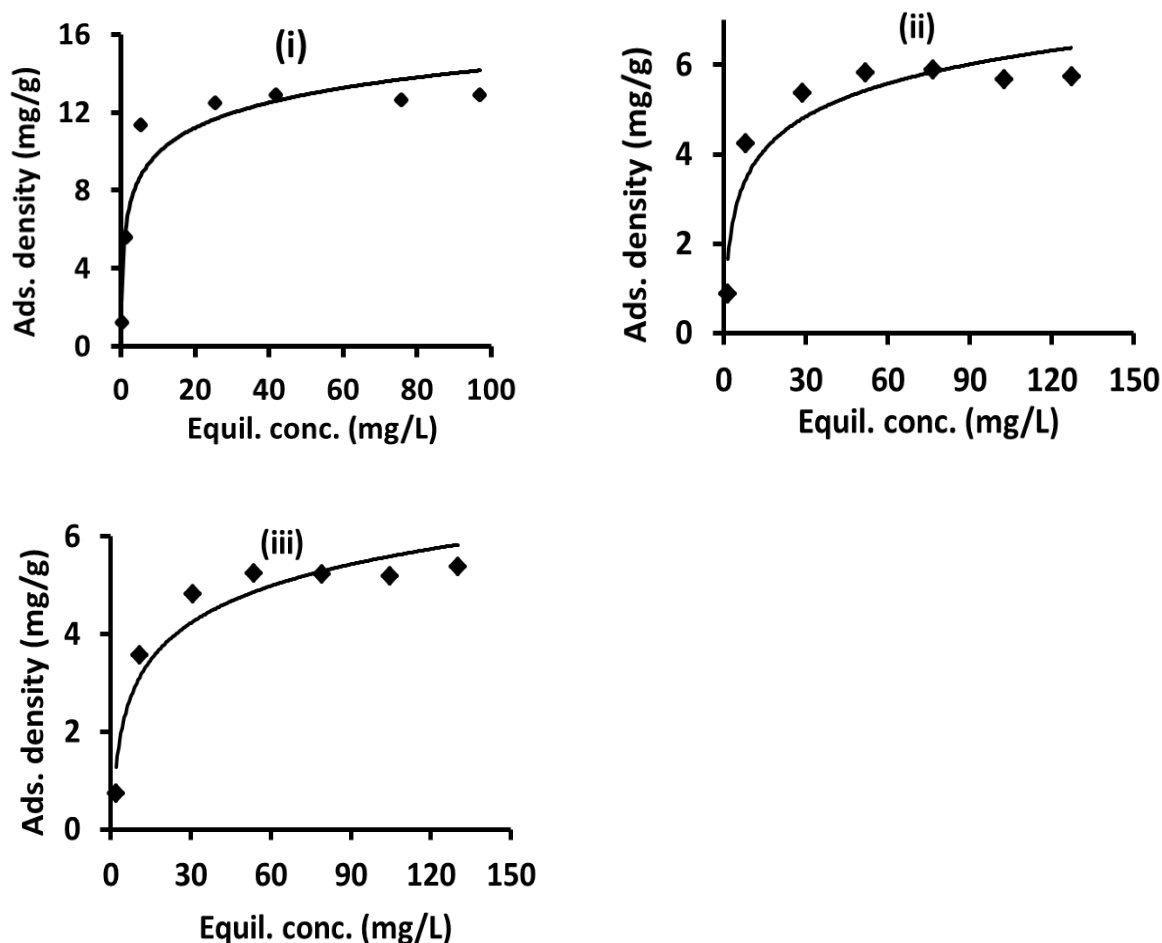


Figure d. Adsorption isotherms of (i) S3, (ii) S2 and (iii) S3 as a function of the equilibrium concentrations at different C_o (adsorbent dose = 4 g, shaking time = 150 min, pH = 2, and $T = 298 \pm 2$ K).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where the term C_e is equilibrium concentration of the metal (mg/L) in the liquid-phase and q_e (mg/g) is the solid-phase concentration of Cr(VI) which is in equilibrium with C_e (mg/L), 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 4.

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

$R_L = 0$ indicates an irreversible adsorption; $0 < R_L < 1$ favourable adsorption, $R_L = 1$ linear and, $R_L > 1$ unfavourable adsorption.

Langmuir and Freundlich isotherm models were applied to the experimental data to establish the relationship between the amount of Cr(VI) adsorbed by the clay soils and its equilibrium concentration in aqueous solution. The plots of C_e/q_e versus C_e for the adsorption of Cr(VI) on the three clay soils (Figures not shown) were found to be linear with r^2 values ranging 0.97 - 0.99. This shows that adsorption of Cr(VI) on the fired clay soils conforms to the linear form of the Langmuir model in the concentration range 5 – 150 mg/L. 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, qm , evaluated from the slopes of the regression equations for the C_e/q_e versus C_e plots for the three clay soils were in the order: S3 (8.77 mg/g) > S2 (4.81 mg/g) > S1 (4.74 mg/g). The orders of qm for the three clay soils was in accordance with the order of their clay contents, i.e., the higher the clay content of a soil, the higher was its qm value. The higher qm value associated with soils of higher clay content indicate that, the maximum quantity of Cr(VI) that can be adsorbed, the affinity of the binding sites and, the energy of adsorption of soils of high clay content for Cr(VI) was high relative to those of low clay content. The calculated R_L values in all cases were also found to be less than 1, indicating a favourable adsorption condition.

Using the qm and SSA values of each of the clay soils, the maximum adsorption density of Cr(VI) ions on the clay soils were calculated in terms of number of Cr(VI) ions adsorbed per unit area of soil. Accordingly, adsorption densities of 5.9, 1.3, and 1.1 Cr(VI) ions per nm^2 area were obtained for S3, S2 and S1 respectively. This revealed that the soil with the highest clay content, S3, did not only possess a higher surface area than S2 and S1, but was also able to bind more Cr(VI) ions on a unit area of the adsorbent. This can be attributed to the existence of a large number of sites on the surface of S3 that are preferred by Cr(VI) ions for adsorption.

The equilibrium data in the current study were also applied to the logarithmic form of the Freundlich model given by equation 5 (Freundlich 1906).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where q_e (mg/g) is the solid-phase concentration of Cr(VI) which is in equilibrium with the liquid-phase concentration C_e (mg/L), K_F (mg/g) and n are the 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 Freundlich isotherm model is considered to be appropriate for describing both multilayer sorption and sorption on heterogeneous surfaces (Ho *et al.*,

2002). The adsorption pattern of Cr(VI) on the clay soils were found to fit well with the Freundlich model with r^2 values of 0.972, 0.971, and 0.971 for S3, S2 and S1 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. The Freundlich constants K_F and n for S3, S2 and S1 respectively, were found to be 0.98, 0.79 and 0.49 L/g and, 1.20, 1.31 and 1.39. It has been shown by McKay *et al.* (McKay *et al.*, 1982) that n values between 1 and 10 values indicate beneficial adsorption. Therefore, the n values obtained in the current study indicate that the adsorptive removal of Cr(VI) on the clay soils under the studied conditions was feasible.

3.8 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 Cr(VI) 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 6 and 7 respectively, were used.

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303} t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \tag{7}$$

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 Cr(VI) 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 2).

Table 2: Rate constants and coefficient r^2 of models of pseudo first and pseudo second order rate equations used to describe adsorption of metals on the studied clay minerals

Adsorbents	Pseudo 1 st order			Pseudo 2 nd order		
	q_e	K_1	r^2	q_e	K_2	r^2
S ₁	0.354	0.004	0.854	0.511	0.0079	0.971
S ₂	0.287	0.004	0.958	0.521	0.0144	0.985
S ₃	0.451	0.007	0.905	0.497	0.0189	0.992

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 Cr(VI) 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 $p < 0.008$ and $p < 0.068$ respectively. This result also supports the fact that the pseudo-second-order kinetic model was a better fit. The pseudo-second-order rate constant of S3 (0.019 g min⁻¹ mg⁻¹) was found to be higher than those of S2 (0.014) and S1 (0.008). This could be an indication of the relatively faster rate at which equilibrium in S3 is attained relative to S₂ or S₁. The amount of Cr(VI) 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 (Weber and Morris 1963) and given by equation 8, (Figure e).

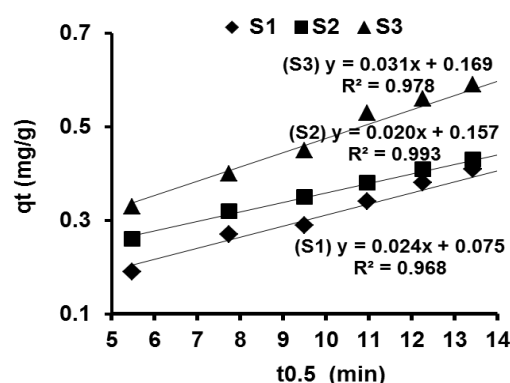
$$q_t = k_p t^{0.5} \quad (8)$$

Where, k_p (mg g⁻¹ min^{0.5}) is the intra-particle diffusion rate constant.

Intraparticle diffusion plays a significant role in controlling the kinetics of the adsorption process, if the plot of q_t versus $t^{0.5}$ yields a straight line passing through the origin, with the slope giving the rate constant, k_p . If the lines do not pass through the origin 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 e show a linear relationship between $t^{0.5}$ and q_t . It is clearly shown in Figure 5 that all the three plots do not pass through the origin, indicating that the diffusion of Cr (VI) species into the pores of the adsorbent was not the dominating factor controlling the mechanisms

of the adsorption process. Similar findings were reported by other researchers (Dave *et al.*, 2012; Sahmoune *et al.*, 2009; Kara and Demirbel 2012; Baral *et al.*, 2008).


Figure e. Intra-particle diffusion curve for the adsorption of Cr(VI) ions on S3, S2 and S1.

4.0 Conclusion:

In this study, the relative ability of fired clay soils to remove Cr(VI) from aqueous solution was investigated. The fired clay soils showed removal efficiencies ranging 64 to 97 % where the highest removal efficiency was recorded for the soil with the highest clay content and the lowest for the soil with the lowest clay content. In general, an increase in adsorption capacity ranging 0.67 to 0.83% 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 Cr(VI) ion, confirmed by the q_m values determined from the Langmuir adsorption isotherm, was highest for the high-clay soil S3 (8.77 mg/g) followed by the two lower clay-content samples, S2 (4.81 mg/g) and S1 (4.74 mg/g). The isotherms can be better described by the Langmuir model (r^2 0.968 - 0.987) than by the Freundlich model (r^2 0.971 - 0.972). 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

Cr(VI) by the three clay soils. The pseudo-second-order kinetic model was found to be a better fit for the adsorption of Cr(VI) by the clay soils.

The findings of the current study in general revealed that the Cr(VI) removal efficiencies of fired clay soils/bricks differ depending on their textural compositions of the clay soils from which the bricks were prepared. Fired clay soils/bricks prepared from raw clay soil of higher clay:silt:sand ratio can remove Cr(VI) 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 Cr(VI) will be necessary for efficient use of the fired clay soil adsorbents.

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