The potential of ball-milled South African bentonite clay for attenuation of heavy metals from acidic wastewaters: Simultaneous sorption of Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} ions

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Abstract

Adsorption of Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} by bentonite clay from polycationic solution was investigated. Mineralogical composition of clay was done using X-Ray Diffraction (XRD), elemental composition using X-Ray Fluorescence (XRF) and Morphology using Scanning Electron Microscopy (SEM) and Electron Dispersion X-ray (EDX). Optimum adsorption conditions were evaluated using batch experimental procedures. Parameters optimized included: adsorbent dosage, shaking time, ions concentration and pH. Interaction of bentonite clay with acidic wastewaters led to an increase in pH and significant reduction in metal species concentration. Optimization experiments revealed that 60 mins of equilibration, 1 g of clay dosage, 50 mg L^{-1} of polycations, pH 6, 250 rpm and $26^{\circ}C$ are the optimum condition for removal of heavy metals from the acidic wastewaters. Removal of metals was > 99% for all chemical species in solution. The metal species sorption affinity varied as follow: Co> Cu> Ni= Zn> Pb. Kinetic studies showed that adsorption by bentonite clay fitted to the pseudo-second-order model with pore diffusion also acting as a major rate governing step. The adsorption data fitted well to Freundlich adsorption isotherm than Langmuir adsorption isotherm hence confirming multilayer adsorption. This comparative study proved that bentonite clay can increase the pH and effectively remove metal species from acidic and metalliferous wastewaters.

Keywords: Bentonite clay; metal species; adsorption; Isotherms; optimization

1   Introduction

Discharge of effluents rich in toxic heavy metals has become a prime issue of ecological concern (Teixeira, et al., 2003, Xu, et al., 2009, Zuhairi Yaacob, et al., 2009, Zou, et al., 2013, Vodyanitskii, 2014). Heavy metals have vast industrial applications and are commonly

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found in wastewater emanating from mining activities, metal finishing industry, refining and smelting of metals, metallurgical processes and manufacturing of batteries (Alloway, 1990, Babel and Kurniawan, 2003, Zuhairi Yaacob, et al., 2009, Andráš, et al., 2012, Balintova, et al., 2013, Chakroun, et al., 2013, Cao, et al., 2014). Wastewater from these industries normally contains Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} ions. The presence of these metals in wastewater is of prime concern to the public due to their toxicity on exposure to terrestrial and aquatic organisms. Heavy metals are non-biodegradable and persistent in the environment. Due to their non-biodegradable nature, heavy metals can bio-accumulate in living organisms and bio-magnification through the food chain. Toxic levels of metal species in the biosphere can also be released into water and soil fluids through natural and anthropogenic processes. These processes allow metal species to enter the food chain, which ends with human consumption. Metal species degrade the ability of the environment to foster life through water and soil pollution (Alloway, 1990, Andráš, et al., 2012, Guillén, et al., 2012, Guo, et al., 2013, Hatar, et al., 2013, Bouzayani, et al., 2014, Cao, et al., 2014, Guo, et al., 2014).

In the quest to come-up with pragmatic remediation techniques that are economically viable and efficient in removal of toxic heavy metals from industrial effluents prior water pollution. The present study was developed to troubleshoot the extent of wastewater pollution and explore the efficiency of vibratory ball milled bentonite clay for attenuation of metal species from acidic effluents. The abundance, versatility and low cost of natural clays, in addition to their potential are of both scientific and industrial interest (Volzone, 2004, Abu-Eishah, 2008, Yuan, et al., 2013, Zhu, et al., 2013, Musso, et al., 2014).

Clay minerals are well-recognized for their excellent adsorption capabilities that explains their extensive industrial, technological, agricultural, and environmental applications (Yuan, et al., 2013). Clays in smectite family, in particular bentonite clay, have been widely applied as adsorbents of metal species from aqueous solutions (Barbier, et al., 2000, Abollino, et al., 2003, Volzone, 2004, Bhattacharyya and Gupta, 2008, Oubagaranadin, et al., 2010, Vieira, et al., 2010, de Pablo, et al., 2011, Sdiri, et al., 2012, Yuan, et al., 2013). The adsorption of metal species from aqueous acidic solutions by clay minerals has been extensively investigated (Volzone, 2004, Sdiri, et al., 2011, Sdiri, et al., 2012, Yuan, et al., 2013).

Clay minerals adsorb metal species from aqueous solutions through cation replacement or by forming surface functional groups that normally observe the selectivity rule of Ca > Hg > Pb > Cu > Mg > Zn > Co > Ni > Cd (Đukić, et al., 2015). Bhattacharyya and Gupta (2008)

described the removal and immobilization of Cd(II), Pb(II) and Cu(II) by montmorillonite in acidic to slightly alkaline media and that of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) by acid-activated montmorillonite. Anomalous adsorption of metal species, which occurs in excess of the cation exchange capacity (CEC) of clay, has been observed for some metal species, e.g., Cu(II) and Zn(II) by H-montmorillonite and Cu(II) by Na- and Ca-montmorillonite (Bhattacharyya and Gupta, 2008, Đukić, et al., 2015). Milling of clay causes the fragmentation, distortion, breakage of crystalline networks and cobwebs, and particle size reduction followed by an increase of the surface area, exfoliation of particles and amorphization, that lead to an increase of metals removal efficiencies (Paik, et al., 2010, Wang, et al., 2011, Djukić, et al., 2013, Hamzaoui, et al., 2015, Zhuang, et al., 2015). To the authors' knowledge, the vibratory ball milled South African bentonite clay has never been used for removal of metals from aqueous solutions. Simultaneous removal of Pb(II), Cu(II), Cd(II), Ni(II) and Zn(II) from wastewater by South African bentonite clay has never been documented. Therefore, the present study examines adsorption by ball milled South African bentonite clay of Cu(II), Co(II), Ni(II), Pb(II) and Zn(II) ions from acidic aqueous solutions.

2 Materials and methods

2.1 Sampling and preparation of bentonite clay

Bentonite clay was supplied by ECCA (Pty) Ltd (Cape Town, South Africa). The raw bentonite was washed by soaking in ultra-pure water and draining after 10 minutes. The ultrapure water used was such that it covered the entire sample in the beaker and was allowed to overflow. The procedure was repeated four times. The washed bentonite was dried for 24 h at 105°C in an oven. The dried samples were milled into a fine powder (Retsch RS 200 mill) (15 minutes of pulverizing and 800 rpm) and sieved pass 32 µm particle size sieve.

2.2 Characterisation of aqueous solution

Chemical analysis of raw and processed water samples was done by Inductively Coupled Mass Spectrometry (ICP-MS) (7500ce, Agilent, Alpharetta, GA, USA). The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. pH was measured using CRISOM MM40 multimeter probe. All experiments were carried out in triplicate and the relative standard deviations were less than 1%.

2.3 Characterisation of bentonite clay

The elemental compositions of the samples were ascertained using X-ray Flourescence spectroscopy (XRF). The Thermo Fisher ARL9400 XP+ Sequential XRF coupled with WinXRF software was used for analyses. The mineralogy of raw materials and synthesis products were identified by XRD on a Phillips PW 1710 X-ray powder diffractometer operating in Bragg-Brentano geometry with Cu-Kα radiation at 40 mA and 40 kV and secondary monochromation. Data collection was carried out in the 2θ range 3-90°, with a scanning step of 0.02°. Morphology of bentonite clay was ascertained using SEM-EDS (JOEL JSM – 840, Hitachi, Tokyo, Japan). Surface area was determined by Brunauer-Emmett-Teller (A Tristar II 3020, Micrometrics BET from Norcross, GA, USA).

2.4 Point of zero charge (PZC) and cation exchange capacity (CEC)

The point of zero charge of the clay, was determined using the solid addition method (Kumar, et al., 2011). The Cation Exchange Capacity (CEC) of bentonite clay was determined using ammonium acetate method (Alloway, 1990).

2.5 Preparation of working solution

Stock solution of 1000 mg L^{-1} Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} prepared as one solution using ultrapure water from lab consumable was used for this study. The working solutions were prepared from this stock solution by appropriate dilutions for the batch experiments.

2.6 Adsorption study

2.6.1 Effect of residence time

Nine 100 mL aliquots with 50 mg L^{-1} of each metal were added into 9, 250 mL high density polyethylene (HDPE) plastics. 1 gram of bentonite clay was added into each container. The samples were equilibrated on a range of 1 – 360 mins using Labcon model 3100E table shaker (pH < 3). After shaking, the mixtures were filtered through 0.45μm pore nitrate cellulose filter membrane. Concentrations of metals and final pH were measured in samples taken at desired time intervals. All experiments were done at ambient temperature.

2.6.2 Effect of adsorbent dosage

Seven 100 mL aliquots with 50 mg L^{-1} of each metal were added into 7, 250 mL HDPE plastics. Varying grams of bentonite clay ranging from 0.1 – 5 g were added into each container. The samples were equilibrated 60 mins using Labcon model 3100E table shaker (pH < 3). After shaking, the mixtures were filtered through 0.45μm pore nitrate cellulose filter membrane. Concentrations of metals and pH were measured using ICP-MS and CRISOM MM40 probe respectively. All experiments were done at ambient temperature.

2.6.3 Effect of adsorbate concentration

Six 100 mL aliquots with concentration ranging from 0.1 - 500 mg L^{-1} were added into 6, 250 mL HDPE plastic. 1 gram of bentonite clay was added into each container. The samples were equilibrated 60 mins using Labcon model 3100E table shaker (pH < 3). After shaking, the mixtures were filtered through 0.45µm pore nitrate cellulose filter membrane. Concentrations of metals and pH were measured using ICP-MS and CRISOM MM40 probe respectively. All experiments were done at ambient temperature.

2.6.4 Effect of supernatant pH

Six 100 mL aliquots with 50 mg L^{-1} of each metal were added into 6, 250 mL HDPE plastic. The pH was adjusted to a range of 2 − 12. One gram of bentonite clay was added into each container. The samples were equilibrated 60 mins using Labcon model 3100E table shaker (pH < 3). After shaking, the mixtures were filtered through 0.45µm pore nitrate cellulose filter membrane. Concentrations of metals and pH were measured using ICP-MS and CRISOM MM40 probe respectively. All experiments were done at ambient temperature.The pH was adjusted to the required ranges using 1 M NaOH and Nitric acid (98%).

2.7 Removal of metals at optimized conditions

Synthetic wastewaters were treated at established optimized conditions in order to assess the effectiveness of bentonite clay for removal of metal species from synthetic wastewaters. The pH and metal species content were determined as described previously.

2.8 Calculation of % removal and adsorption capacity

Percentage removal and adsorption capacity was using (1) and (2) as shown below.

$$\text{Percentage removal (\%)} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

$$\text{Adsorption capacity } (q_e) = \frac{(C_i - C_e)V}{m} \qquad (2)$$

Where: C_o = initial concentration, C_e = equilibrium ion concentration and V = volume of solution

2.9 Adsorption model

Adsorption kinetics was done using pseudo-first-order, pseudo-second-order kinetics and itra-particle diffusion models. Adsorption isotherms were determined using Langmuir and Freundlich adsorption isotherm. An error analysis was carried out to evaluate the fitness of

the adsorption isotherms to experimental data. In the present study, the linear coefficient of determination (R^2) was employed for the error analysis. The linear coefficient of determination was calculated by using the equation:

$$r = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{n(\sum x^2) - (\sum x)^2} - \sqrt{(\sum y^2) - (\sum y)^2}}$$ (3)

Theoretically, the R^2 value varies from 0 to 1. The R^2 value shows the variation of experimental data as explained by the regression equation. In most studies, the coefficient of determination, R^2, is applied to determine the relationship between the experimental data and the models.

2.10   geochemical modelling

To complement chemical solution results, the ion association model PHREEQC was used to calculate speciation of metal species based on the pH and solution concentrations of major ions in supernatants that were analysed (Parkhurst and Appelo, 1999).

3   Results and discussions

3.1   Mineralogical Characterization by X-ray diffraction

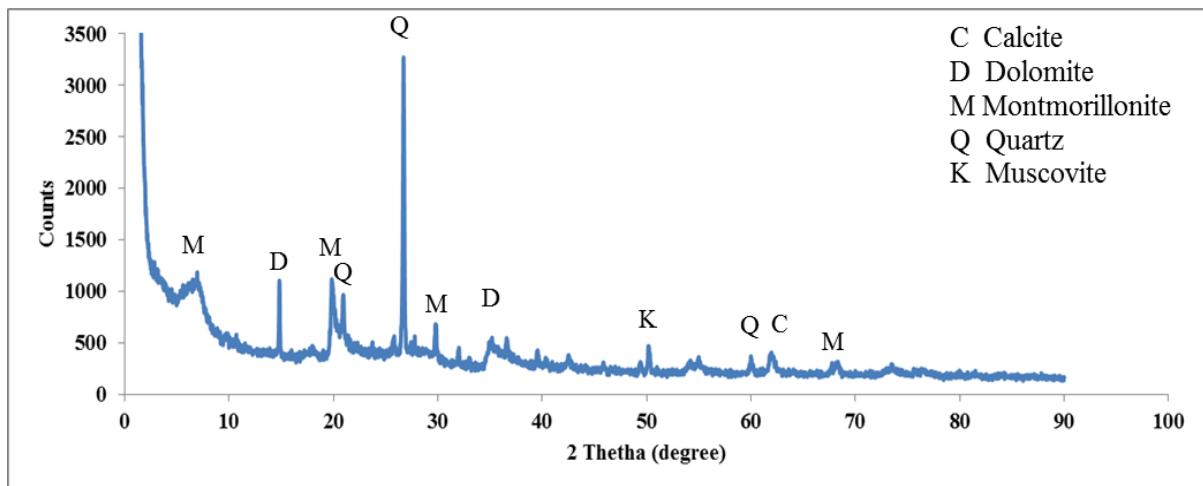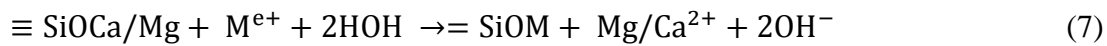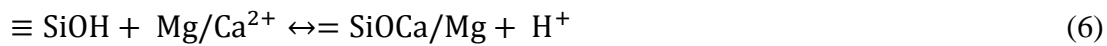Mineralogical composition of bentonite clay is shown in **Figure 1**.

Figure 1: mineralogical composition of bentonite clay

The prominent peak found in the bentonite clay appears at 27° (2θ). It was observed that bentonite clay was comprised of quartz, montmorillonite, calcite, muscovite and dolomite.

Similar results were obtained by Dukic et al. (2013). The availability of quartz, calcite and dolomite will contribute to an increase in pH of aqueous solution. This corroborated study by Gitari (2014). Calcium/magnesium will react with acidity to form calcium/magnesium ions and water

$$Ca/MgOH^+ + H^+ \rightarrow Ca/Mg^{2+} + H_2O \qquad (4)$$

Silicate will react with acidity through ion exchange and lead to pH increase thus promoting the precipitation of metals

$$\equiv SiOH \leftrightarrow SiO^- + H^+ \qquad (5)$$

$$\equiv SiOH + Mg/Ca^{2+} \leftrightarrow= SiOCa/Mg + H^+ \qquad (6)$$

$$\equiv SiOCa/Mg + M^{e+} + 2HOH \rightarrow= SiOM + Mg/Ca^{2+} + 2OH^- \qquad (7)$$

3.2 Elemental composition by X-ray fluorescence

Elemental compositions of raw and reacted bentonite clays are shown in **Table 1.**

Table 1: Elemental composition of raw and reacted bentonite clay

% Composition	Raw bentonite clay	Reacted bentonite
SiO$_2$	67	65
Al$_2$O$_3$	17	15
Fe$_2$O$_3$	4	5
MnO	0.1	0.1
MgO	3.5	0.1
CaO	1.5	0.1
Na$_2$O	1.5	0.1
K$_2$O	0.5	0.1
CuO	< 0.01	1.7
CoO	< 0.01	1.6
ZnO	< 0.01	1.1
PbO	< 0.01	1.2
NiO	< 0.01	2
LOI	6	7
Total	100	100

Bentonite clay is characterised by Al and Si oxides as the main components hence indicating that the material used in this study is aluminosilicate. Mg, Ca, Na and K are present as exchangeable cations. These elements contribute to high cation exchange capacity of the clay. Before interaction, concentration of Co, Cu, Ni, Pb, and Zn was <0.001 %. After interaction of bentonite clay with metal rich wastewaters, Co, Cu, Ni, Pb, and Zn concentrations increased to > 1 % indicating adsorption of the metal cations by bentonite clay. The reduction of Mg, Ca, Na and K indicate that these were the base alkali and earth alkali metals that were exchanged from bentonite clay interlayers.

3.3   Morphology and elemental composition

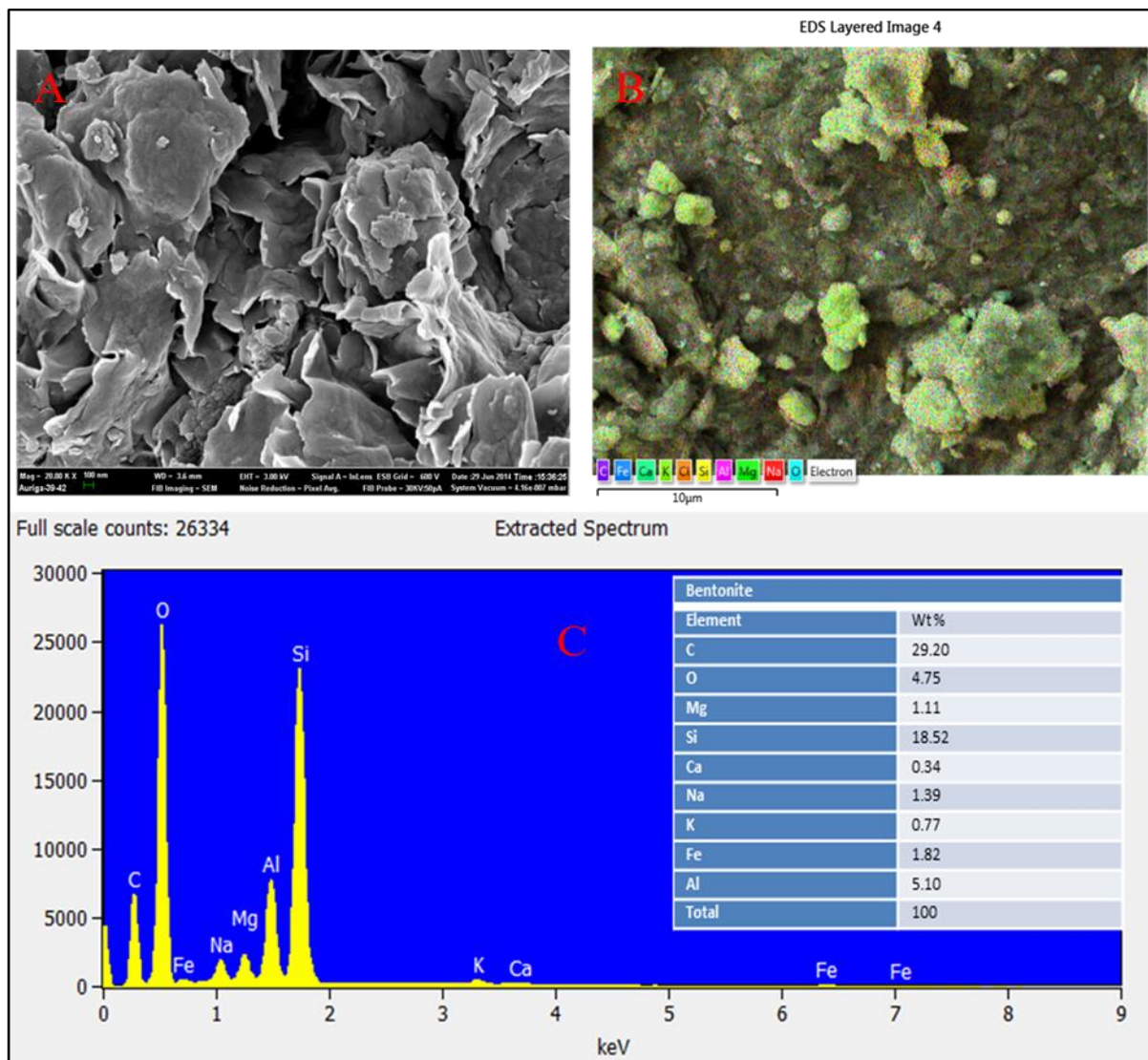Morphology and elemental composition of bentonite clay is shown in **Figure 2.**

Figure 2: Morphology (A), mapping (B) and elemental composition (C) of bentonite clay

Morphology of the raw clay can be seen in Figure 2, expressing the characteristic leafy structure. The micrographs reveal the heterogeneous nature of surface morphology of the bentonite clay sample which also shows predominance of smectite crystals, the crystals presented a foliated form. In the bentonite clay sample micrograph, it was observed crystals of small size belonging to the hexagonal crystalline system, these crystals can be attributed the quartz accessory minerals. Mapping indicated that the elements are uniformly distributed on bentonite clay surfaces.

3.4 Surface area, pH_{pzc} and cation exchange capacity (CEC)

The results for surface area, CEC and pH_{PZC} for bentonite clay are shown in **Table 2**.

Table 2: Surface area of bentonite clay, pHpzc and CEC

Parameters		Bentonite
Surface area (m^2/g)		
Single point surface area		37.05
BET surface area		37.21
Adsorption cumulative surface area pore		20.32
Pore volume (cm^3/g)		
Single point pore volume		0.08
Cumulative volume of pores		0.08
Pore size (nm)		
Adsorption average pore width		8.98
Adsorption average pore diameter		16.49
Point of Zero Charge (pH_{PZC})		8.1
CEC (meq $100g^{-1}$)	**pH 5.4**	**262**
	pH 7.4	265

Bentonite clay had 37 m^2/g of surface area and a single point pore volume and cumulative pore volume of 0.08 cm^3/g hence indication that the clay is porous. The pore size was determined to be 8.98 nm in width and 16.49 nm in diameter respectively. pH_{pzc} was observed to be 8.1. pH_{pzc} gives an insight on the type of chemical species that are more likely to be removed from aqueous solution during the reaction. When pH_{pzc} is greater than the supernatant pH the adsorbent will adsorb anions and when the pH of the supernatant is above

the pH_{pzc} the adsorbent will adsorb cations from the solution. The high pH_{PZC} in bentonite clay is an attribute of the presence of aluminium and iron oxide or hydroxides in the clay matrix. The pH_{pzc} value of a material is a reflection of the individual pH_{pzc} values of the components present. The CEC of bentonite clay was observed to be 262 meq $100g^{-1}$ at pH 5.4 and 265 meq $100g^{-1}$ at pH 7.4 hence indicating that it is independent of pH of media.

3.5 Adsorption optimization experiments

Results of optimization of the adsorption conditions for metal species by bentonite clay are presented in this section.

3.5.1 Effects of residence time

The effects of equilibration time on sorption of metal species from synthetic wastewaters are shown in **Figure 3**.
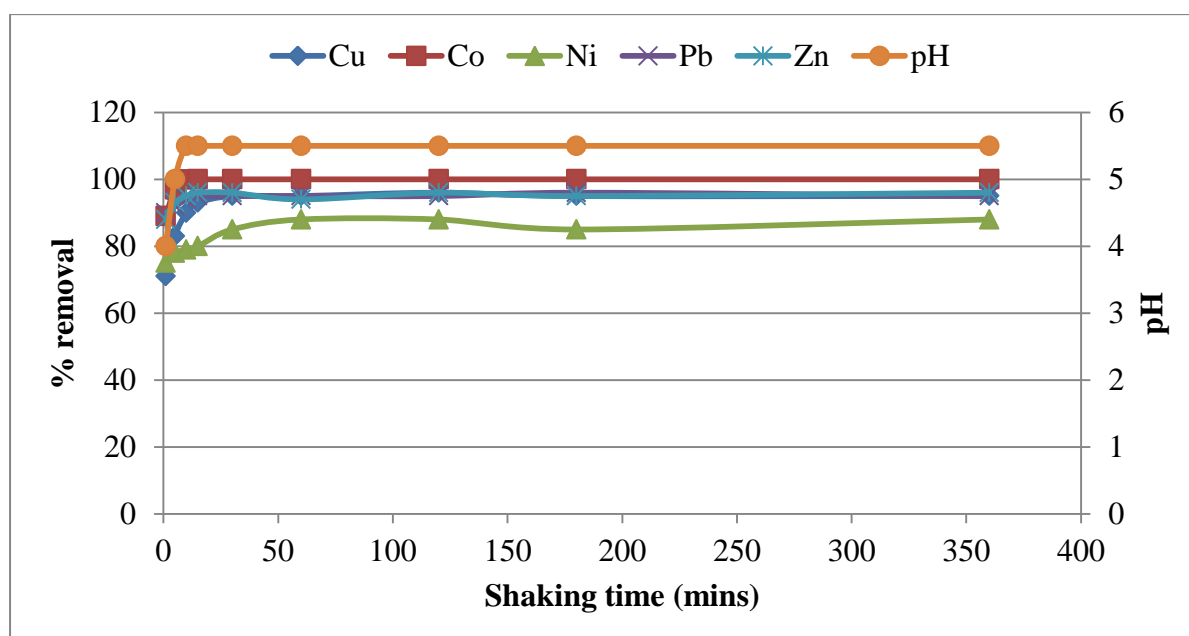

Figure 3: Effects of residence time on sorption of metal species from wastewaters (Conditions: pH < 3, 1g of bentonite clay dosage, 50 mg L^{-1} of adsorbate concentration, 250 rpm shaking speed, 1: 100 S/L ratios, 100 mL solution, < 32 μm particle size and room temperature).

To determine the time required for equilibrium adsorption, we varied the contact time between adsorbent and adsorbate. **Figure 3** shows the effect of shaking time on simultaneous adsorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) from wastewaters. It is clear that the increase in contact time from 1 to 60 min increased the amount of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) adsorbed, followed by a constant adsorption upon further increasing the

contact time (60 mins onwards) hence indicating that the reaction kinetics has approached a steady state. The metals sorption affinities followed this sequence: Co> Pb= Zn = Cu > Ni. The pH of the supernatant solution was observed to be > 5.5. This may be due to dissolution of alkali, earth alkali, calcite and dolomite to aqueous solution. The release of hydroxyl ions on clay matrices may also contribute to an increase in pH. Equilibrium adsorption was reached within a short period of 60 mins for all concentrations of the dissolved metal ions. Based on these results, an equilibrium time of 60 mins was selected as the agitation time for subsequent experiments.

3.5.2 Effects of bentonite clay dosage

The effects of bentonite clay dosage on sorption of metals species from synthetic wastewaters is shown in **Figure 4**.
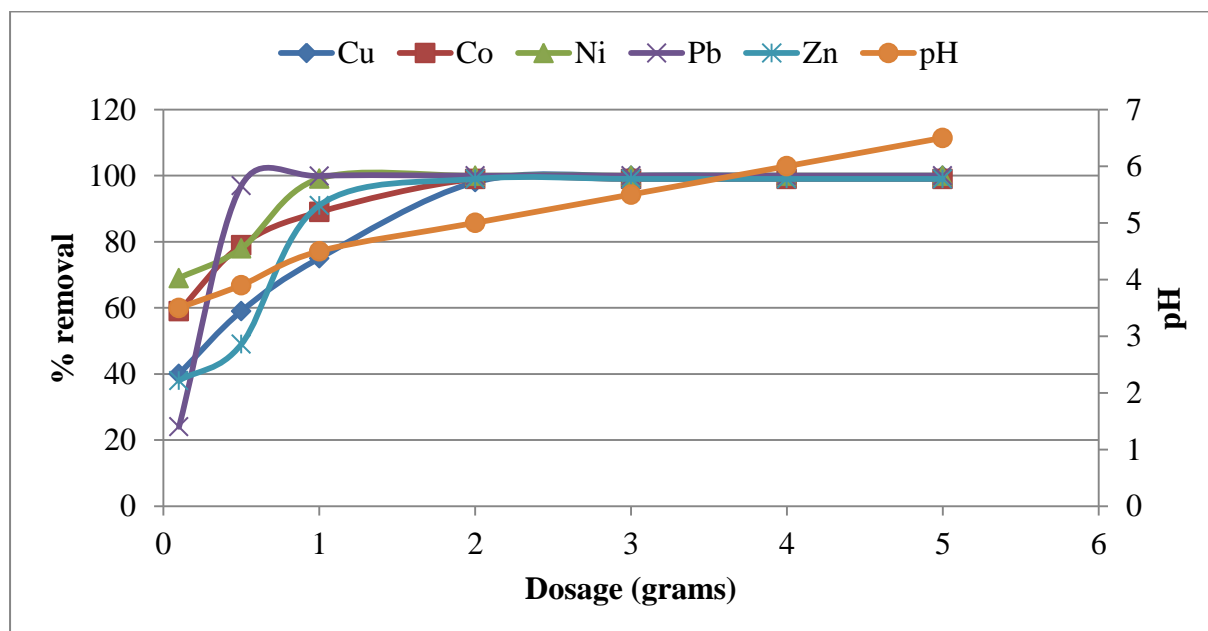

Figure 4: Effects of bentonite clay dosage on sorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) from wastewaters (Conditions: pH < 3, 60 mins of shaking, 100 mg L^{-1} of adsorbate concentration, 250 rpm shaking speed, 1: 100 S/L ratios, 100 mL solution, < 32 μm particle size and room temperature).

The results of the dependence of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) adsorption on amount of bentonite clay used are shown in **Figure 4**. Increasing the mass of bentonite clay slightly increased the percentage removal of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II). As the amount of adsorbent increases, the number of adsorbent sites increases; therefore, these particles attach more ions to their surfaces. The pH of the solution was also observed to

increase with an increase in bentonite clay dosage. This is attributed to the release of base cations, and hydroxyl ion, and dissolution of calcite and dolomite from clay matrices. The sorption affinity of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) to bentonite clay matrices was Cu(II) > Co(II) > Zn(II) > Ni(II)> Pb(II). Since the sorption of 100 mg/L of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) was > 80 % at 1 g, the optimum dosage for removal metals from aqueous solution was chosen to be 1 g.

3.5.3   Effects of adsorbate concentrations

The effects of concentration on sorption of metals species from synthetic wastewaters is shown in **Figure 5**.
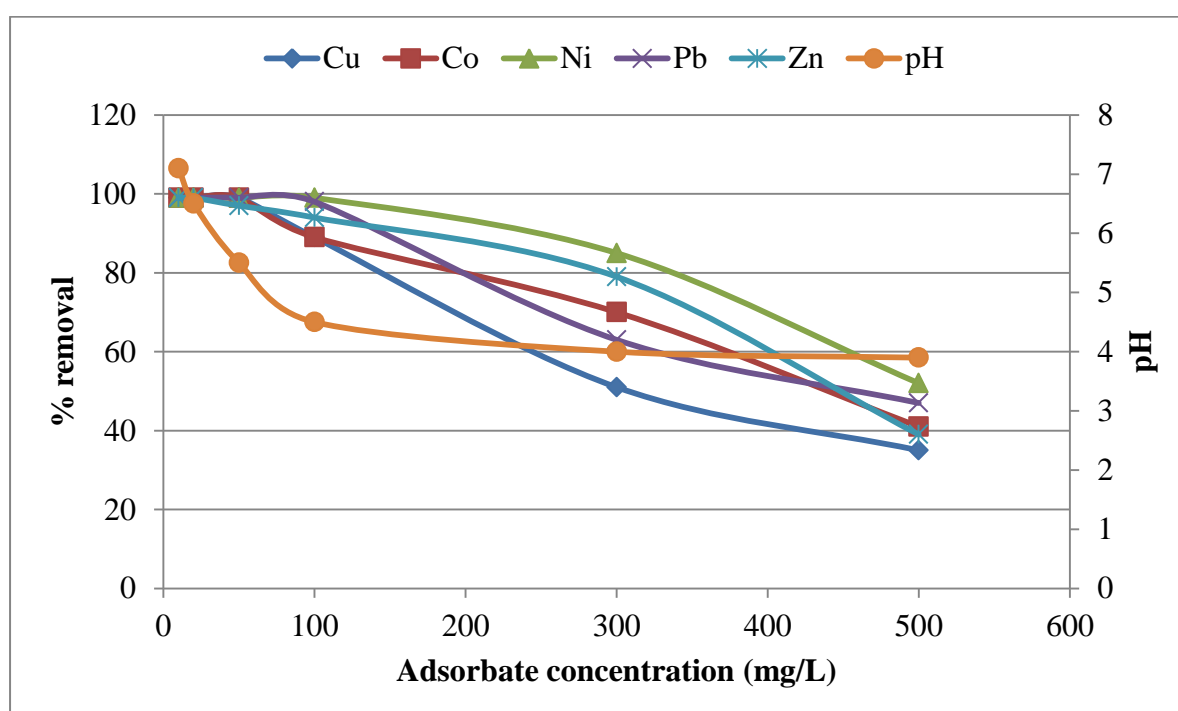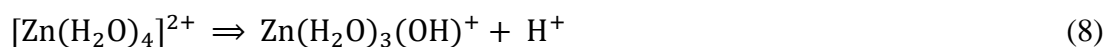

Figure 5: Effects of species concentration on sorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) from wastewaters (Conditions: 60 mins of shaking, pH < 3 , 1g of bentonite clay dosage, 250 rpm shaking speed, 1: 100 S/L ratios, 100 mL solution, < 32 μm particle size and room temperature).

As can be observed from figure 5, an increasing concentration of the Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) ions in solution resulted in a decrease in % removal with an increase in ion concentration, it was observed that the final pH of the solution was decreasing from 7 at 10 mg/L to 4 at 500 mg/L. This is due to hydrolysis of the metal cations with subsequent release of protons (for example, equation 8). The metals removal affinity was as follow: Zn < Co =

Cu = Ni = Pb. Moreover, it was observed that 50 mg L^{-1} can be the optimum concentration that 1 gram of bentonite clay can remove from aqueous solution.

$$[Zn(H_2O)_4]^{2+} \implies Zn(H_2O)_3(OH)^+ + H^+ \qquad (8)$$

3.5.4 Effects of pH

The effect of pH on sorption of metals species ions from synthetic wastewaters is shown in **Figure 6**.
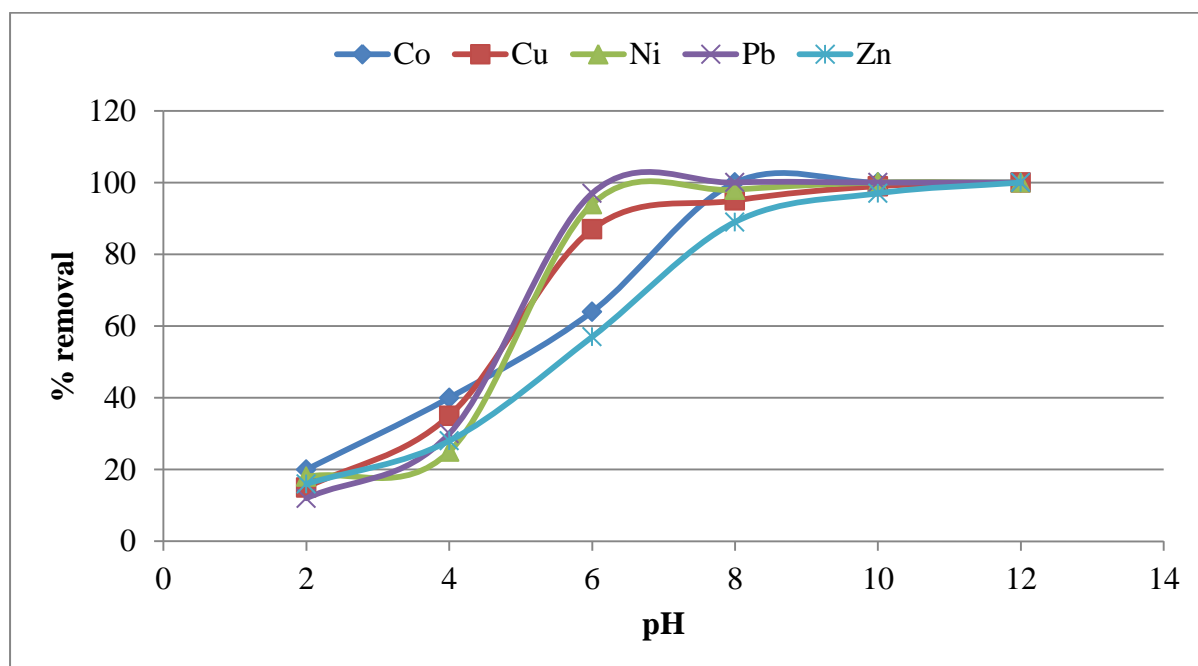

Figure 6: Effects of pH on sorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) from wastewaters (Conditions: 60 mins of shaking, 1g of bentonite clay dosage, 50 mg L^{-1} of species concentration, 250 rpm shaking speed, 1: 100 S/L ratios, 100 mL solution, < 32 μm particle size and room temperature).

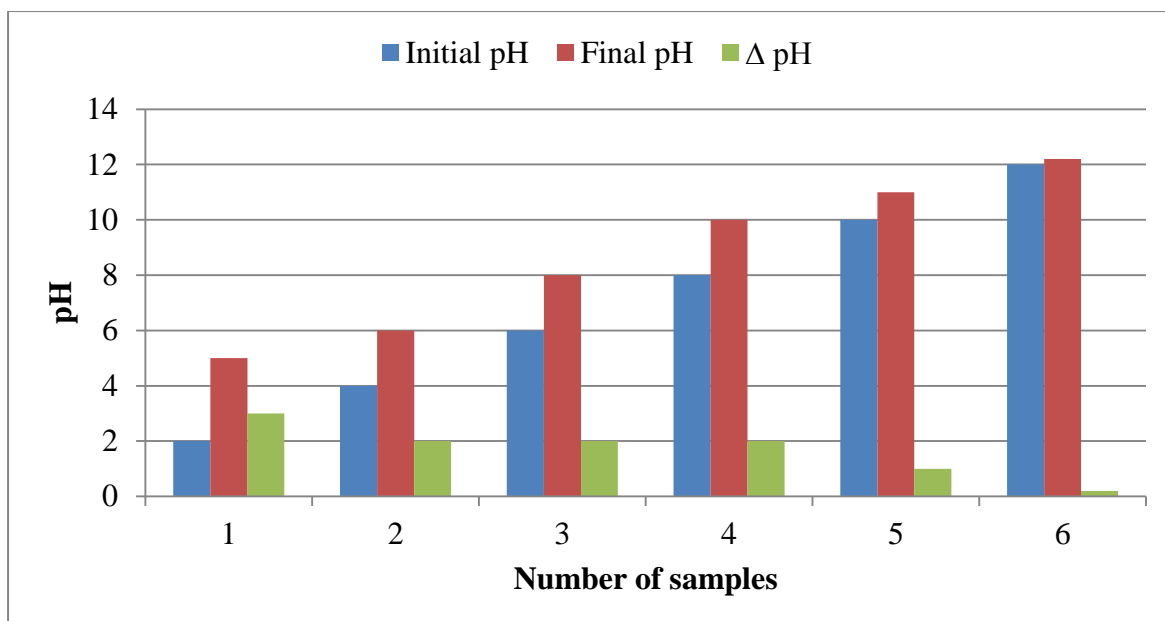Variation between initial and final pH is shown in **Figure 7**

Figure 7: Variation between initial and final pH of the supernatants (Conditions: pH < 3, 1g of bentonite clay dosage, 60 mins of shaking, 250 rpm shaking speed, 1: 100 S/L ratios, 100 mL solution, < 32 μm particle size and room temperature).

The pH of the aqueous solution is an important variable which controls the adsorption of the metal at the clay–water interfaces. Hence, the influence of pH on the adsorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto bentonite clay was investigated in the pH range of 2–12. **Figure 7** shows the effect of pH on adsorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto bentonite clay. It can be observed from the results that the adsorption of Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) ion increases with an increase in pH of the solution. Clays are known to possess a negative surface charge in solution. As pH changes, surface charge also changes, and the sorption of charged species is affected (attraction between the positively charged metal ion and the negatively charged clay surface). It is conceivable that at low pH values, where there is an excess of H_3O^+ ions in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the negatively charged clay surface. As the pH increases and the balance between H_3O^+ and OH^- are more equal, more of the positively charged metal ions in solution are adsorbed on the negative clay surface and thus the percentage removal of the metal ions increases. On the other hand, precipitation of metal hydroxides may also occur as the pH in solution increases, which will lead to a corresponding decrease in the amount of metal ions adsorbed onto the clay. Britton (1929) observed precipitation of metal hydroxides from dilute solutions to within a specific pH range. He observed that Cu^{2+} would precipitate at pH 5.3, Pb^{2+} at 6.0,

Ni^{2+} at 6.7, Zn^{2+} at 7.0 and Co^{2+} at 6.8. An observation of figure 6 indicates that there is increased removal of the metal species between pH 4-8 which corresponds to the pH range of precipitation of the investigated metal species. This could indicate that metal hydroxide precipitation was a significant mechanism of removal of these metal species.

3.6 Modelling

3.6.1 Adsorption kinetics

The effect of contact time on removal of chemical species from aqueous solution was evaluated using different kinetic models to reveal the nature of the adsorption process and rate limiting processes. A Lagergren pseudo first order kinetic model is a well-known model that is used to describe mechanisms of metal species adsorption by an adsorbent. It can be written as follow (Albadarin, et al., 2012, Iakovleva, et al., 2015):

$$\ln(q_e - q_t) = \ln q_{e-} k_1 t \qquad (9)$$

Where k_1 (min^{-1}) is the pseudo-first-order adsorption rate coefficient and q_e and q_t are the values of the amount adsorbed per unit mass at equilibrium and at time t, respectively. The experimental data was fitted by using the pseudo-first-order kinetic model by plotting $\ln(q_e - q_t)$ vs. t, and the results are shown in **Table 3.** The pseudo-first-order was applied and it was found to fairly converge with the experimental data, and the correlation coefficients were > 0.95. Moreover, the calculated amounts of Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions adsorbed by the bentonite clay [qe, calc (mgg-1)] were less than the experimental values [$q_{e, exp}$ (mgg^{-1})] (**Table 3**). The finding indicated that the Lagergren pseudo-first-order kinetic model is inappropriate to describe the adsorption of Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions from aqueous system by ball milled bentonite clay.

The pseudo-second-order kinetic model is another kinetic model that is widely used to describe the adsorption process from an aqueous solution. The linearized form of the pseudo-second-order rate equation is given as follow:

$$\frac{t}{qr} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

Where k_2 [g(mg min^{-1})] is the pseudo-second-order adsorption rate coefficient and q_e and q_t are the values of the amount adsorbed per unit mass at equilibrium and at time t, respectively. An application of the pseudo-second-order rate equation for adsorption of chemical species to

the bentonite matrices portrayed a good fit with experimental data (**Figure 8 and Table 3**). The obtained results confirms that pseudo-second-order model is the most suitable kinetic model to describe adsorption of Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions by bentonite clay from aqueous system. Moreover, this also confirms that the mechanism of metals species removal from aqueous solution is chemisorption. Different kinetic model parameters for adsorption of Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions on bentonite clay are shown in **Table 3**. Note the theoretical adsorption capacity is close to the experimental adsorption capacity further confirming that this model describes the adsorption data. The overall kinetics of the adsorption from solutions may be governed by the diffusional processes as well as by the kinetics of the surface chemical reaction. In diffusion studies, the rate is often expressed in terms of the square root time

$$q_t = k_{id}t^{1/2} + C_i \tag{11}$$

Where k_{id} (mgg^{-1} min$^{-1/2}$) is the Intraparticle diffusion coefficient (slope of the plot of q_t vs. $t^{1/2}$) and C_i is the Intraparticle diffusion rate constant. The results also showed that the Intraparticle diffusion model was partially applicable for the present process due to correlation coefficients > 0.84. Therefore, pore diffusion factor could potentially exist and pose a greater effect on transportation of Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) towards the interlayers and internal surfaces of bentonite clay.

Table 3: Different kinetic model parameters for adsorption of metals species on bentonite clay

Pseudo-first-order kinetic model

Element	$q_{e, exp}$ (mgg^{-1})	$q_{e, calc}$ (mgg^{-1})	K_1 (min^{-1})	R^2
Co(II)	9.5	12.9	0.41	0.99
Cu(II)	9.9	-33.3	-0.66	0.99
Ni(II)	8.8	-47.2	-0.37	0.96
Pb(II)	9.5	-47.1	0.64	0.97
Zn(II)	9.6	-9.99	4.15	0.99

Pseudo-second-order kinetic model

Element	$q_{e, exp}$ (mgg^{-1})	$q_{e, calc}$ (mgg^{-1})	K_2 (g.mg. min^{-1})	R^2
Co(II)	9.5	10	2.1	1
Cu(II)	9.9	10	1.79	1
Ni(II)	8.8	8.7	1.0	0.99
Pb(II)	9.5	9.5	-7.4	1
Zn(II)	9.6	9.5	1.8	1

Intra particle diffusion kinetic model

Element	$q_{e, exp}$ (mgg^{-1})	C_i (mgg^{-1})	K_{id} (mgg^{-1} min$^{-1/2}$)	R^2
Co(II)	9.5	-10.76	1.60	0.86
Cu(II)	9.9	-34.24	3.97	0.95
Ni(II)	8.8	-36.31	4.97	0.98
Pb(II)	9.5	-63.66	7.16	0.84
Zn(II)	9.6	-38.11	4.40	0.77

The correlation coefficient (R^2) for adsorption of metal species on bentonite clay is shown in **Figure 8**.
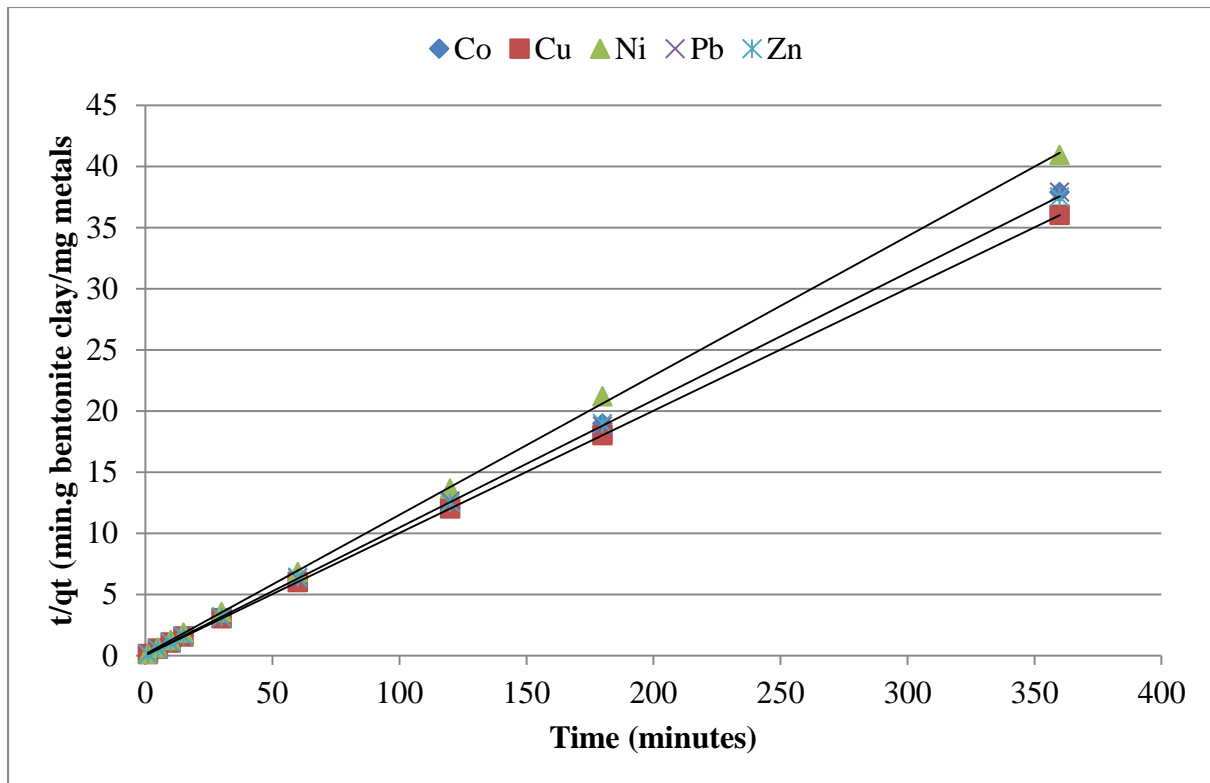
Figure 8: Pseudo-second-order plots of metals species adsorbed on bentonite clay.

3.6.2   Adsorption isotherm

The relationship between the amount of ions adsorbed and the ions concentration remaining in solution is described by an isotherm. The two most common isotherm types for describing this type of system are Langmuir and Freundlich adsorption isotherms. These models describe adsorption processes on a homogenous (monolayer) or heterogeneous (multilayer) surface respectively. The most important model of monolayer adsorption came from Langmuir. This isotherm is described as follows:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{12}$$

The constant Q_0 and b are characteristics of the Langmuir equation and can be determined from a linearized form of equation. The Langmuir isotherm is valid for monolayer sorption due to a surface with finite number of identical sites and can be expressed in the following linear form:

$$\frac{Ce}{q_e} = \frac{1}{Q_m b} + \frac{Ce}{Q_m} \tag{13}$$

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as:

$$R_L = \frac{1}{1 + bC_o} \tag{14}$$

Where, Ce = Equilibrium concentration (mg L^{-1}), Qe = Amount adsorbed at equilibrium (mg g^{-1}), Qm = Langmuir constants related to adsorption capacity (mg g^{-1}) and b = Langmuir constants related to energy of adsorption (L mg^{-1}). A plot of Ce versus Ce/Qe should be linear if the data is described by the Langmuir isotherm. The value of Qm is determined from the slope and the intercept of the plot. It is used to derive the maximum adsorption capacity and b is determined from the original equation and it represents the intensity of adsorption.

The Freundlich adsorption isotherm describes the heterogeneous surface energy by multilayer adsorption. The Freundlich isotherm can be formulated as follows:

$$q_e = kCe^{1/n} \tag{15}$$

The equation may be linearized by taking the logarithm of both sides of the equation and can be expressed in linear form as follows (equation 16):

$$\log q_e = \frac{1}{n} \log C + \log K \tag{16}$$

Where Ce = Equilibrium concentration (mg L^{-1}), q_e = Amount adsorbed at equilibrium (mg g^{-1}), K = Partition Coefficient (mg g^{-1}) and n = Intensity of adsorption. The linear plot of $\log Ce$ versus $\log q_e$ indicates if the data is described by Freundlich isotherm. The value of Kf implies that the energy of adsorption on a homogeneous surface is independent of surface coverage and n is an adsorption constant which reveals the rate at which adsorption is taking place. These two constants are determined from the slope and intercept of the plot of each isotherm. Data listed in **Table 4** shows the Langmuir and Freundlich adsorption isotherm parameters for adsorption of Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} ions onto bentonite clay.
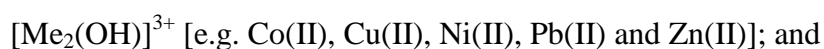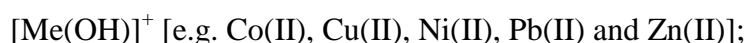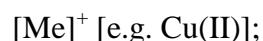
Table 4: Langmuir and Freundlich adsorption isotherm parameters for Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} ions

	Langmuir adsorption isotherm				Freundlich adsorption isotherm		
Species	R^2	Qm (mg/L)	b (L mg^{-1})	R_L	R^2	K_f (mg/L)	n
Co^{2+}	0.98	0.9	-370	-0.0003	0.99	2	0.2
Cu^{2+}	0.94	0.94	-21.3	-0.0003	0.99	3.3	1.2
Ni^{2+}	0.94	0.94	-21.3	-0.0003	0.99	1.3	1.2
Pb^{2+}	0.95	0.91	-7.9	-0.0002	0.98	4.2	2.4
Zn^{2+}	0.98	0.8	-0.8	-0.0003	0.98	2.1	0.2

Table 4 shows that the adsorption data fitted well to Freundlich adsorption isotherm than Langmuir adsorption isotherm. This was determined by the regression coefficient of the obtained results. This confirms that the type adsorption process is taking place on multilayer surfaces. High K_f indicate that adsorption is taking place on heterogeneous surface and n shows that the adsorption was taking place at a fast and favourable rate. The negative R_L values indicate that the adsorption was not favourable (Sparks, 1995, Selim, et al., 2001, Selim and Kingery, 2003, Vicente, et al., 2013)

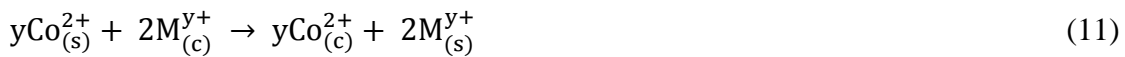### 3.7   Mechanisms of metals species removal

Several factors are governing the removal of metals from aqueous solution. From the modelling experiments, it was shown that multilayer adsorption is predominant and the type of chemical reaction is chemisorption. Due to an increase in pH, metal species tend to precipitate as metals hydroxide, thus making precipitation one of the modes of chemical species removal. pH has a stronger influence on the removal of metals. An explanation for such behaviour should consider both the hydration of metallic ions in solution and formation of equilibrium of hydrocomplexes. This was predicted using PHREEQC geochemical model. In the pH range 1-4, different hydrochemical species of metals are presented in solution, namely:

$[Me]^+$ [e.g. Cu(II)];

$[Me(OH)]^+$ [e.g. Co(II), Cu(II), Ni(II), Pb(II) and Zn(II)];

$[Me_2(OH)]^{3+}$ [e.g. Co(II), Cu(II), Ni(II), Pb(II) and Zn(II)]; and

$[Me_2(OH)_2]^{2+}$ [e.g. Co(II), Cu(II), Ni(II), Pb(II) and Zn(II)]. The basic medium favours the formation of some anionic hydrocomplexes forms that do not influence the adsorption process. Consider the following equilibrium:

$$[Me(H_2O)_x]^{2+} + H_2O \leftrightarrow [Me(H_2O)_{x-1}(OH)]^+ + H_3O^+ \qquad (10)$$

Under low acidity (pH < 4), the equilibrium is moved to the left and generates a decrease of the hydrocomplex form. Due to net negative charge on clay surfaces, those hydrocomplexes will be adsorbed by clay surface. Ion exchange is also a prevalent mechanism that governs that removal of metals from aqueous system through isomorphous substitution. The interaction between the heavy metals ions and clay are:

$$yCo_{(s)}^{2+} + 2M_{(c)}^{y+} \rightarrow yCo_{(c)}^{2+} + 2M_{(s)}^{y+} \qquad (11)$$

$$yCu_{(s)}^{2+} + 2M_{(c)}^{y+} \rightarrow yCu_{(c)}^{2+} + 2M_{(s)}^{y+} \qquad (12)$$

$$yNi_{(s)}^{2+} + 2M_{(c)}^{y+} \rightarrow yNi_{(c)}^{2+} + 2M_{(s)}^{y+} \qquad (13)$$

$$yPb_{(s)}^{2+} + 2M_{(c)}^{y+} \rightarrow yPb_{(c)}^{2+} + 2M_{(s)}^{y+} \qquad (14)$$

$$yZn_{(s)}^{2+} + 2M_{(c)}^{y+} \rightarrow yZn_{(c)}^{2+} + 2M_{(s)}^{y+} \qquad (15)$$

Where y is the exchangeable cations valence M (Na, K, Ca, Mg, Mn) and subscripts (s) and (c) denote solution and clay phases, respectively.

3.8   Treatment of wastewater at optimized conditions

The results of metal species sorption when bentonite clay was reacted with metalliferous acidic effluents are shown in **Table 5**.

Table 5: Chemical composition of metalliferous wastewater before and after treatment (chemical species in mg L^{-1} except pH and EC)

Parameter	DWA guidelines	Synthetic wastewater	Product water
pH	6 – 10	3	6
TDS (mg/L)	0 – 1200	1009	872
EC (µS/cm)	0 – 700	1899	1611
Cu (mg/L)	0 – 1	50	0.5
Zn (mg/L)	0 – 0.5	50	0.1
Pb (mg/L)	0 – 0.01	50	0.01
Co (mg/L)	NA	50	0.9
Ni (mg/L)	0 - 0.07	50	0.1

Bentonite showed a significant increase in pH and reduction in metals concentration. This showed that the treatment is effective for wastewater with low metal concentrations. A reduction in TDS and EC is indicating that there was sorption of metals from aqueous solution to clay matrices. Metal species concentration was reduced to within DWA water quality guidelines. The adsorption affinities varied as follows: Co> Cu> Ni= Zn> Pb.

3.9 Comparison adsorption capacity of different materials

Comparison of percentages of metal species removed from aqueous solution using different materials in similar single or multicomponent species solutions is shown in **Table 6**.

Table 6: Comparison of adsorption trends of different materials using similar single or multicomponent species solutions

Adsorbent	Co^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
Bentonite clay (Present study) (mg g^{-1})	2	3.3	1.3	4.2	2.1
Clinoptilolite (mg g^{-1})	-	3.1	0.4	5.7	-
Na- Clinoptilolite (mg g^{-1})	0.8	2.2	0.7	34	1.5
Montmorillonite/kaolinite clay (mg g^{-1})	-	4.7	-	6.7	2.4
Montmorillonite/kaolinite clay-TiO$_2$ composite (mg g^{-1})	-	16.4	-	26.2	6.56
Magnesite/bentonite clay composite (mg g^{-1})	1	1.3	2	1.3	1.1

The metals removal capacities as measured according to Freundlich (K_f) for various adsorbents are given in **Table 6**. It is evident that the removal capacity of the bentonite clay towards Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} is comparable to other available adsorbents though other materials showed superior adsorption capacity as compared to raw bentonite clay.

4   Conclusions

To respond to an alarming degradation of aquatic ecosystems, it is essential to find low-cost techniques suitable for the removal of pollutants such as metal species from drinking as well as industrial wastewater. In this context, bentonite clay was used to remove metal species Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from wastewaters in a single step. Optimum conditions established for their removal were 60 minutes of equilibration, 1 g of bentonite clay, 50 mg L^{-1} of Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} concentration, 250 rpm, 32µm, 25◦C temperature, 100 mL solution, 1:100 S/L ratios. In this study bentonite clay achieved > 99 % removal efficiencies for metal species in acidic wastewaters. The sorption affinity varied as follows: Co> Cu> Ni= Zn> Pb. Interaction of bentonite clay and metal species showed a decrease in base cations on the clay matrices hence proving that ion exchange is also governing the removal of metal species. Adsorption kinetic revealed that pseudo-second-order kinetics better confirmed that removal of metals was governed by chemisorption as rate limiting the chemical reaction. Long range intra-particle diffusion was also determined to control the percolation of particle to bentonite clay interlayers. Adsorption data fitted better to the Freundlich adsorption isotherms as compared to Langmuir adsorption isotherm, confirming multilayer adsorption. From the results, it was concluded that bentonite clay can be used for treatment of acidic wastewaters.

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