Int. J. Environ. Sci. Technol. (2015) 12:3417–3426
DOI 10.1007/s13762-015-0769-2

ORIGINAL PAPER

Kinetics, thermodynamics and competitive adsorption of lead and zinc ions onto termite mound

N. Abdus-Salam · M. O. Bello

Received: 10 January 2014 / Revised: 29 November 2014 / Accepted: 27 January 2015 / Published online: 17 February 2015

Abstract The elemental composition of termite mound was determined by XRF which revealed K, Ti and Mn as minor constituents while Ca and Fe as major constituents. The dominant functional groups of termite mound are Fe–OH, Fe–O and O–H. The Pb(II) and Zn(II) adsorption capacities (mg g^{-1}) are in order of Pb(II) (13.07) > Zn(II) (12.40) > Pb(Pb/Zn) (11.72) > Zn(Pb/Zn) (7.62). The Langmuir adsorption isotherm fitted the adsorption data better than Freundlich isotherm. The adsorption process was best described by pseudo-second-order kinetic model for single and binary solutions, and the rate constants k_2 (g mg^{-1} min^{-1}) are 0.036, 0.016, 0.024 and 0.015, and the calculated value of q_e (mg g^{-1}) is 12.33, 12.25, 11.52 and 7.84 for Pb(II), Zn(II), Pb(Pb/Zn) and Zn(Pb/Zn), respectively. The regression coefficient, R^2 values, for these solutions ranged between 0.9966 and 0.9978. The ΔH (kJ mol^{-1}) values were positive for single and binary solutions in the order Pb(II) (32.0) > Pb(Pb/Zn) (30.8) > Zn(Pb/Zn) (28.0) > Zn(II) (19.0), while ΔS (kJ mol^{-1} K^{-1}) are in the order of Pb(II) (0.103) > Pb(Pb/Zn) (0.097) > Zn(Pb/Zn) (0.082) > Zn(II) (0.06). The ΔG value for Zn(II) is positive in both single and binary systems, while that for Pb(II) was positive between 313–333 and 323–333 K for single and binary systems, respectively. The data show that the use of neglected termite mound for Pb(II) and Zn(II) removal from aqueous solutions is economically significant in wastewater treatment.

Keywords Termite mound · Competitive adsorption · Kinetics · Thermodynamics · Binary solution

Introduction

Technological advancement has made man to be increasingly dependent on materials whose production generates large quantities of industrial wastes, often containing heavy metals. Research findings have shown that the toxicity due to annual metallic discharge into the environments far exceeds the combined total toxicity of radioactive and organic wastes as measured by the quantity of water required to dilute such wastes to meet the quality of drinking water standard (Abdus-Salam and Adekola 2005a). Natural environment has the ability to sequester these heavy metals but whenever the waste exceeds the environmental tolerance levels, specific effects are noticed in man. The leaching of waste rich in heavy metals, discharge of industrial effluents or dumping of waste rich in heavy metals into aquatic systems frequently cause critical pollution levels to be exceeded (Mendiguchia et al. 2007). For example, lead and cadmium are commonly found in the wastewater of industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp (Iqbal and Edyvean 2005). Thus, effluents from these industries when discharged into body of water will pose health challenges on aquatic life and man that depends on water.

The conventional methods of heavy metal removal include chemical precipitation, ultra filtration, biochemical treatment and ion exchange (Abdus-Salam and Itiola 2012). There are shortcomings associated with these methods ranging from poor efficiency when the metal concentration is lower than 10 mg L^{-1}, disposal problem

N. Abdus-Salam (✉) · M. O. Bello
Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria
e-mail: nasalami2002@yahoo.co.uk

of large volume of organic solvent, the cost of reagents and energy consumption (Abdus-Salam and Itiola 2012). Adsorption process is an efficient and alternative method to the conventional methods because the process is free from the above shortcomings. The process is simple, efficient and cost-effective. The adsorbent for adsorption process is often obtained from raw or modified natural and synthetic materials. The volume of available literature on biomass compared to other natural materials shows that there is greater attention on adsorbents prepared from biomass, while less attention is given to other natural materials. Some agricultural by-products that have been used as adsorbents are rubber wood sawdust (Srinivasakannan and Abu Baker 2004), dates stone (Alhamed and Bamufleh 2009), bamboo-based [Hameed et al. 2007], coconut shell [Torregrosa-Macia et al. 1997; Tan et al. 2008], clay and clay materials (Appel and Ma 2002; Rouff et al. 2005; Omar and Al-Itawi 2007) and oxides of iron (Abdus-Salam and Adekola 2006).

Activated carbon (AC) is the most widely used adsorbent for wastewater treatment. There has been increasing research into alternative adsorbents with comparative performance advantage to AC. The need was partly due to high cost of procurement of AC and high cost associated with its regeneration emanating from high degree of loses in operational process (Olgun and Atar 2012, Atar and Olgun 2009). Termites are social insects that build nests in soil or wood (Eggleton et al. 2002). The mounds are features built from subsoil taken from a depth as low as 3 metres below the earth surface; thus, the composition of mound soil is closely related to the nature of adjacent subsoil (Semhi et al. 2008). Recently, the use of termite mound (TM) to remove Pb(II) (Abdus-Salam and Itiola 2012) and Cr(VI) (Araujo et al. 2013), and defluoridation of groundwater (Fufa et al. 2013) were reported. The permissible limits of both lead and zinc in drinking water are 0.1–0.05 and 5.0 mg l^{-1}, respectively (WHO 1996; Arias and Sen 2009). The accumulation of Pb and Zn in living organism is known to cause serious health problems such as brain disorder, kidney dysfunction, anaemia, vertigo and pancreas damage (Zhu et al. 2010; Veli and Alyuz 2007).

The potential of using TM for water pollution remediation is growing with little attention on the influence of co-ions on the adsorption process. Therefore, this present work was aimed at investigating the physicochemical properties of the termite mound and the effect of some dependable parameters such as adsorbent dose, agitation time, temperature and pH on metal adsorption and examines the adsorption from single and binary solutions of lead and zinc onto TM. This research was carried out in the Department of Chemistry, University of Ilorin, Nigeria, and it spans between January 2012 and March 2013.

Materials and methods

The TM for this research was sourced from Federal Ministry of Agriculture Root and Tuber Expansion Farm, Km 5, Ajasepo, Offa Road, Kwara State, Nigeria. The TM sample was pretreated as earlier described (Abdus-Salam and Itiola 2012). The fraction that passed through 300-nm sieve aperture was used for subsequent analysis. This fraction was further pretreated to remove non-clay materials and concentrate the active minerals that will improve the adsorption property of the TM.

The pH of the TM was determined potentiometrically in 0.1 M $CaCl_2$ solution in the ratio 1:2.5. The moisture content was determined by oven drying at 376 K (Hesse 1997). The pHzc of the sample was determined by both potentiometric and by mass titration methods (Noh and Schwarz 1989; Balderas-Hernandez et al. 2006). The cation exchange capacity, CEC, was determined using potassium acetate method (James et al. 2008), and the amount of potassium exchange was measured using Genway model PP120 flame photometer.

Adsorption capacity

A 25 ml of Pb(II) (or Zn(II)) solution with initial concentrations ranging between 100 and 1,000 mg l^{-1} was added onto 0.5 g of TM in 100-ml Erlenmeyer flask. The sample was agitated on orbital shaker for 7 h at 303 K. The supernatant liquid was filtered, the residual metal analysis was carried out using Buck Scientific Model 210 VGP Atomic Absorption Spectrophotometer (AAS), and the quantity adsorbed was calculated from Eq. 1 (Megat et al. 2007):

$$q_e = \frac{C_i - C_e}{M} \times V \tag{1}$$

and the extent of adsorption was calculated from Eq. 2 (Bhattacharyya and Sen Gupta 2006):

$$\%\text{Adsorption} = \frac{C_i - C_e}{C_i} \times \frac{100}{1} \tag{2}$$

where q_e is the quantity of metal adsorbed (mg l^{-1}); C_i and C_e are the initial and final concentrations of the metals (mg l^{-1}), V is the volume of the metal solution (l), and M is the mass of the termite mound soils (g) used. The quantity adsorbed was plotted against the initial concentration to determine the adsorption capacity of the mound for Pb(II) and Zn(II). These optimal concentrations were used subsequently for determination of other dependable factors.

Effect of agitation time

A 0.5 g adsorbent dose was contacted with 25 ml of the optimum metal concentration for Pb(II), Zn(II) (600 and

800 mg l^{-1}, respectively) and the binary solution of ratio 1:1 Pb(II)/Zn(II) mixture. The effect of agitation time was investigated for 10, 15, 20, 30, 45, 60, 90 and 180 min. The mixtures in reactors were then agitated on a flat orbital shaker and allowed to equilibrate at different time intervals. The mixtures were filtered at designed time intervals, and the un-adsorbed metals were analysed using AAS, while the amount adsorbed was calculated from Eq. 1.

Effect of temperature

A 25 ml of the optimum concentration for Pb(II) (or Zn(II)) was added to 0.5 g of the TM sample in a 100-ml conical flask. The mixture was equilibrated for 7 h at temperature 303, 313, 323 and 333 K, respectively. This was repeated for the binary solution Pb(II)/Zn(II) mixture. The mixtures were filtered, and the un-adsorbed metals were analysed using AAS, while the amount adsorbed was calculated from Eq. 1.

Effect of pH

A 25 ml of the optimum concentration for Pb(II) and Zn(II), respectively, was added to 0.5 g of the TM in a 100-ml conical flask. The pH of the resulting solutions was adjusted between 2 and 7 by gradual addition of 0.1 M HNO_3 or 0.1 M KOH solution. The solution was equilibrated for 7 h, filtered and the un-adsorbed metals were analysed using AAS, while the amount adsorbed was calculated from Eq. 1.

Results and discussion

Physicochemical characterization of TM

Table 1 Some physicochemical properties of termite mound

Properties	Results
Colour	Brown
Texture	Fine
pH	6.9
C.E.C	13.2
Organic matter (OM)	1.60
Moisture content	17.4

The physicochemical properties of the termite mound are presented in Table 1. The pH in water suspension was much closed to neutral (6.9). Soil pH plays a major role in the sorption of heavy metals as it controls the solubility and hydrolysis of metal hydroxides, carbonates and phosphates. It also significantly enhances ion-pair formation and solubility of organic matter (Tokalioglu et al. 2006). The moisture content of the air dried sample was 17.4 %. Although % moisture of a sample may reflect the degree of dryness to which the sample is exposed, it could also give information on the pore size of the sample. Soil water is held by adhesive and cohesive forces within the soil, and an increase in pore space will lead to increase in water holding capacity of soil. Therefore, 17.4 % moisture content translates to the average pore. In a related research, 12.0 % was obtained (Manuwa 2009). The difference in these results may be due to the period of sampling and geology of the underlying soil materials. The percentage organic carbon content is 1.60 % and the organic matter (OM) is 2.77 %, which shows that the OM value is higher when compared with average value reported for similar soil materials (Stanley 1975). The CEC of the TM was measured to be 13.2 meq 100 g^{-1}. Values of CEC for different soil types are in the range of 1.0–100 meq 100 g^{-1}, least for sandy soil and most for clay soil. A higher CEC value reflects the dominance of 2:1, and lower values reflect the presence of 1:1 mineralogical arrangement (Dube et al. 2000). The higher the OM content of the mound, the higher the value of its CEC, and inferably, the higher the availability of exchangeable ions that confer higher adsorption on the adsorbent (Abdus-Salam and Itiola 2012).

The point of zero charge (pzc) by potentiometric titration was 5.9 which is lower (7.8) than what was obtained for similar material taken from a different source (Abdus-Salam and Itiola 2012). A lower OM value is known to influence the pzc making it slightly higher (Schwertmann and Fechter 1982). The obtained OM value in this research is 2.77 % as compared to 3.45 % obtained in a similar research work (Abdus-Salam and Itiola 2012). The mineralogical compositions of the dried TM as determined by XRF showed that K, Ti and Mn are present as minor elements, while Ca and Fe are major constituents. The FTIR spectral assignments and interpretations were done according to literature reports (Halavay et al. 1977; Nakamato 1978; Abdus-Salam and Adekola 2005b). The FTIR revealed that the absorption peaks at 3,620.51 and 3,437.26 cm^{-1} were assigned to OH stretching frequency, 1,112.96, 1,033.88 and 1,008.80 cm^{-1} were attributed to Fe-OH bending modes, while 540.09 and 470.65 cm^{-1} were assigned to Fe–O stretching frequency of water.

Adsorption capacity of TM

Figure 1 depicts the adsorption of varying concentrations of Pb(II) and Zn(II) from single adsorbate solution onto

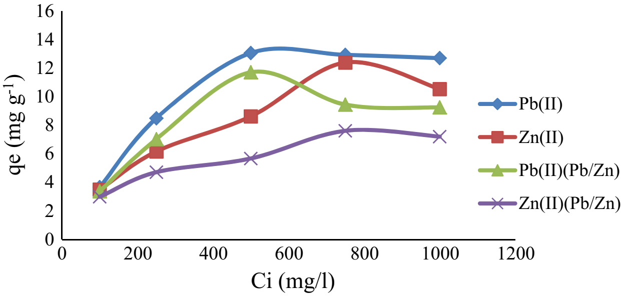

Fig. 1 Quantity of Pb(II) and Zn(II) adsorbed from single and binary solutions

TM. The adsorption of both Pb(II) and Zn(II) increased with increase in concentration until about 600 and 800 mg l^{-1} initial concentration at which 13.07 and 12.40 mg g^{-1} of Pb(II) and Zn(II), respectively, were adsorbed. There was a slightly higher adsorption of Pb(II) than Zn(II) under the same experimental conditions. This observation was in agreement with a similar work on volcanic ash soil (Esmaili et al. 2003). Figure 1 also shows the adsorption capacity for Pb(II) {or Zn(II)} from binary solution of Pb(II)/Zn(II) onto TM. It was observed that the quantity of Pb(II) or Zn(II) adsorbed decreased as compared with single metal dose adsorption. This showed that efficiency of metal ion adsorption was influenced by the presence of other ions in binary or multi-system solutions. This may be due partly to competitiveness of ions for the same available active sites and partly to repulsion of ions with similar charges.

Although both Pb(II) and Zn(II) have the same ionic charges but the ionic radius and electronegativity of Pb(II) are higher than those of Zn(II). Some important ionic parameters of both Pb(II) and Zn(II) are presented in Table 2. Although, both ions were favourably adsorbed, Pb(II) was more favourably adsorbed than Zn(II) which could be attributed to higher values of ionic radius and electronegativity of Pb(II) than those of Zn(II) (Depci et al. 2012; Lu and Xu 2009).

Effect of agitation time

The effect of contact time on the adsorption of Pb(II), Zn(II) as single adsorbate solution as well as Pb(Pb/Zn) and Zn(Pb/Zn) from binary solutions on TM is shown in Fig. 2. The curves represented three stages of adsorption behaviour. The time interval between 0 and 15 min represents fast kinetics with 77.40 % Pb and 69.30 % Zn adsorption. This is followed by a slow kinetic rate (15–45 min) within which 100 % Pb and 87.30 % Zn adsorption was attained. The third stage (45–180 min) represents a practically constant kinetics.

Similar trend was observed in binary solution although with lower metal adsorption. The 0–15 min represents fast kinetic where 69.80 % Zn(Pb/Zn) and 81.30 % Pb(Pb/Zn) were adsorbed. This was followed by 15–45 min time interval that represents the slow kinetic and 86.62 % Zn(Pb/Zn) and 87.72 % Pb(Pb/Zn) adsorption. The initial rapid increase in adsorption may be due to the presence of vacant adsorption sites on TM and un-restricted active sites with similar energy. However, as more and more active sites are filled up, the rate of adsorption slowed down and the ease of adsorption becomes more difficult (Bhattacharyya and Sen Gupta 2006) until equilibrium is reached. The quantity of Pb(II) adsorbed was greater at any given time in single and binary solutions than that of Zn(II) in the same adsorption environment. The lower adsorption of Pb(II) or Zn(II) from binary solution as compared to single adsorbate solution suggests competitiveness of the two ions.

Effect of temperature

The effect of temperature on the adsorption capacity is represented by the plot of temperature versus quantity adsorbed (Fig. 3) for both single and binary solutions. There was increase in the quantity adsorbed with increase in temperature for both Pb(II) and Zn(II) for single and binary solutions. The quantity adsorbed for Pb(II) was greater at any given temperature in single and binary solutions than that for Zn(II) in the same adsorption environment. The lower adsorption of Pb(II) or Zn(II) from binary solution as compared to single adsorbate solution suggests ionic influence on adsorption. The effect of ionic interaction in a binary solution on the sorption process may also be represented by the ratio of the adsorption capacity for one metal ion in the presence of the other metal ions, q_b (q_{binary}), to the adsorption capacity for the same metal when it is present alone in the solution, q_s (q_{single}) (Mohan and Singh 2002), such that for:

$q_b/q_s > 1$, the sorption is promoted by the presence of other metal ions;
$q_b/q_s = 1$, there is no observable net interaction; and
$q_b/q_s < 1$, sorption is suppressed by the presence of other metal ions. The ratio was found to be <1 which is an indication that the presence of one ion suppressed the adsorption of the other ion, and the higher the influence of co-ion on the adsorption of primary ion, the lower the ratio of q_b/q_s. Similar results were obtained, in similar

Table 2 Some atomic properties of lead and zinc

Properties	Metals	
	Pb	Zn
Oxidation state	+2, +4	+2, +1
Electronegativity (Pauli scale)	2.33	1.65
First ionization energy (kJ/mol)	715.6	906.4
Atomic radius (pm)	175	134
Covalent radius (pm)	146 ± 5	122 ± 4
Ionic radius (M^{2+}), 4-coordinate (pm)	98	60
Ionic radius (M^{2+}), 6-coordinate (pm)	119	74

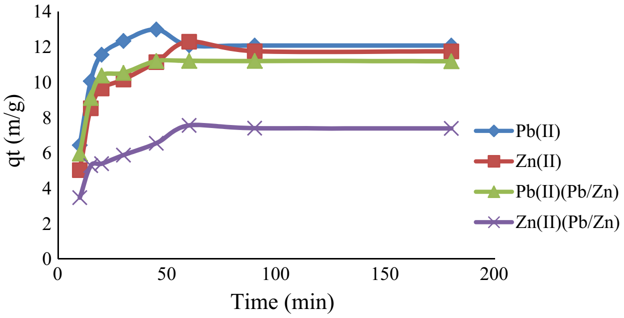

Fig. 2 Quantity of Pb(II) and Zn(II) adsorbed versus time from single and binary solutions

works, for Pb and Zn in binary solutions (Mohan and Singh 2002; Depci et al. 2012).

An increase in adsorption with increase in temperature is an indication that the adsorption process was endothermic (Hefne et al. 2008; Dandamozd and Hosseinpur 2010). The endothermic nature of the adsorption processes may be attributed to an increase in the kinetic energy of the ions which enhances the adsorption onto the active sites or causing the metal ions to be better solvated (Naseem and Tahir 2001).

Effect of pH

At constant adsorbate concentration and time, pH of the solution was varied from 2.0 to 7.0 as most metals tend to precipitate out of solution at pH > 7.0 (Bayramoglu et al. 2003). Figure 4 represents the effect of variable pH on the adsorption of Pb(II) and Zn(II). It is observed that the adsorption of both Pb(II) and Zn(II) is pH dependent. The quantities adsorbed increase with increasing pH with Pb(II) being more influenced than Zn(II). There was an increase in the quantity adsorbed up to the pH of 5 for Pb(II) and 6 for Zn(II).

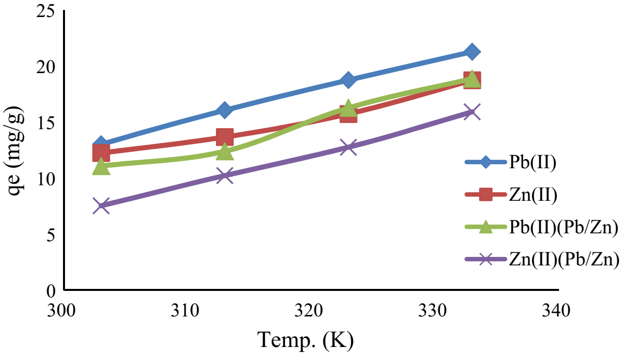

Fig. 3 Effect of temperature on adsorption Pb(II) and Zn(II) in single and binary solutions

The TM surface charge transformation which becomes more negative as the pH of the solution matrix increases conferred greater affinity for positive ions onto TM. Generally, the medium in which an adsorbent is suspended, the presence of anionic species or complexing agent has strong influence on the surface charge characteristics and may confer a net negative charge on the surface at pH below pzc (Appel and Ma 2002). Otherwise the net surface charge characteristic is positive at a pH below pzc, negative above pzc and neutral at pH = pzc. The adsorption of Pb(II) and Zn(II) at pH below pzc can only be justified by the presence of anionic species of the salts of metals used. Near the pzc (5.9) of TM, the net negative charge attained its maximum and hence maximum adsorption of Pb(II) and Zn(II). Moreover, when the pH of the adsorbing medium was increased, there was an increase in the deprotonation of the surface OH group on TM leading to a decrease in H^+ ion on the TM surface sites. This created more negative charges and enhanced adsorption of positively charged species (Ghanem and Mikkelsen 1988).

Adsorption isotherms

Two adsorption isotherms, Langmuir and Freundlich models were tested using the experimental data of the equilibrium adsorption. Adsorption isotherm was studied to determine the adsorption capacity and potential for selecting adsorbents for heavy metal remediation.

Langmuir adsorption isotherm

The linear form of the Langmuir isotherm was applied in form of Eq. 3:

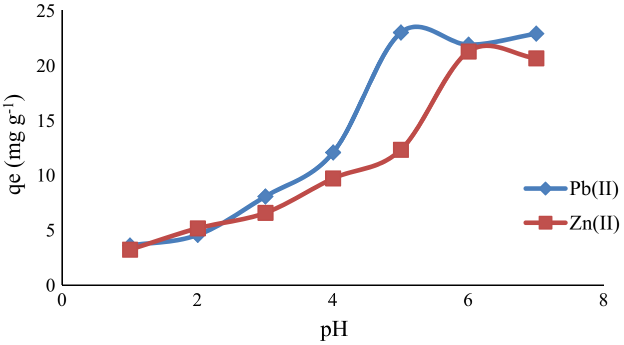

Fig. 4 Plot of pH versus adsorbed quantity of Pb(II) and Zn(II)

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

where b and q_m are Langmuir coefficients representing the equilibrium constant for the adsorbate–adsorbent equilibrium and the monolayer capacity, respectively, C_e is the equilibrium concentration of the solute in bulk solution (mg l^{-1}), and q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}).

The Langmuir plots of equilibrium concentration, C_e (mg l^{-1}) versus C_e/q_e, were linear for Pb(II) and Zn(II), respectively (figure not shown). The adsorption data of both Pb(II) and Zn(II) as single and binary solutions fitted well into Langmuir isotherm with regression coefficient (R^2) of 0.9944 (Pb), 0.9634(Zn), 0.9841 [Pb(Pb/Zn)] and 0.9776 [Zn(Pb/Zn)]. The calculated Langmuir parameters are shown in Table 3. The value of b indicates that the TM has stronger affinity for Pb(II) than Zn(II) and is in agreement with earlier report (Serrano et al. 2005). The mono-layer maximum adsorption capacity, q_m, is 14.08 mg g^{-1} (Pb), 12.66 mg g^{-1} (Zn), 9.90 mg g^{-1} [Pb(Pb/Zn)] and 8.20 mg g^{-1} [Zn(Pb/Zn)]. The calculated q_m for Pb(II) is higher than that for Zn(II) and higher for single adsorbate than for binary solution which follows the observed experimental trend. The b value, however, was greater for binary system than for single adsorbate system for the two ions, that is, 0.037 (0.020) and 0.010 (0.009) l g^{-1} for Pb(II) and Zn(II), respectively. Higher b value is related to the specific adsorption of metals at high-energy surfaces (Serrano et al. 2005). The increase in the b value suggests that competition for sorption sites promotes the retention of both metals on more specific adsorption sites (Li et al. 2012). However, the b value of Pb(Pb/Zn) was more than Zn(Pb/Zn), and this confirmed the higher competitive role of Pb(II) over Zn(II) in a binary solution.

Freundlich adsorption isotherm

Equilibrium data were treated using Freundlich isotherm according to equation as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where K_f is the constant related to overall adsorption capacity (mg g^{-1}), n is a constant related to sorption intensity known as Freundlich sorption intensity constant, q_e is the amount of solute adsorbed per unit weight (mg g^{-1}), and C_e is the equilibrium concentration of the solute in the bulk solution (mg l^{-1}). The isotherm model yielded linear plots (figure not shown) with correlation coefficient, R^2, of 0.8287 (Pb), 0.9645 (Zn), 0.7302 [Pb(Pb/Zn)] and 0.9647 for [Zn(Pb/Zn)]. The Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies (Atar and Olgun 2009). The Freundlich adsorption intensity constant, n, and maximum diffusion constant, K_f, for Pb(II) and Zn(II) in single and binary solutions are reported in Table 3. The n values for binary solutions are higher than those for the single adsorbate solution. This confirmed the ionic interactions in binary solutions. The n value indicates whether the nature of adsorption is favourable or otherwise. A value less than 1 indicates that sorption intensity is favourable over the entire range of concentration,

Table 3 Langmuir and Freundlich isothermal constants and correlation coefficients

Metal ions	Langmuir isotherm			Freundlich isotherm			q_b/q_s
	R^2	q_m (mg/g)	b (L/g)	R^2	K_f (L/g)	n	
Pb	0.994	14.08	0.020	0.828	1.37	2.42	
Pb(Pb/Zn)	0.984	9.90	0.037	0.730	1.37	2.69	0.70
Zn	0.964	12.66	0.009	0.964	1.0	2.74	
Zn(Pb/Zn)	0.977	8.20	0.010	0.964	1.01	3.31	0.65

while a value greater than 1 favours sorption at higher concentration (Adekola et al. 2011). It could be concluded from the value obtained that the adsorption is favourable at higher concentrations for both Pb(II) and Zn(II).

Adsorption kinetics

The adsorption kinetics describes the solute uptake rate, which in turn governs the residence of the adsorbed species. It is also used to express the efficiency of the adsorption process. The kinetic data for the adsorption of Pb(II) and Zn(II) onto TM were tested with two different adsorption kinetic models: the Lagergren pseudo-first-order equation (Eq. 5) and pseudo-second-order equation (Eq. 6)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (6)$$

The Lagergren pseudo-first-order plot of log $(q_e - q_t)$ against t (min) for both Pb(II) and Zn(II) in single adsorbate and binary solution was linear but the R^2 is ≪less than 1. The same data were tested with pseudo-second-order kinetic model by plotting t/q_t versus t (min).

The plots in Fig. 5 fulfil the conditions that yielded q_e values that are very close to the experimental values. The experimental and calculated values of q_e, the pseudo-second-order constant (k_2) and coefficient of correlation, R^2, are presented in Table 4. Linearity of the plots with R^2 values that are very close to unity indicates that the adsorption processes followed pseudo-second-order kinetic model. A number of adsorption processes on clay materials have been reported to fit well into second-order kinetic model (Solener et al. 2008; Bhattacharyya and Sen Gupta 2006; Mohapatra et al. 2010). The decrease in the value of k_2 in binary solutions when compared to single adsorbate solution supports the interactions of ions in binary solution.

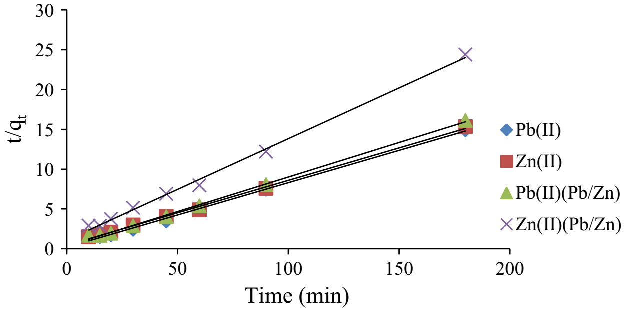

Fig. 5 Plot of t/q_t versus t for Pb(II) and Zn(II) in single and binary solutions

Table 4 Pseudo-second-order kinetics parameters for the adsorption of Pb(II), Zn(II), Pb(Pb/Zn) and Zn(Pb/Zn) on TM

System	Parameters			
	R^2	k_2 (g mg^{-1} min^{-1})	Q_e (mg g^{-1})	
			Calc.	Exp.
Pb(II)	0.9969	0.036	12.33	13.07
Zn(II)	0.9975	0.016	12.25	12.40
Pb(II)(Pb/Zn)	0.9978	0.024	11.52	11.72
Zn(II)(Pb/Zn)	0.9966	0.015	7.84	7.62

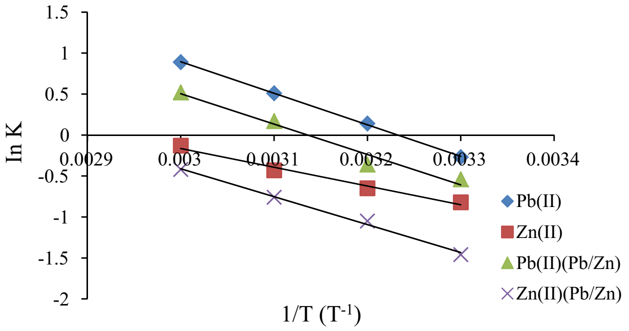

Fig. 6 Plot of InK versus 1/T for Pb(II) and Zn(II) in single and binary solutions Chart Title

Adsorption thermodynamics

The Gibb's free energy (ΔG^0), enthalpy (ΔH^0) and entropy changes (ΔS^0) for the sorption were calculated using the following equations:

$$\Delta G = -\mathrm{RT}\mathrm{In}K \qquad (7)$$

$$\mathrm{In}K = {}^{\Delta S}\!/_{R} - {}^{\Delta H}\!/_{T} \qquad (8)$$

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

where R is the ideal gas constant (kJ mol^{-1} K^{-1}), $K = C_{ads}/C_e$, and T is the temperature (K). ΔH^0 and ΔS^0 values were obtained from the slope and intercept, respectively, of Van't Hoff plots (Mohan and Singh 2002). The plot of InK versus 1/T (K^{-1}) is represented by Fig. 6 for single and binary adsorbate solutions. The calculated parameters are given in Table 5, and from the table, it could be observed that the heat of adsorption, ΔH, for both single and binary solutions was all endothermic but is lower in binary for Pb(II) than the single adsorbate solution. This confirms the fact that Pb(II) is influenced by the presence of Zn(II) since lower heat of adsorption was

Table 5 Thermodynamics parameters for the adsorption of Pb(II), Zn(II), Pb(Pb/Zn) and Zn(Pb/Zn) on TM

System	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔG (kJ mol^{-1})			
			303 K	313 K	323 K	333 K
Pb(II)	32.0	0.103	0.65	−0.36	−1.36	−2.46
Zn(II)	19.0	0.06	0.33	1.69	1.15	0.35
Pb(Pb/Zn)	30.8	0.097	1.36	0.94	−0.46	−1.44
Zn(Pb/Zn)	28	0.082	3.68	2.73	2.24	1.16

required for the binary system. A lower heat of adsorption favoured Zn(II) removal in single adsorbate solution when compared with its binary solution. This indicates that Zn(II) adsorption was unfavourable in the presence of Pb(II), and much heat of adsorption is needed to overcome the restriction in the binary solution as compared to single process.

The thermodynamic factors are reported in Table 5. The values of ΔS for Pb(II), Zn(II), Pb(Pb/Zn) and Zn(Pb/Zn) are positive which indicate increased disorderliness and randomness at the solid–solution interface of TM. The ΔS value in binary system for Pb(II) is practically lower than that in the single system, which suggests the influence of ionic interactions in binary solution (Depci et al. 2012). However, ΔS value for Zn(II) in binary system is higher than the value for single solution system. This is an indication that Zn(II) suffered more of ionic interactions, and there is need for more heat of adsorption before Zn(II) adsorption takes place. The negative value of ΔG for Pb(II) at 313 up to 333 K indicates spontaneity of the adsorption of Pb(II) in single adsorbate system and negative at 323 and 333 K in binary system onto TM. Although adsorption of Zn(II) is not spontaneous, it can be improved upon by increasing the temperature of the adsorption process since positive ΔG value for Zn(II) decreases with increase in temperature (Omar and Al-Itawi 2007). The ΔG value was more positive in binary Zn(Pb/Zn) solution than in the single Zn(II) system. Similar trend was observed for ΔH values between single and binary systems for Zn(II) adsorption. This implies that more heat will be needed to promote the adsorption of Zn(II) on TM due to competing ions.

Conclusion

TM has great potential as adsorbent for lead and zinc removal from aqueous solutions. The processes of both Pb(II) and Zn(II) adsorption are found to be pH and agitation time dependent. Pseudo-second-order kinetic model was found applicable to describe the processes. The equilibrium adsorption data of both Pb(II) and Zn(II) on TM are better fitted to Langmuir than Freundlich adsorption isotherm model in single and binary systems. The calculated adsorption capacity values are very close to experimental values. The effect of competing ion was observed in the adsorption capacities of Pb(II) and Zn(II) in binary solution as compared with the single solution. The adsorption capacities, q_m, of Langmuir are in the order of Pb(II) > Pb(II)(Pb/Zn) and Zn(II) > Zn(II)(Pb/Zn). Thermodynamic studies showed that ΔH and ΔS are positive and that the process is endothermic. ΔG was negative (spontaneous) at 313 and 323 up to 333 K for Pb(II) and Pb(II)(Pb/Zn), respectively, while that for Zn(II) and Zn(II)(Pb/Zn) is positive but decreases with increase in temperature.

Acknowledgments The authors are grateful to Mr. M. A. Adebayo (Chief technologist), Mr. J. Adamu and other technologists in the Department of Chemistry and Central Research Laboratories, University of Ilorin, for their support.

References

Abdus-Salam N, Adekola FA (2005a) The influence of pH and adsorbent concentration on adsorption of lead and zinc on natural goethite. AJST 6(2):55–66

Abdus-Salam N, Adekola FA (2005b) Physico-chemical characterization of some Nigerian goethite mineral samples. Ife J Sci 7(1):131–137

Abdus-Salam N, Adekola FA (2006) Comparative dissolution of natural goethite samples in HCl and HNO_3. JASEM 10(2):11–17

Abdus-Salam N, Itiola AD (2012) Potential application of termite mound for adsorption and removal of Pb(II) from aqueous solutions. J Iran Chem Soc 9:373–382

Adekola FA, Abdus-Salam N, Abdulrauf LB (2011) Removal of arsenic from aqueous solution by synthetic hematite. J Chem Soc Niger 36(2):52–58

Alhamed YA, Bamufleh HS (2009) Sulfur removal from model diesel fuel using granular activated carbon from dates' stones activated by $ZnCl_2$. Fuel 88:87–94

Appel C, Ma LQ (2002) Concentration, pH, and surface charge effects on Cd and Pb sorption in three tropical soils. J Environ Qual 31:581–589

Araujo BR, Reis JOM, Rezend EIP, Mangrich AS, Wisniewski A Jr, Dick DP, Romao LPC (2013) Application of termite nest for adsorption of Cr(VI). J Environ Manag 129:216–223

Arias F, Sen TK (2009) Removal of heavy metal ion, Zn(II) from aqueous solution by kaoline clay mineral: a kinetic and equilibrium study. Colloid Surf A 348:100–108

Atar N, Olgun A (2009) Removal of basic and acid dyes from aqueous solutions by a waste containing boron impurity. Desalination 249:109–115

Balderas-Hernandez P, Ibanez JG, Godinez-Ramirez JJ, Almada-Calvo F (2006) Microscale environmental chemistry: part 7. Estimation of the Point of Zero Charge (pzc) for simple metal oxides by a simplified potentiometric mass titration method. Chem Educ 10(10):267–270

Bayramoglu G, Bektas S, Arica MY (2003) Biosorption of heavy metal ions on immobilized white-rot fungus Trametes versicolor. J Hazard Mater 101(3):285–300

Bhattacharyya KG, Sen Gupta S (2006) Pb(II) uptake by kaolinite and montmorillonite in aqueous medium: influence of acid activation of the clays. Colloids Surf A Physicochem Eng Asp 277(1–3):191–200

Dandamozd F, Hosseinpur AR (2010) Thermodynamic parameters of zinc sorption in some calcareous soil. J Am Sci 6(7):1–7

Depci T, Kul AR, Onal Y (2012) Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van pulp: study in single- and multi- solute systems. Chem Engr J 200:224–236

Dube A, Zbytniewski R, Kowalkowski T, Cukrowska E, Buszewski B (2000) Adsorption and migration of Heavy metals in soil. Pol J Environ Stud 10(1):1–10

Eggleton P, Bignell DE, Hauser S, Dibog L, Norgrove L, Madong B (2002) Termite diversity across an anthropogenic gradient in the humid forest zone of West Africa. Agric Ecosyst Environ 90:189–202

Esmaili A, Nasseri S, Mahvi AH, Atash-Dehghan R (2003) Adsorption of lead and zinc ions from aqueous solution by volcanic ash soil (VAS). In: Proceedings of the 8th international conference on environmental science technology, Lemnos Island, Greece, pp 8–10

Fufa F, Alemayehu E, Lennartz B (2013) Defluoridation of groundwater using termite mound. Water Air Soil Poll 224:1552–1566

Ghanem SA, Mikkelsen DS (1988) Sorption of zinc on iron hydrous oxide. Soil Sci 146(1):11–21

Halavay J, Jonas K, Elek S, Inczedy J (1977) Characterization of the particle size and crystallinity of certain minerals by infrared spectrophotometry and other instrumental methods-1. Investigation on clay minerals. Clay Miner 23:425–456

Hameed BH, Din ATM, Ahmad AL (2007) Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. J Hazard Mater 141:819–825

Hefne JA, Mekhemer WK, Alandis NM, Aldayel OA, Alajyan T (2008) Kinetic and thermodynamic study of the adsorption of Pb(II) from aqueous solution to the natural and treated bentonite. Int J Phys Sci 3(11):281–288

Hesse PR (1997) A textbook of soil chemical analysis, illustrated. Chem. Pub. Co., John Murray, London, p 152

Iqbal M, Edyvean RGJ (2005) Loofa sponge immobilized fungal biosorbent: a robust system for cadmium and other dissolved metal removal from aqueous solution. Chemosphere 61(4):510–518

James OO, Mesubi MA, Adekola FA, Odebunmi EO, Adekeye JID (2008) Beneficiation and characterization of a Bentonite from North-Eastern Nigeria. J NC Acad Sci 124(4):154–158

Li T, Jiang H, Yang X, He Z (2012) Competitive sorption and desorption of cadmium and lead in paddy soil of eastern china. Environ Earth Sci. doi:10.1007/s12665-012-1853-2

Lu SG, Xu QF (2009) Competitive adsorption of Cd, Cu, Pb and Zn by different soils of Eastern China. Environ Geol 57:685–693

Manuwa S (2009) Physico-chemical and dynamic properties of termite mound soil relevant in sustainable food production. In: 9th African crop science, conference proceedings, Cape Town, South Africa, pp 365–369

Megat MAK, Wan Ngah WS, Zakaria H, Ibrahim SC (2007) Batch study of liquid-phase adsorption of lead ion using lalang (imperata cylinderical) leaf powder. J Biol Sci 7(2):222–230

Mendiguchia M, Moreno C, Vargas M (2007) Evaluation of natural and anthropogenic influences on the Guadalquivir River (Spain) by dissolved heavy metals and nutrients. Chemosphere 69(10):1509–1517

Mohan D, Singh KP (2002) Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. Water Res 36:2304–2318

Mohapatra M, Mohapatra L, Singh P, Anand S, Mashra BK (2010) A comparative on Pb(II), Cd(II), Cu(II) and Co(II) adsorption from single and binary aqueous solutions on additive assisted nano structured goethite. Int J Eng Sci Technol 2(8):81–103

Nakamato K (1978) Infrared spectral of inorganic and coordination compounds, 3rd edn. Wiley, New York, p 239

Naseem R, Tahir SS (2001) Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent. Water Res 35(16):3982–3986

Noh SJ, Schwarz JA (1989) Effect of point of zero charge of simple oxides by mass titration. J Colloid Interface Sci 130(1):157–164

Olgun A, Atar N (2012) Equilibrium, thermodynamic and kinetic studies for the adsorption of lead (II) and nickel (II) onto clay mixture containing boron impurity. J Ind Eng Chem 18:1751–1757

Omar W, Al-Itawi H (2007) Removal of Pb+2 Ions from Aqueous Solutions by adsorption on kaolinite clay. Am J Appl Sci 4(7):502–507

Rouff AA, Reeder RJ, Fisher NS (2005) Electrolyte and pH effects on Pb(II)-calcite sorption processes: the role of the $PbCO_{3(aq)}$ complex. J Colloid Interface Sci 286(1):61–67

Schwertmann U, Fechter H (1982) The point of zero charge of natural and synthetic ferrihydrite and its relation to adsorbed silicate. Clay Miner 17:471–476

Semhi K, Chaudhuri S, Claurer N, Boeglin JL (2008) Impact of termite activity on soil environment: a perspective from their soluble chemical components. Int J Environ Sci Tech 5(4):431–444

Serrano S, Garrido F, Campbell CG, Garcia-Gonzalez MT (2005) Competitive sorption of cadmium and lead in acid soils of Central Spain. Geoderma 124:91–104

Solener M, Tunali S, Ozcan AS, Ozcan A, Gedikbey T (2008) Adsorption characteristics of lead(II) ions onto the clay poly(methoxyethyl) acrylamide composite from aqueous solutions. Desalination 223:308–322

Srinivasakannan C, Abu Baker MZ (2004) Production of activated carbon from rubber wood sawdust. Biomass Bioenergy 27(1):89–96

Stanley EM (1975) Environmental chemistry, 2nd edn. Willard Grant Press, USA, p 293

Tan IAW, Ahmad AL, Hameed BH (2008) Preparation of activated carbon from coconut husk: optimization study on removal of

2,4,6-trichlorophenol using response surface methodology. J Hazard Mater 153:709–717

Tokalioglu S, Kartal S, Gultekin A (2006) Investigation of heavy metal uptake by vegetables growing in contaminated soil using the modified BCR sequential extraction method. Int J Environ Anal Chem 88(6):417–430

Torregrosa-Macia R, Martin-Martinez JM, Mittelmeijer-Hazeleger MC (1997) Porous texture of activated carbons modified with carbohydrates. Carbon 35(4):447–453

Veli S, Alyuz B (2007) Adsorption of copper and zinc from aqueous solutions by using natural clay. J Hazard Mater 149:226–286

WHO (World Health Organization) (1996) Guidelines for drinking-water quality, 2nd ed. Vol. 2. Health criteria and other supporting information. World Health Organization, Geneva

Zhu J, Yang J, Deng B (2010) Ethylenediamine-modified activated carbon for aqueous lead adsorption. Environ Chem Lett 8:277–282