Removal of Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} cations and AsO_4^{3-} anions from aqueous solutions by mixed clay from Tundulu in Malawi and characterisation of the clay

SMI Sajidu[1], I Persson[2], WRL Masamba[1], EMT Henry[3]* and D Kayambazinthu[4]
[1] *Chemistry Department, University of Malawi, PO Box 280, Zomba, Malawi*
[2] *Department of Chemistry, Swedish University of Agricultural Sciences, Box 7015, 75007 Uppsala, Sweden*
[3] *School of Science, University of Fort Hare, Private Bag X1314, Alice, 5700, Republic of South Africa*
[4] *Forestry Research Institute of Malawi, PO Box 270, Zomba, Malawi*

Abstract

Water and wastewater studies in Malawi have revealed very high levels of heavy metals in most streams and other water bodies particularly within urban areas. The metals are produced and released during industrial and agricultural activities, and also in vehicular emissions. These metals may pose serious threats to both human health and the environment. This study investigated the potential of mixed clay, obtained from the Tundulu area, in removing, Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} cations and AsO_4^{3-} anions from aqueous solutions using batch equilibrium technique. Qualitative mineralogical characterisation of the clay revealed that the clay contains illite, distorted kaolinite, mixed layer minerals and non-clay mineral carbonate fluoroapatite. pH_{pzc} for the raw clay, as determined by potentiometric titrations, was 9.66 while pH_{pzc} of pretreated clay was 9.63. Pretreatment of the clay involved removal of carbonates, iron oxides and organic matter. Initial total metal concentrations ranged from 3 to 5 mg/ℓ. pH metal sorption dependence of the clay revealed Cr^{3+} removal from pH of 3 to complete removal at pH 5 with over 90% of the removal attributable to adsorption on the clay while the remaining 10% attributable to both adsorption and $Cr(OH)_3$ precipitation. Zn^{2+} complete removal occurred at pH above 7 with 92% attributable to adsorption while the rest could be from both adsorption and hydroxide precipitation. Cu^{2+} was removed from pH 4 and completely above pH 6.8 with 50% due to adsorption. Cd^{2+} removal was between pH of 6 and 9 with 85% due to adsorption to the clay. Lead was completely removed at pH greater than 7.67. Removal of Hg^{2+} at total Hg^{2+} concentration of 0.023 mM was pH independent fluctuating between 30 and 60%. No effective removal of AsO_4^{3-} anion was observed.

Keywords: heavy metals, illite, kaolinite, mixed layer minerals, carbonate fluoroapatite, pH_{pzc}

Introduction

Heavy metal water pollution is an area of major concern today in both developed and developing countries. Heavy metals occur naturally in soils, and they are widely used in industry especially in electronics and the rapidly growing information technology sector. Common anthropogenic sources include agricultural activities, atmospheric deposition, road run off, discharges from industrial plants and sewage works, acidic mine effluents and building of reservoirs. Agricultural activities provide important non-point sources of heavy metal pollutants such as cadmium, lead, and iron from phosphatic fertilisers. Phosphatic fertilisers, for example, are the most ubiquitous source of cadmium contamination because the rock phosphates used for the manufacture of fertilisers have relatively high concentrations of cadmium (Alloway, 1995; Harrison, 1996). The presence of high levels of these metals in the environment may cause long-term health risks to humans and ecosystems. It is therefore mandatory that their levels in drinking water, wastewater, and water used for agricultural and recreational purposes must be reduced to within the maximum allowable concentrations recommended by national and international health authorities such as the World Health Organisation (WHO, 2004).

Studies in Malawi have revealed high levels of particular heavy metals in several streams and soils in different areas of the country (Saka and Ambali, 1999; Lakudzala et al., 1999; Masamba and Chimbalanga, 2001; Kadewa, 2002). A recent quality inventory compilation of Blantyre streams (Limbe, Nasolo, and Mudi) and wastewater treatment plants (Limbe and Soche) reported levels of lead from 0.027 to 0.118 mg/ℓ, cadmium from 0.002 to 0.015 mg/ℓ, zinc from 0.166 to 0.630 mg/ℓ, chromium from 0.028 to 0.479 mg/ℓ, iron from 0.761 to 7.280 mg/ℓ and copper from 0.006 to 0.046 mg/ℓ (Sajidu et al., 2005). The concentrations at some sampling points were substantially higher than the World Health Organisation (WHO, 2004) maximum allowable limits for drinking water, which are 0.01, 0.003 and 0.05 mg/ℓ please for lead, cadmium and chromium respectively.

Many processes for the removal of heavy metals from water and wastewater have been investigated. Chemical precipitation, physical treatment such as ion exchange, solvent extraction and adsorption are amongst the conventional methods for the removal of heavy metals. However, these methods are unsustainable in developing countries due to high maintenance costs and chemical importation with scarce convertible foreign currency and the general dwindling revenue base of water treatment companies or urban authorities. Recently, natural materials, which are good sorbents and inexpensive have received much attention in sorption of heavy metals from contaminated solutions. Their use would be a viable replacement or supplement to these chemicals.

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* To whom all correspondence should be addressed.
☎ +2740 653 2341 or +2784 608 2136; fax: +27 40 653 1669;
e-mail: ehenry@ufh.ac.za

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Among the natural materials, clay minerals such as montmorillonite (Brigatti et al., 1995; Auboiroux et al., 1996; Zeng and Jiang, 2005; Brigatti et al., 2005), allophane (Okada et al., 2005), sepiolite (Brigatti et al., 1996; Brigatti et al., 2000), smectites (Arpa et al., 2000), kaolinite (Srivasta et al., 2005), bentonite (Khan et al., 1995; Al-Qunaibit et al., 2005; Donat et al., 2005), illite (Elzinga et al., 2001; Echeverria et al., 2005) and vermiculite (Brigatti et al., 2005) are some of the most useful heavy metal sorbents owing to their high cationic exchange capacity (CEC) and different mechanisms of heavy metal uptake by the clays have been proposed. Natural and synthetic hydroxyapatites have also been investigated for heavy metal uptake (Takeuchi and Arai, 1990; Ma, 1994; Singh et al.„ 2001; Lusvardi et al., 2002).

Removal of metal cations by clay minerals is controlled by parameters such as charge characteristics of the clay. Charge characteristics include the magnitude of the active sites and cation exchange capacity which has two components; namely, the permanent negative charge generated by isomorphous substitution within the octahedral and tetrahedral sheets of the silicate layers and the pH dependent charge arising from dissociation of edge hydroxyl groups. The pH-dependent charge may also be contributed by dissociation of other acid groups present such as humic acids particularly in un-purified clay minerals (Adhikari and Singh, 2003; Serrano et al., 2005). In addition to the clay charge properties, metal uptake is also influenced by the characteristic of the metal ion itself such as its ionic radius, charge size and hard – soft acid – base properties (McBride, 1994). Many researchers have investigated the influence of other factors on metal uptake by clays and soils in general such as metal concentrations (Coles and Yong, 2002), presence of competing ions (Auboiroux et al., 1996; Breen et al., 1999), pH (Maguire et al., 1981; Barrow et al., 1981; Barbier et al., 2000; Coles and Yong, 2002; Echeverria et al., 2005), temperature (Adhikari and Singh, 2003; Bektas et al., 2004) and ionic strength (Auboiroux et al., 1996; Breen et al 1999; Echeverria et al., 2005). Of all these factors, pH is considered the 'master variable' controlling ion exchange, dissolution/precipitation, reduction/oxidation, adsorption and complexation reactions (McBride, 1994). For each adsorbent and metal ion there is a narrow pH interval of less than 2 pH units within which uptake of the given metal ion increases from nearly zero to almost 100%. The pH increases the negative charges on the adsorbing material, modifies the metal speciation, displaces surface complexation reaction equilibria and also controls the direction of metal cation/proton competition reactions for the negative sites on the adsorbent (Stumm, 1992). The metal cation can be up taken either by cation exchange or by specific chemical sorption. Absorption onto the clay adsorbent structure and precipitation on the surface are also possible uptake mechanisms (Harter, 1983). These metal sorption mechanisms may occur at different solution pHs for different metals with a possibility of a combination of them at some pH ranges. Metal surface adsorption is characteristic of an inner sphere complex formation. An inner sphere complex can be distinguished from an outer sphere complex by dependence of the metal sorption on ionic strength. Strong dependence on ionic strength indicates formation of an outer sphere while a weak dependence on ionic strength is characteristic of an inner sphere complex formation (Stumm, 1992; Lutzenkirchen, 1997). pH_{pzc} values can also be used to distinguish inner and outer sphere complex formation. 100 percent metal sorption occurring below adsorbent's pH_{pzc} value is typical of an inner sphere complex while adsorption metal uptake occurring above pH_{pzc} is characteristic of an outer sphere complex. The opposite is true for anion uptake.

While most metal uptake studies by clay minerals have used single clay minerals, this study investigated the dependence of heavy metal uptake on pH by a natural mixed clay material. The clay which has been reported to contain about 10% $P_2O_{5,}$ is found at Tundulu in the Phalombe District in Malawi and is being investigated as a low- cost adsorbent for heavy metal remediation. This work also qualitatively characterised the clay by powder X-ray diffraction. Acidic and basic properties were determined by potentiometric titrations. The heavy metal cations studied were Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} and the anion AsO_4^{3-}.

Materials and methods

Natural clay samples

The clay samples used for heavy metal removal work in this study were collected from the Geological Survey Department of Malawi (GSoM) but originally came from Tundulu in the Phalombe District, Malawi. There was no report about their full mineralogical composition except information on the phosphorus content of about 10% (Lukhele, 2001). Characterisation and heavy metal adsorption experiments were done on both purified and raw clays. Discrimination in this paper is such that the purified clays are labelled 'purified Tundulu clays' (simply PTC) while the raw clays are labelled 'raw Tundulu clays' (simply RTC). The clay purification procedures for the removal of carbonates, iron oxides and organic matter were done as described in literature (Kunze and Dixon, 1986; Ammann, 2003). Cation exchange capacity (CEC) for both PTC and RTC was determined by adsorption of copper ethylenediamine complex as described by Bergaya and Vayer (1997). The CEC values were 9.61 ± 0.18 $cmol_c$/Kg for PTC and 19.73 ± 0.73 $cmol_c$/Kg for RTC which are typical CEC values of illite clay minerals of 0 to 40 $cmol_c$/kg (Gustafsson et al., 2005).

Powder X-ray diffraction

Room temperature XRD patterns for the RTC and PTC were collected in transmission mode using a PW1710 diffractometer (at the department of Forest Soils, SLU) with monochromatic $CuK_{\alpha 1}$ and $CuK_{\alpha 1}$ (λ_1=1.54060Å and λ_1= 1.54439 Å) radiation that was selected using a 0.01 mm Ni-filter. X-rays which were produced at the X-ray source (copper radiation) were passed through the 0.01 Ni-filter for homogenising the X-ray radiation giving pure CuK_α radiation which was diffracted by the sample. The data were collected in the range from 2.0 to 60.0° (2θ) by a linear PSD which was set at a step size of 0.020° (2θ) and counting time of 1.0 s per step. The diffractometer was operated by computer software from Phillips called automatic powder diffraction (APD).

Identification of minerals in the clay from the XRD patterns was performed 'by hand' using search-match JCPDS-files published by the Joint Committee on Powder Diffraction Standards (JCPDS, 1974) together with diffraction profiles obtained from standards of clay minerals as reported in literature (Duda and Rejl, 1990; Brindley and Brown, 1980). The final plot of the powder pattern was created using Microsoft Excel software on raw data text files.

Potentiometric titration

Suspensions of 6.0 g sample/ℓ (both for the PTC and RPC) were prepared. 50 mℓ of the clay suspension in 0.1 M $NaNO_3$

TABLE 1
Metal speciation in stock solution as calculated by Visual MINTEQ program

Reagent	Solution concentration (mM)	Solution pH	Species	Species concentration (mM)
$Pb(NO_3)_2$	0.50	5.43	Pb^{2+} $PbNO_3^+$ $PbOH^+$	0.491 0.006 0.002
$Cd(NO_3)_2.4H_2O$	0.60	5.76	Cd^{2+} $CdNO_3^+$	0.598 0.002
$Cu(NO_3)2.H_2O$	1.25	5.33	Cu^{2+} $CuNO_3^+$ $CuOH^+$ $Cu_2(OH)_2^{2+}$	1.235 0.008 0.005 0.001
$Zn(NO_3)_2.6H_2O$	1.25	5.31	Zn^{2+} $ZnNO_3^+$	1.244 0.006
$Na_2HASO_4.7H_2O$		8.17	$HASO_4^{2-}$ $H_2ASO_4^-$	0.946 0.054

background electrolyte was titrated with 0.0213M nitric acid stepwise from 0 to 20 mℓ at increments of 0.1 mℓ using Metrohm 665 Dosimat titrator. The pH reading after equilibration of each step was recorded using Ross Sure Flow combination electrode Orion No. 8172. During titration the flask containing the suspension was covered with parafilm to avoid formation of carbonates at pH greater than 6. A similar titration on a new suspension was done with 0.02M NaOH. The volume, $V_{e,}$ corresponding to total proton monolayer coverage (which in turn is used to calculate the total concentration of acid-base active sites, $\{\equiv SOH_{tot}\}$) was calculated from pH vs. V_t (volume of acid added) plot. The concentration of surface charge, [Q], which is the difference between positive and negative surface sites at every titration point and the mean number of protons per surface site (Z) were also calculated.

Plots of apparent pK_a, $pK_{aap.}$, values vs. Z for both the base and acid titrations were made for the determination of intrinsic pK_as, pK^s_{a1intr} and pK^s_{a2intr}, while points of zero charges, pH_{pzc} , for the clays were calculated as:

$$pH_{pzc} (= 0.5\ (pK^s_{a1intr} + pK^s_{a2intr}))$$

AsO_4^{3-}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} adsorption

Metal solutions preparation

Pb^{2+} of 0.50 mM (103.6 mg/ℓ) stock aqueous solution was obtained from dissolution of $Pb(NO_3)_2$ AR grade reagent (declared impurity of less than 0.5%) (BDH).Cd^{2+} was prepared from AR grade reagent $Cd(NO_3)_2.4H_2O$ (declared impurity of less than 1%) (BDH) to give a stock concentration of 0.6 mM (67.44 mg/ℓ). Cu^{2+} and Zn^{2+} were prepared from AR grade reagent $Cu(NO_3)_2.3H_2O$ (declared impurity of less than 0.5%) (MERCK) and $Zn(NO_3)_2.6H_2O$ (declared impurity of less than 0.2%) (Mallinckrodt Chemical Works) at a stock concentration of 1.25 mM (78.44 and 81.74 mg/ℓ respectively). AsO_4^{3-} was prepared from $Na_2HASO_4.7H_2O$ (declared impurity of less than 0.5%) (MERCK) at a stock concentration of 1.00 mM (74.92 mg/ℓ). Hg^{2+} was prepared from $Hg(CF_3SO_3)_2$ a concentration of 0.50 mM (100.3 mg/ℓ). Cr^{3+} of 2.10 mM (109.2 mg/ℓ) was prepared from dilution of stock solution of 1.4M $Cr(ClO_4)_3.6H_2O$. pH values of the solutions are shown in Table 1. Theoretical calculations performed from computer program Visual MINTEQ, Version 2.32 (Gustafsson, 2005) at the solutions' pH values indicate that most of the metal species in solution are free metal cations (Table 1). $Cr(ClO_4)_3.6H_2O$ and $Hg(CF_3SO_3)_2$ are not available in the program's list of components for the solution speciation.

Metal adsorption experiments

7.5 mℓ of 0.1 M $NaNO_3$ was pipetted into each of 12 centrifuge tubes. 2.5 mℓ of clay suspension (either PTC or RTC) and 0.5 mℓ of a given metal solution from its stock concentration were added to the centrifuge tube. An appropriate amount of acid (20 mM HNO_3) or base (20 mM NaOH) was added to adjust the pH to a certain value. The mixture was shaken for 48 h and then centrifuged for 15 min at 3 000 r/min using a KUBOTA KS-5200C centrifuge. 3 to 4 mℓ of the supernatant was taken, acidified with a drop of concentrated HNO_3 and analysed for the given metal concentration on an atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) in the case of Cd^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+}. $Pb^{2+,}$ As^{5+} and Hg^{2+} determination in the supernatant was done using an inductively coupled plasma emission spectrometer at the Department of Soil Sciences (SLU). The pH in the remaining supernatant in the centrifuge tubes was recorded as the equilibrium solution pH. Percentage metal uptake (%E) was calculated by use of Eq. (1)

$$\%E = \frac{(C_o - C)x100}{C_o} \qquad (1)$$

where:

C_0 and C are the initial and final concentrations respectively of the metal ions in solution.

Results and discussion

Powder X-Ray diffraction patterns of the clay material

The RTC and PTC XRD patterns are shown in Figs. 1a and 1b. Depending on the randomly packed samples the abundance of clay minerals is underestimated on behalf of primary rock-forming minerals. For a good analysis of the clay minerals oriented preparates (e.g. clay mineral-oriented specimen samples) and saturation with magnesium are recommended. However, the intention of this investigation was to obtain an approximate indication of the mineralogical composition of the Tundulu clay and to account for the clay's heavy metal cation adsorption properties based on this knowledge.

An interpretation of the d-values for the peaks point at an occurrence of illite, disordered kaolinite and carbonate fluoro-

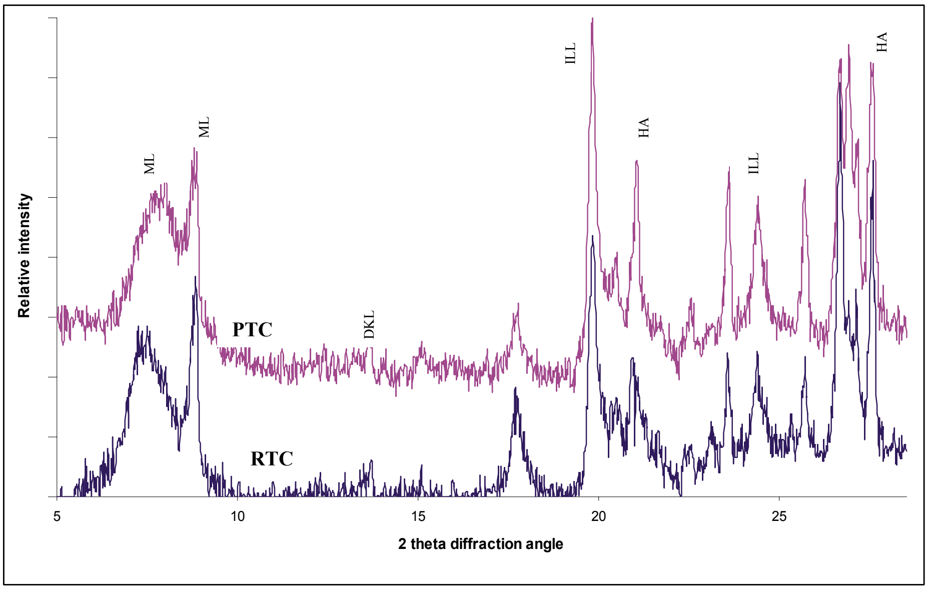

Figure 1a
PXRD patterns of Raw Tundulu Clays (RTC) and Purified Tundulu Clays (PTC).
ML = Mixed clay mineral, DKL = Distorted kaolinite, HA = Halloysite, ILL = Illite

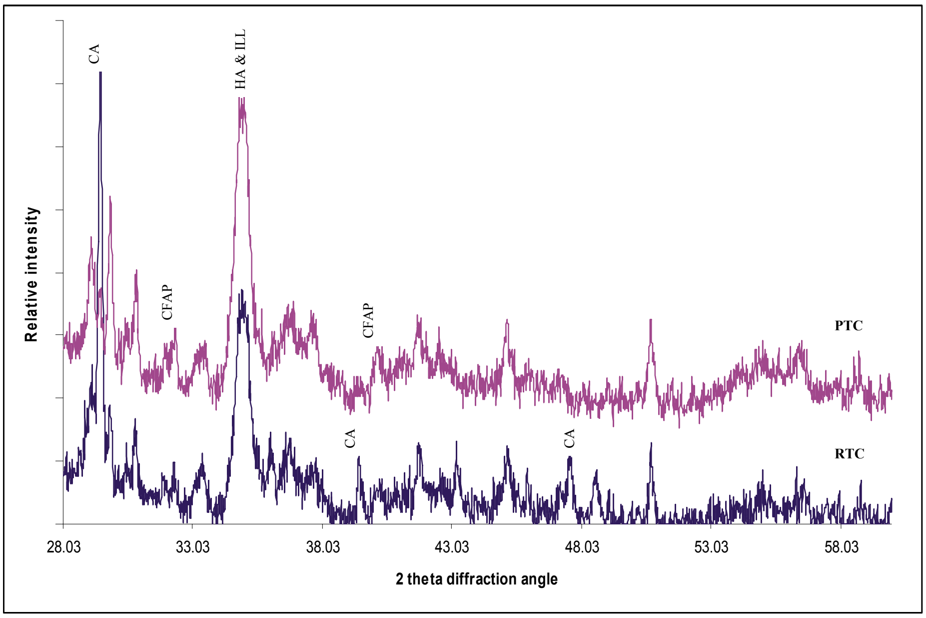

Figure 1b
PXRD patterns of raw Tundulu clays (RTC) and purified Tundulu clays (PTC). CA = calcite,
CFAP = carbonate fluoroapatite, HA = halloysite, ILL = illite

apatite (JCPDS, 1974: 21-145; 19-272). The kaolinite is said to be disordered because of the weak reflection at d-value of 7.17 Å which is quite intense in well-crystallised kaolinite. The carbonate fluoroapatite reflections at d-values of 2.78 Å, 2.68 Å and 2.24 Å are all weak indicating that fluoroapatite is not the dominant component of the sample. The reflections at 4.32 Å and 3.33 Å could be due to presence of halloysite which has a 1:1 layer structure as kaolinite but differs from kaolinite by having a single sheet of water molecules between the layers. The 3.33 Å peak is rather explained as a third order peak from illite. There is an indication from the broad intense reflections at 12.25 Å and 9.97 Å that the material could contain mica, smectite or vermiculite mixed layer (ML) mineral as well. The probability for mica occurrence in the clay fraction is low and instead illite ought to be abundant. It is obvious is that there must be some kind of ML-mineral especially as there is a prominent peak at 24 Å. The peaks at 10 Å, 5 Å and 3.33 Å provide clear evidence for illite and the 9.97 Å peak could be due to mica. The presence of calcite is detected in the RTC (reflections at 3.03 Å, 2.28 Å and 2.09Å) but not in the PTC, which has been treated for removal of calcite and iron compounds. This implies that calcite is fully removed during the clay purification process. It is interesting to note that quartz, one of the most common primary rock-forming minerals inherited from the bedrock, is not detected in the sample. The absence of quartz suggests the material is heavily weathered.

Another explanation for a broad peak at 4.46 Å (or 4.47 Å) instead of badly crystallised kaolinite is that the peak could come from dioctahedral mica with a peak in the interval 4.49 to 4.45 Å. Because there is a peak near 10 Å the probability for the occurrence of a mica peak at 4.46 Å is high.

Potentiometric titrations

The Tundulu mixed clay is highly alkaline as indicated by initial pH values of greater than 9 in Figs. 2a and 2b for the purified sample (PTC). This is also the case for the raw sample (RTC) as shown in Figs. 2d and 2e. For PTC $\{\equiv SOH_{tot}\}$ is 5.112x10^{-4}M (8.52 x10^{-5} mole/g) calculated from the equilibrium volume obtained in Fig. 2a and 3.166 x 10^{-3}M (5.277 x 10^{-4} mole/g) for RTC in Fig. 2d. RTC indicated pH buffer properties in the pH range of 4.0 to 6.0 and also in the range of 7.0 to 8.0. The buffering property in the range of 4.0 to 6.0 could be attributed to low water-soluble organic acids such as oxalic, citric, formic and lactic acids. De-protonation of water-soluble carboxylic groups of humic acids could also contribute to buffering in this range. In the pH region of 7.0 to 8.0, the buffering property could be attributable mainly to soluble inorganic phosphates (since dihydrogen phosphate has a pKa of 7.2). These water-soluble organic and inorganic acids were removed during the purification processes; hence, the absence of buffering properties in the PTC sample. However, the PTC curve in the pH region of 4.45 to 7 is not as smooth as it would have been in the case of the absolute absence of any water-soluble acids. There is an indication of some reactions which could be attributed to dissolutions and de-protonation of small amounts of acids retained from the purification processes. In addition to the clay minerals, the presence of organic matter in the RTC would render the RTC more effective at cation adsorption than

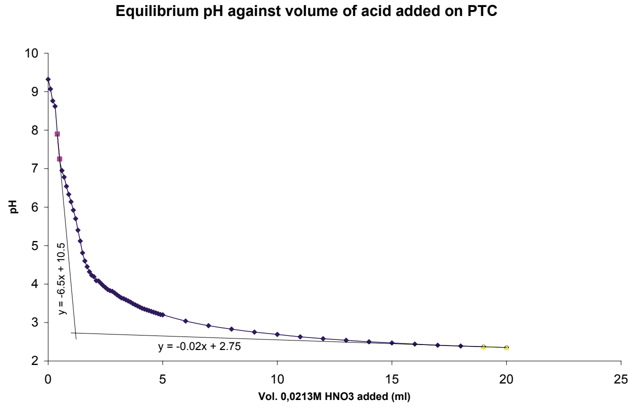

Figure 2a
Acidimetric titration of the purified Tundulu clays (PTC)

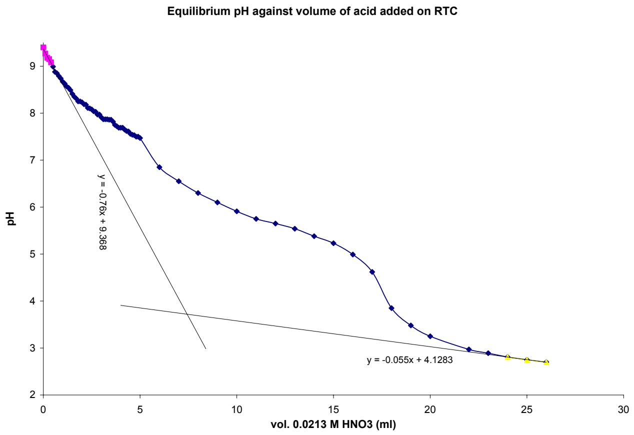

Figure 2d
Acidimetric titration of the raw Tundulu clays (RTC)

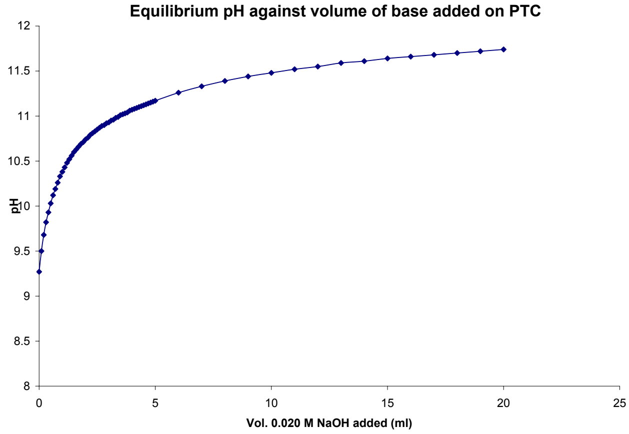

Figure 2b
Alkalimetric titration of the purified Tundulu clays (PTC)

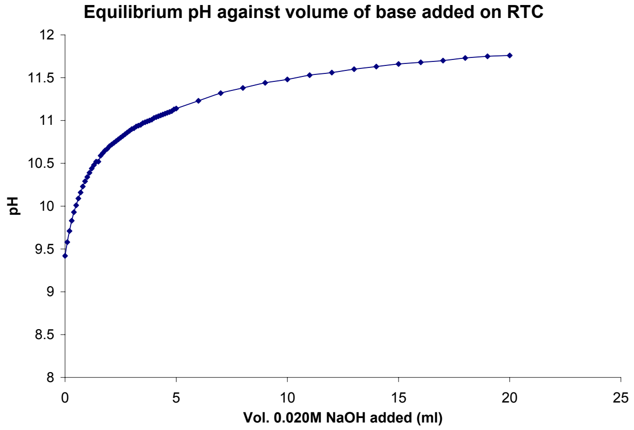

Figure 2e
Alkalimetric titration of the raw Tundulu clays (RTC)

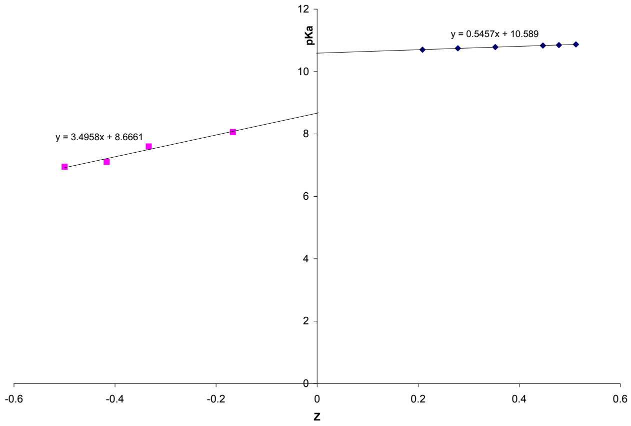

Figure 2c
Apparentacidity constants (pK_a app.) calculated from figures a and b plotted against Z for PTC. Note that the negative Zs for pK_{a1} app. have just been used for simplicity of the diagram. They are actually positive values.

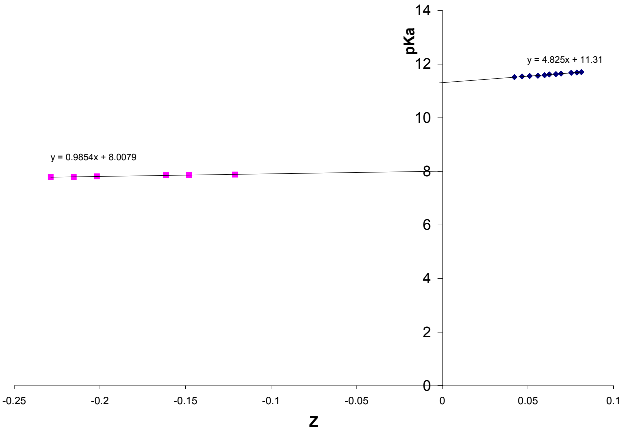

Figure 2f
Apparent acidity constants (pK_a app.) calculated from figures d and e plotted against Z for RTC. Note that the negative Zs for pK_{a1} app. have just been used for simplicity of the diagram. They are actually positive values.

the PTC. pH_{pzc} which is an average of $pK^s_{a1int_r}$ and $pK^s_{a2int_r}$ and is found to be 9.63 for PTC (Fig. 2c) and 9.66 for RTC (Fig. 2f).

Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} cation and AsO_4^{3-} anion adsorption from aqueous solutions

Adsorption of chromium

Figure 3a shows per cent chromium adsorbed at varying suspension pH. The results indicate that complete chromium removal is achieved between pH of 3 and 5. The solubility product constant (K_{sp}) for $Cr(OH)_3$ at 25°C is 6.3 x 10^{-31}. This implies that precipitation of $Cr(OH)_3$ at total Cr concentration of 0.1 mM occurs at pH greater than 5.27. Since 100% of the Cr^{3+} ions are removed below pH 5 by the PTC, such removal is solely attributable to adsorption on the clay mineral surfaces. However, in the case of RTC, only 90% of Cr^{3+} is removed below pH 5.27. The removal of the remaining 10% at higher pH could thus be due to combination of adsorption on clay minerals and precipitation of $Cr(OH)_3$. At pH values below 5, RTC adsorption of Cr^{3+} is greater than

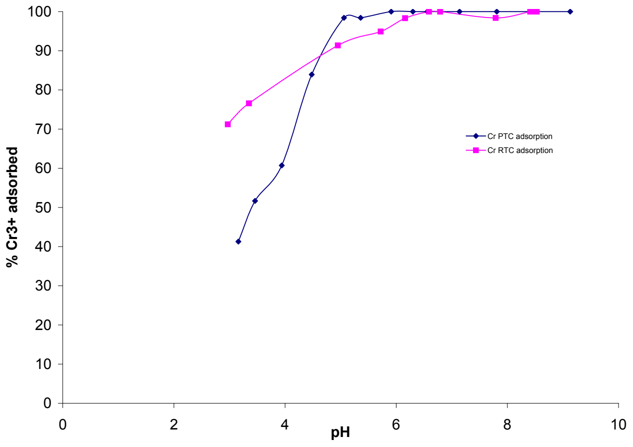

Figure 3a

% adsorbed Cr^{3+} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total Cr^{3+} concentration was 0.1 mM (5.2 mg/ℓ)

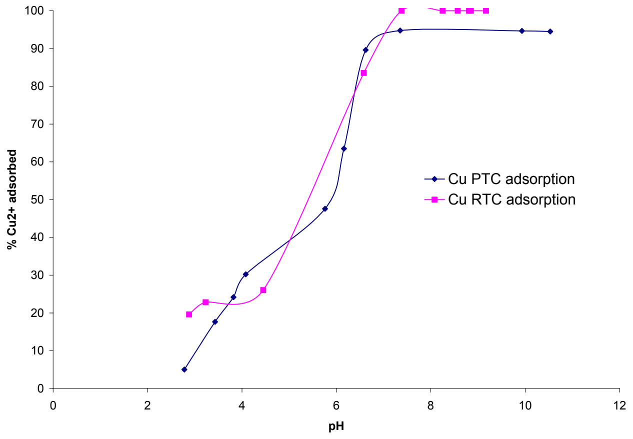

Figure 3b

% adsorbed Cu^{2+} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total Cu^{2+} concentration was 0.06 mM (3.8 mg/ℓ)

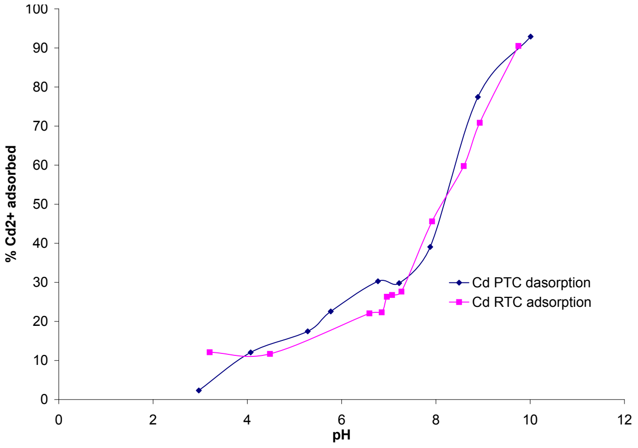

Figure 3c

% adsorbed Cd^{2+} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total Cd^{2+} concentration was 0.03 mM (3.4 mg/ℓ)

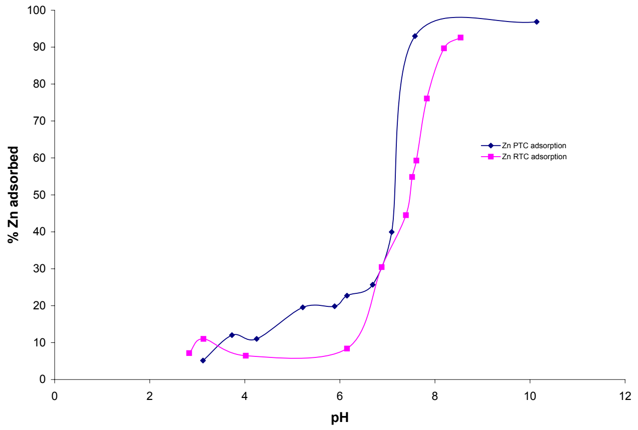

Figure 3d

% adsorbed Zn^{2+} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total Zn^{2+} concentration was 0.06 mM (3.9 mg/ℓ)

that of PTC. This is expected because in addition to adsorption on clay minerals, Cr^{3+} uptake by the untreated clay may also be governed by surface complexation to iron oxides and organic complexation as well. Adsorption to carbonates may also occur in the case of the RTC. Since the adsorption is below the material's pH_{pzc}, formation of inner sphere complexes is expected.

Adsorption of copper

Copper removal is achieved between pH 4 and 6.8 (from about 20% to 100%) (Fig. 3b). At total Cu^{2+} concentration of 0.06 mM with Cu $(OH)_2$ K_{sp} of 2.2×10^{-20}, precipitation of the hydroxide is expected to start at pH 6.28. At this pH already 50% and 65% of Cu^{2+} have been removed by PTC and RTC respectively. RTC in general indicated greater adsorption capacity at each pH value than PTC. The maximum Cu^{2+} removal capacity for the RTC was 100% while the PTC was 95%. In addition to adsorption and hydroxide precipitation, copper removal by the RTC may also be enhanced by precipitation of malachite ($Cu_2(OH)_2CO_3$). Formation of an inner sphere complex in the adsorption case is expected due to its occurrence below the material's pH_{pzc}.

Adsorption of cadmium

Similar Cd^{2+} adsorption trends were observed for both PTC and RTC (Fig. 3c). $Cd(OH)_2$ precipitation which is expected to start at pH of 9.46 when total concentration of Cd^{2+} is 0.03 mM could not account for the Cd^{2+} removal in this study because at pH 9.46 already 85% of Cd^{2+} had been adsorbed. However, Cd^{2+} adsorption by the clays was not as strong as Cu^{2+} and Cr^{3+} adsorption since 100% removal could not be achieved and even at high pH of 10 there was only 90% removal. It is reported (Gustafsson et al., 2005) that Cd^{2+} has a lower tendency to adsorb and form organic complexes than Pb^{2+} and Cu^{2+}. This is clearly seen in Fig. 3c where Cd^{2+} adsorption by RTC is generally lower than that of PTC at every pH point; contrary to the observations in the case of Cu^{2+} in Fig. 3b. The adsorption process occurs below pH_{pzc}; hence, the formation of inner sphere complexes is proposed.

Adsorption of zinc

Precipitation of solid $Zn(OH)_2$ at total Zn concentration of 0.06 mM is expected at pH greater than 7.65 since K_{sp} for $Zn(OH)_2$ is 1.2×10^{-17}. At pH 7.58, 92% Zn removal (Fig. 3d) by PTC is achieved which is attributable to adsorption either through surface complexation or ion exchange on the clay minerals. Just as for Cd adsorption in Fig. 3c, Zn adsorption by RTC is lower than that of PTC at given pH values probably due to the low tendency of Zn to adsorb and form organic complexes. This behaviour is a clear manifestation of chemical similarity between Zn and Cd.

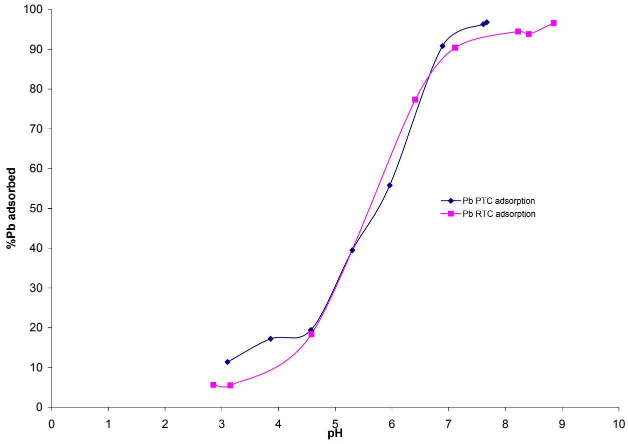

Figure 3e
%adsorbed Pb^{2+} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total Pb^{2+} concentration was 0.024 mM (4.9 mg/ℓ)

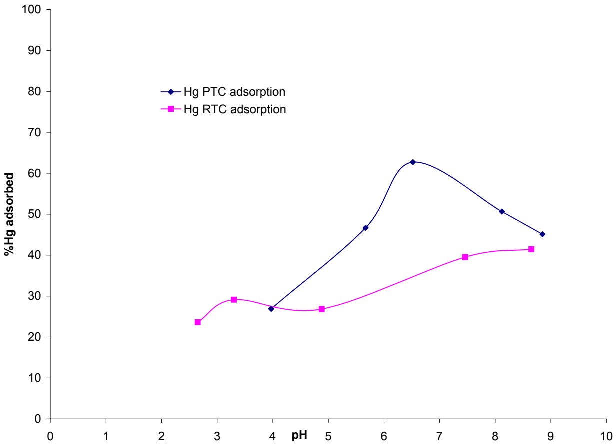

Figure 3f
%adsorbed Hg^{2+} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total Hg^{2+} concentration was 0.023 mM (4.78 mg/ℓ)

100% Zn removal could not be achieved even at high pH value of 10 as in the case of Cd. The adsorption process occurs below pH_{pzc}; hence, formation of inner sphere complexes is proposed.

Adsorption of lead

In a solution containing total Pb concentration of 0.024 mM precipitation of $Pb(OH)_2$ is expected to start at pH 8.85. However, over 95% removal of Pb (Fig. 3e) is achieved at pH of 7.6 and above. This shows that Pb^{2+} is strongly bound to the clay materials. The extent of adsorption by both PTC and RTC is similar at a given pH value.

Adsorption of mercury

It can be observed from Fig. 3f that Hg^{2+} adsorption is almost pH independent with sorption capacity fluctuating between 30 and 60 %. In dilute solutions Hg^{2+} ions hydrolyse readily to produce neutral mononuclear species $Hg(OH)_2$ even at pH as low as 3 or less (Baes and Mesmer, 1986). These species remain in solution and have a very low tendency to bind to adsorbing surfaces. Other species produced in small amounts are $HgOH^+$, $Hg(OH)_3^-$ and Hg_2OH^{3+}. It is probably the coulombic interactions between these small amounts of charged species that give rise to the observed constant binding capacity of the clay

Adsorption of arsenate

Insignificant adsorption of AsO_4^{3-} , as shown in Fig. 3g, was observed at all pH values. Clay minerals are either neutral or possess permanent negative charges. Their cation exchange capacity is a result of the permanent negative charge or the acid base reactions of their surface hydroxyl groups. Since As^{5+} occurs as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} in the pH range < 2; 3 to 6; 8 to 10; and >12 respectively (Gustafsson et al., 1983) which indicates that it is an anionic species within the study pH range, it is not surprising that the clay-arsenic interactions in this study are not favourable for adsorption.

Conclusions

The work has demonstrated the successful application of Tundulu mixed clays for heavy metal detoxification as a cheap and environmentally friendly method. The removal of Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+} cations by the clays does not require any addition of a base or acid because at a pH of about 7 (pH of water/wastewater in Malawi ranges from 6.5 to 8) removal of greater than 70% of these metals was obtained. However, the anionic species, AsO_4^{3-}, requires a different type of adsorbent for its uptake. Further work is being considered on desorption properties of the clays, treatment of the heavy metal containing sediments and pilot testing. The pH metal adsorption profiles indicate that metals can be recovered and clays regenerated for reuse by reducing the pH to low values.

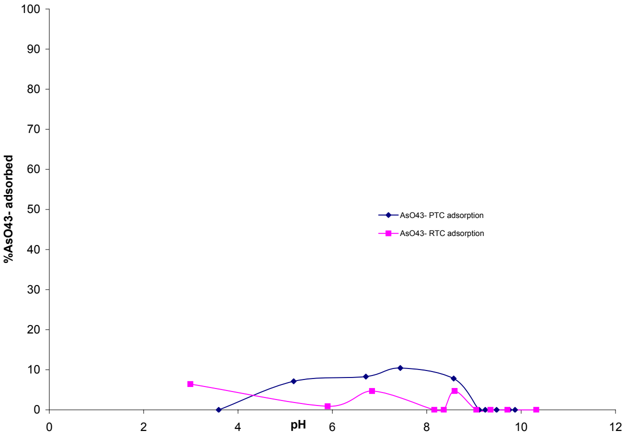

Figure 3g
%adsorbed AsO_4^{3-} against pH for RTC and PTC. 0.1M $Na(NO)_3$ was used as background electrolyte. The total AsO_4^{3-} concentration was 0.048 mM (3.57 mg/ℓ)

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