Sorption of Zn and Mn ions from single and binary metal solutions by Kaolinite: *Influence of physico-chemical factors*

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Abstract: Batch equilibrium sorption studies of Zn and Mn in kaolinite under single and binary metal systems were carried out in order to assess the controlling experimental and physico-chemical conditions on the adsorption process. The experimental data show that the equilibrium isotherms of Mn and Zn onto kaolinite correlate well with both Langmuir and Freundlich models. Increase in the estimated maximum adsorption (M, mg/g) for Zn and Mn uptake/removal were observed with increasing pH from 2.5 to 8.5 under binary metal solution system while similar trend were only observed between pH 2.5 and pH 5.5 under single metal solution system. However, the observed influence of sorbent mass is appreciable at pH of 2.5 with >20% reduction in adsorption capacity (when solution-solid ratio was increased from 10ml/g to 20ml/g) for Zn and Mn under both single and binary metal solution systems. Also, increase in metal concentration from 50 to 100mg/l and from 100 to 200g/l resulted in about 10% reduction in adsorption capacity at pH of 2.5 and about 10-15% reduction at pH of 5.5 under both single and binary systems. However, the reduction of less than 2% at pH of 8.5 especially under binary system could be attributed to complementary co-precipitation of metal hydroxides. Further evaluation had shown that the adsorption mechanism of both metals is characterized by ion-exchange process most especially at pH of 2.5. Finally, based on the overall assessment, this study highlighted the potentials of clay materials as cheap sorbents for removal of trace/heavy metals from contaminant aqueous wastes.

Key words: Sorption, Kaolinite, Batch equilibrium test, single and binary metal solution.

Introduction

Over the last century, there have been increasing environmental contamination/pollution problems associated with exponential growth of the world's population on one hand and with the corresponding increase in exploitation of the earth's raw mineral materials on the other hand. These had undoubted led to build-up of waste products, of which trace/heavy metals are of particular environmental concern. Usually soils serve as important sinks for contaminant metals, however clay and organic contents are important components that control the sorption/retention capacity of soils in respect of the contaminant trace metals. Nonetheless, the nature of heavy metal retention depends on the species and concentration of the respective heavy metal, soil constituents, pH, redox conditions, and other physico-chemical characteristics of the solid–solution system. Furthermore, the

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overall behavior of heavy metals in a soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, most especially the clay components (APPEL AND MA, 2002).

Hence understanding mechanisms of metal sorption in soils is important as these reactions dictate the strength of the metal–soil surface interaction. The stronger the interaction with the soil surface, the less is the likelihood of environmental contamination. On a relative basis, exchange reactions (i.e. reversible electrostatic or outer-sphere reactions) are said to render metals most labile. However, inner sphere complex formation and co-precipitation with soil surfaces (i.e., bond formation between contaminant metal and soil surface) cause metals to be retained strongly and in most cases nearly irreversibly (MCBRIDE, 1994). Consequently, metal immobilization through precipitation and adsorption processes is considered a common mechanism to decrease the hazards of heavy metal in contaminated soils (MA ET AL., 1993; MALAKUL ET AL., 1998). However, a number of available common methods for removing metals in contaminated soils are said to be economically unfavorable (e.g. conventional ion exchange, electrolyte or liquid extraction, electrodialysis) or technically complicated (e.g. precipitation, cementation, reverse osmosis) (HORACEK ET AL., 1994, BROWN ET AL, 2000). In addition to these constraints, most of the modern remediation and removal methods are not always available in typical developing countries. Hence, the need to look at clay materials as effective and alternative low cost, natural adsorbents for the removal of metal ions from polluted aqueous wastes in developing countries. Clay materials, besides serving as excellent hydraulic barri-

ers, can attenuate contaminant migration via geochemical processes such as adsorption, precipitation, and co-precipitation (LIM ET AL., 2002 AND SEZER ET AL., 2003). The effectiveness of clay / clay minerals (e.g. smectite, illite and kaolinite) as well as artificial commercial adsorbents (e.g. activated carbon and zeolite) as adsorption and/or ion-exchange media for dissolved metal ions has been known and studied extensively (GRIFFIN AND AU, 1977; YONG ET AL., 1990 AND 1993; SPARK ET AL., 1995; LOTHENBACH ET AL., 1998; KRAEPIEL ET AL., 1999).

However this study focus on the influence of pH, solution-solid ratio (SSR) and initial metal concentrations on the adsorption characteristics of kaolinite clays in single and in binary metal system and to assess possible metal interference on adsorption using batch equilibrium sorption tests. Furthermore, the abundance of weathered clay in tropical environment that characterized most of the developing regions warrants renewed investigation into the heavy metal immobilization potential of clay materials as cheap natural adsorbent in contaminated sites as well as in application as barrier fills in waste disposal systems.

STUDY CONCEPT

Background to the Study Approach: Equilibrium adsorption isotherms, or capacity studies are of fundamental importance in the design of adsorption systems since they indicate how the metal ions partition themselves between the media and liquid phase with increasing concentration at equilibrium. Usually, the batch equilibrium test (BET) is used to determine such adsorption character-

istics in clay materials. However, the metal uptake process is complex and dependent on the chemistry of the metal ions, specific surface properties of the clays and the physico-chemical influence like pH, temperature, and metal concentration (GOYAL ET AL., 2003). From the experimental results of BET, the amount of respective metals (in this case, Mn and Zn) removed from the solution per gram of clay (soil) sample (mg/g) at specific pH and test/reaction period of about 12-24 h can be calculated using the equation below:

$$q = \{(C_i - C_e) * V\} / (M * 1000) \qquad (1)$$

where:

q =   Amount of metal contaminant removed from solution or sorbed per unit mass of soil material (mg/g or ug/g)

C_i = Initial concentration of metal contaminant in the solution before the experiment (mg/l or ug/l)

C_e = Concentration of the metal contaminant left in the solution after the BET experiment (mg/l or ug/l)

V = Volume of solution used in the BET experiment (ml)

M = Mass of soil or clay material used in the in BET experiment (g)

Hence, the above equation represents the fundamental quantification of the sorption potentials of the clay sorbent and forms the basis of further evaluation and assessment employed in this study.

MATERIALS AND METHODS

The sorbents selected for this study was mainly kaolinite clay. The dry clay samples were grounded and pulverized into fine powder and stored in sealed polyethylene sample bags prior to the laboratory experiments. Mineralogical composition and characters of the kaolinite clay was determined on duplicate samples via X-ray diffraction (XRD) analysis using CuKα radiation with the aid of computer controlled MAC-Science XRD machine (model M18XHF). An example of the X-ray diffractogram of the kaolinite, which was scanned between 2 to 50° at 2°θ/min on glass plate, is pesented in Figure 1.

Prior to the experiment, all the laboratory wares used for the experiments were thoroughly washed and double rinsed with
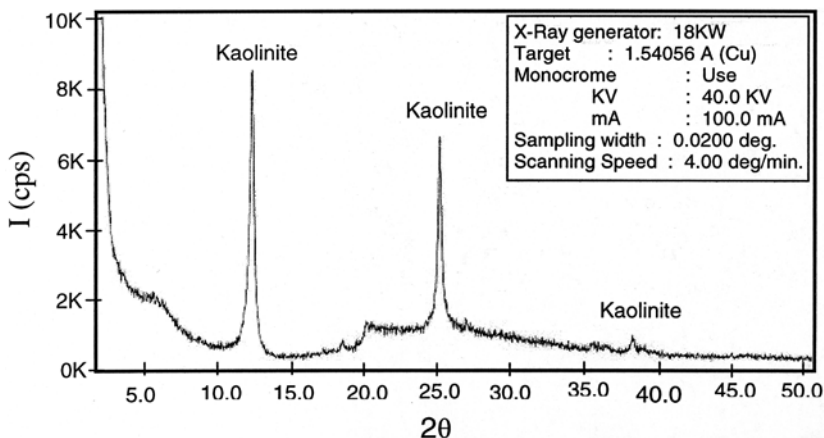
Figure 1. XRD Diffractogram of the analyzed Kaolinite sample used for the BET tests.

Table 1. Characteristics of metals and sorbates

Metal	Valency	*Ionic radius	*IP	Atomic Weight	Salt Formula	Molecular Weight (salt)	% Purity
Zn	2+	0.83	2.4	65.37	$ZnCl_2$	136.28	98.0
Mn	2+	0.92	2.2	54.94	$MnCl_2.4H_2O$	197.91	99.0

*IP = Ionic potencial
*Source = TAYLOR & EGGLETON, 2001

distilled and MilliQ water. The test stock solutions were prepared by dissolving the analytical grade chloride salts of the respective metals in MilliQ water; stock solution of Zn was obtained by dissolving 1.020g of dried $ZnCl_2$ salt (98 % purity) in 1 litre of MilliQ water, while that of Mn solution was prepared by dissolving 1.010 g of crystallized $MnCl_2.4H_2O$ salt (99 % purity) in 1litre of MilliQ water, given a corresponding concentration of 480mg/l Zn and 278mg/l Mn respectively. The stock solutions were then refrigerated at 4°C and subsequently used to make the various dilutions; single–metal component and binary–metal component systems with concentrations of 50, 100 and 200 mg/l used for the experiments. The characteristics of the metals and their salts are presented in Table 1.

Experimental equilibrium adsorption studies were performed to determine the relationship between capacity of the kaolinitic clay media for the metal ions and equilibrium metal ion concentration under different pH (2.5, 5.5 and 8.5) and initial solution concentrations. For the adsorption capacity studies, solutions with concentrations of 50, 100 and 200 mg/l of Zn and Mn in single-component and binary-component systems were prepared from stock solution. Prior to mixing with the clay materials, the pH of each test solutions were adjusted to the required value using 0.1 M HNO_3 and 0.1M of NaOH depending on the situation. Forty milliliters (40 ml) of each concentra-

tion were mixed separately with 2g and 4g of kaolinite clay in conical flasks sealed with parafilm. These were shaken for 18-hours at about 180rev/min on a platform rotary shaker (Model TAITEC-R20 mini) at room temperature (25° +/-3°C). After equilibration, the samples were centrifuged using a centrifuge machine (model KUBOTA KN-70) and the supernatant were collected and refrigerated (4°C) prior to analyses of trace metals. Subsequent analyses were performed using Inductively Coupled Plasma - Atomic Emission Spectrophotometer (ICP-AES; Perkin Elmer Model OPTIMA 3000). To ensure precision and accuracy of the ICP-AES, a series of check standards were analyzed 3 times in the course of each analysis operation to ensure that drift do not occur. Each sample was analyzed three times by the ICP-AES and a mean concentration calculated by averaging. The relative standard deviation (RSD) for each sample was estimated on percent basis while RSD greater than 10 % were excluded from the subsequent data evaluation.

Data evaluation

Subsequent to the experimental phase and estimation of the amount of metal sorbed from the difference between the initial concentration and the portion remaining in solution after equilibration using Equation (1), the following data evaluations were carried on in order to adequately assess and discuss Mn and Zn adsorption on kaolinite under

the varied experimental conditions used in this study. Adsorption isotherms provide the adsorption behavior of soil or clay suspension at equilibrium with the contaminant solutions. In this study, adsorption isotherms were obtained by plotting the amounts of heavy metal species removed from solution (q in mg/g or ug/g of the clay sample) as a function of the equilibrium ion concentration in the filtrate solution (C_e in mg/l or ug/l). Naturally, different soils materials will show different capacities to adsorb heavy metals in response to their respective physico-chemical characteristics.

In adsorption-desorption studies, three major adsorption isotherm equations, which describe the relationship between the solution concentration and species adsorbed, are available from the literature, namely: the constant linear model, the Freundlich model and the Langmuir model (GRIFFIN AND SHIMP 1978; YONG ET AL., 1992; MAJONE ET AL., 1993; MOHAMED ET AL., 1994). However, the Langmuir model is often preferred according to FARRAH ET AL., (1980), as it allows the calculation of capacity values and the constant, which is considered to reflect the relative bonding strength.

The Langmuir model used in this study are given by the following equations:

$$q = K_L M/(1+KC_e) \qquad (2)$$
Langmuir Model

where q and C_e are as explained earlier; a and b are linear constants, M and K_L are the Langmuir model constants. The Langmuir equation (Equation 2) can be linearized as shown in Equation (3) below by plotting C_e/q as a function of C_e (Lamgmuir model):

$$C_e/q = C_e/M + 1/K_L M \qquad (3)$$

For the Langmuir model, constants M, as the adsorption maximum and K_L as a constant related to bonding energy of the adsorption to the adsorbent can be obtained from the intercept and slope of the linear graph respectively.

RESULTS AND DISCUSSION

Equilibrium Isotherms and Adsorption Capacities: Figure 2a and Figure 2b shows adsorption isotherm plots for Mn and Zn in
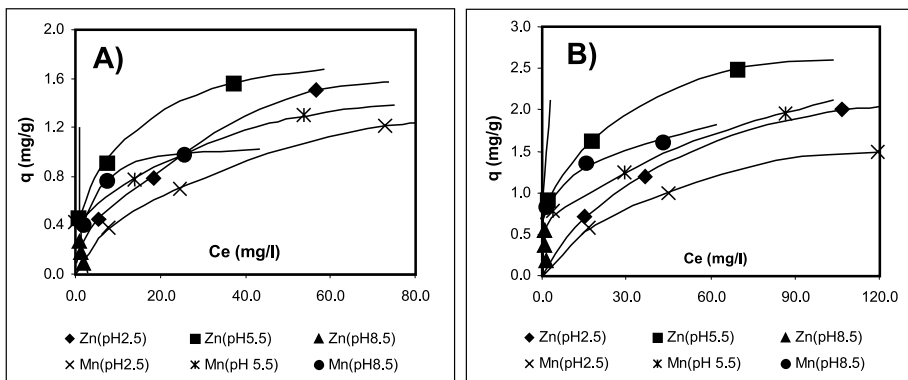
Figure 2. Sorption isotherms of Mn and Zn at SSR of 10ml/g (a) and SSR of 20ml/g (b) under single metal solution system.

single metal system at varied initial pH and under varied solution-solid ratio of 10 and 20 ml/g respectively, while Figure 3a and Figure 3b presents data for binary metal system under similar operating conditions.

As shown in Figure 2 and Figure 3, both Mn and Zn revealed similar adsorption characteristic under both single and binary metal systems.

The curves revealed more or less a two-stage trend as also recognized by KAN ET AL., 1994 in sorption of organic contaminants, involving a relatively fast initial adsorption followed by a gradual slower adsorption phase.

The first stage is characterized by physical adsorption (i.e. ion exchange) at the surface of the kaolinite functional group, which in this study accounts for about 70% and 80% adsorption of Mn and Zn respectively by the kaolinite samples. Such adsorption process is characterized by substitution of hydrogen ion in the outer sheet of the hydroxil group

of kaolinite as well as the negatively charged kaolinite surface as represented below:

$$nSi\text{-}OH + Me^{n+} \rightarrow (Si\text{-}O)n\text{-}Me + nH^+ \tag{6}$$

$$nSiO^- + Me^{n+} \rightarrow (Si\text{-}O)n\text{-}Me \tag{7}$$
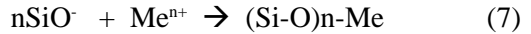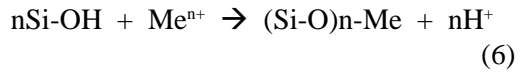
Kaolinite is a layered alumino-silicate mineral with the tetrahedral and octahedral sheets dominated by Si and Al respectively in a 1:1 ratio. Consequently, adsorption of metal cations seems to take place at the proton-bearing surface of the functional group (silanols and aluminols) exposed at the edge of the kaolinite sheets. This adsorption process/ mechanism is said to be favour by the low permanent structural charge and low CEC i.e. low base saturation (40 meq/kg) of kaolinite (DREVER, 1988, YAVUZ ET AL., 2003).

Nonetheless, the adsorption capacity (in mg/g) is much higher at SSR of 20ml/g compared to SSR of 10ml/g for both metals on one hand
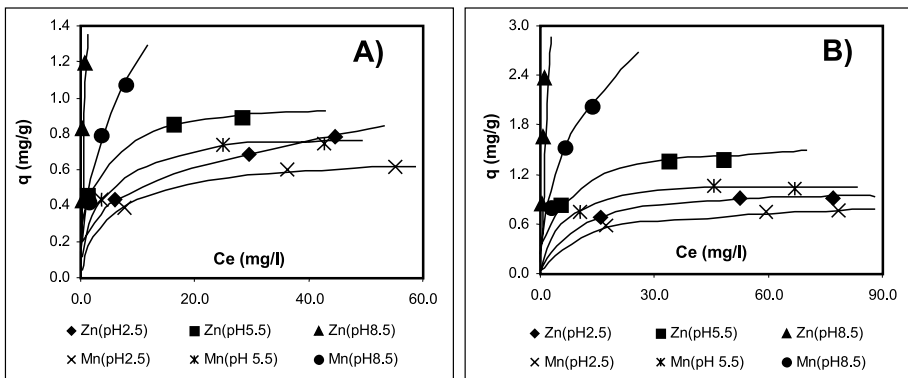

Figure 3. Sorption isotherms of Mn and Zn at SSR of 10ml/g (a) and SSR of 20 ml/g (b) under binary metal solution system.

Table 2. Profiles of the Langmuir constants with respect to pH and SSR variations

Experiment Condition			Kaolinite-Single Metal System				Kaolinite-Binary Metal System			
System	pH	SSR	M(mg/g)	M(mmol/g)	K(l/mg)	R^2	M(mg/g)	M(mmol/g)	K(l/mg)	R^2
Mn	2.5	10	1.70	0.031	0.03	0.98	0.68	0.012	0.18	0.99
Mn	5.5	10	1.38	0.025	0.22	0.96	0.75	0.014	0.52	0.99
Mn	8.5	10	1.10	0.020	0.32	1.00	1.59	0.029	0.26	0.99
Mn	2.5	20	2.25	0.041	0.02	0.99	0.84	0.015	0.13	1.00
Mn	5.5	20	2.11	0.038	0.08	0.97	0.98	0.018	0.65	0.98
Mn	8.5	20	1.67	0.030	0.44	0.99	3.41	0.062	0.11	0.98
Zn	2.5	10	2.15	0.033	0.04	0.95	0.89	0.014	0.14	0.99
Zn	5.5	10	1.71	0.026	0.26	0.99	0.93	0.014	0.74	1.00
Zn	8.5	10	0.05	0.001	-1.25	0.98	4.55	0.070	0.51	0.39
Zn	2.5	20	2.96	0.045	0.02	0.99	1.00	0.015	0.14	0.99
Zn	5.5	20	2.69	0.041	0.14	0.99	1.51	0.023	0.23	1.00
Zn	8.5	20	0.07	0.001	-1.18	0.79	14.68	0.225	0.18	0.24

and it is also higher for Zn compared to that of Mn on the other hand. While the former scenario could be attributed to quantity effect, characterized by saturation of the most active sites at high SSR, the latter could be attributed to differences in ionic radius as well as ionic potential of the two metals (see Table 1). Zinc is readily more adsorbed compared to Mn because of its smaller ionic radius and thus able to be more competitively fix into the pores of the kaolinite clay.

Generally the results of experimental adsorption measurements are usually expressed in the form of one or more equilibrium adsorption isotherm models. The Langmuir isotherm model was tested in this study due to its wider application in contaminant sorbent investigations. The Langmuir (1916 and 1918) isotherm theory assumes a mono-layer adsorption and that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in solution is constant at different solution concentrations.
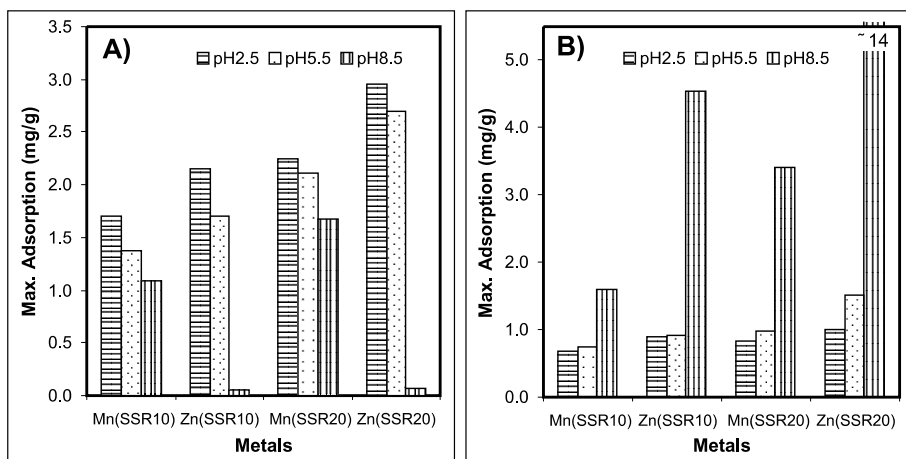
Figure 4. Estimated Langmuir maximum adsorption capacity (M, mg/l) for Mn and Zn at different SSR under (a) Single metal solution system and (b) binary metal solution system.

To quantify the adsorption capacity of the kaolinite for removal of Zn and Mn, typical Langmuir model was applied to the experimental data using to Equation 3, while the estimated Langmuir constants (M and K_L) there-from, are presented in Table 2 (above).

The correlation coefficients (R^2) for the linear regression were >0.90, which is an indication that the experimental data for both metals can be fitted into both Langmuir equation. As indicated in Table 2, sorption parameters for kaolinitic clay show variability between Mn and Zn ions, as reflected by their sorption maximum, Langmuir affinity constants. It can be seen that the maximum adsorption (M, mg/g) generally decreases with increasing pH for both Zn and Mn in single metal solution system, while increasing maximum adsorption with increasing pH is observed in the case of binary system (see Figure 4a and Figure 4b above).

The latter trend for the binary system can be attributed to the fact that the aluminol and silanol groups are more protonated at low pH and hence less available to retain or adsorb the metals. However, the trend in the single metal solution system can be attributed to the interplay of proton input at low pH, which causes hydrolysis of the exchangeable silicate base of the kaolinite (mostly Al in this case) on one hand and cation exchange reaction and in other words the removal of Zn and Mn from solution on the other hand. Therefore, it can be concluded that while hydrolysis and surface adsorption reaction characterized the adsorption mechanism in the single metal system, cation exchange with functional group characterized the adsorption process in the binary metal solution system.

Sorption of Zn and Mn as a function of pH: In soil/clay material pH plays a major role in the sorption of heavy metals as it directly controls the solubilities of metal hydroxides (APPEL AND MA, 2002) while increasing pH is said to increases cationic heavy metal retention to clay/soil surfaces via adsorption, inner-sphere surface complexation, and/or precipitation type reactions (McBRIDE, 1994; SPARKS, 1995; ZUHAIRI, 2003). However, the
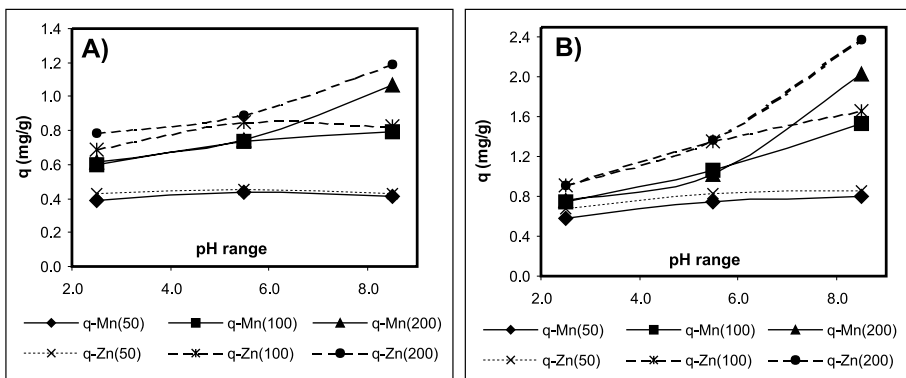
Figure 5. Variation of metal adsorption (q, mg/g) against pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under binary metal solution system.

effects of pH on the adsorption capacity of clay materials are said to depend on the respective isoelectric points (e.g. roughly 3.5 for kaolinite). This is due to the fact that at pH above the isoelectric point, the net negative charge and the ionic states of active sites and hydroxyl groups do promote exchange reactions (DREVER, 1988). For this study, the adsorption of Zn and Mn followed the expected trend of increasing metal uptake/ removal with increasing pH from 2.5 to 8.5, most especially under binary metal system (see Figure 5a and Figure 5b above).

However this trend is observable under single metal system only between pH 2.5 and   pH 5.5 and at low initial concentration (50mg/l) for both metals while the sorption capacities are greatly reduced at higher pH of 8.5 with higher metal concentration of 100 and 200 mg/l most especially for Zn (Figure 6a and Figure 6b).

This could be attributed to the co-precipitation of the metal hydroxides at higher pH (>6.5 for Zn and >8.0 for Mn), which implies that most of the metal ions rather than participated

in the exchange adsorption were precipitated from the solution as hydroxide at operating pH of 8.5 as represented below:

$$Me^{2+} + OH^- = Me(OH)^+ + OH^- = Me(OH)_2 \tag{8}$$
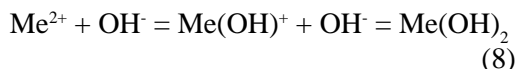
The above assertion is supported by the fact that metal concentrations in solutions are said to be unstable at higher pH due to precipitation of metal hydroxides (PLASSARD ET AL., 2000). Hence, the estimated percentage adsorption are >90% (at pH 8.5 for both metal) as presented in Table 3 imply a combination of those actually adsorbed and those precipitated directly out of the solution.

Therefore it can be concluded that the increasing adsorption capacity with pH under binary system is related to the influence of silanol and aluminol groups that are less protonated with increasing pH and thus more available for the adsorption of the metal ions. This is also supported by the fact that at higher pH active sites on the clay surface are more or less negatively charged and thus
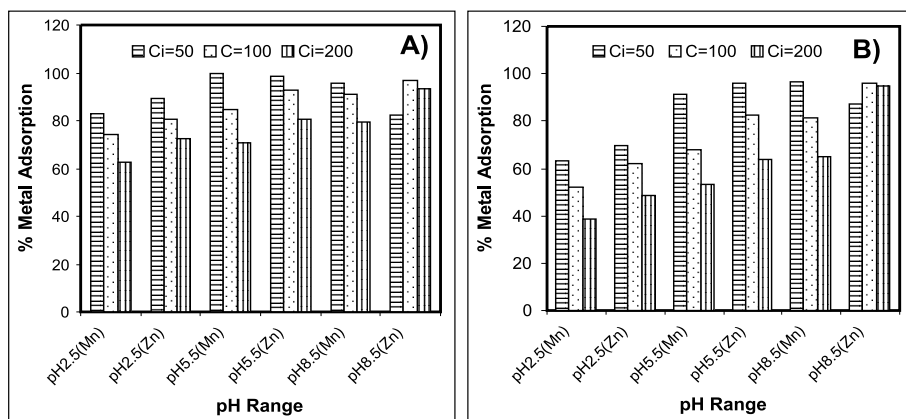
Figure 6. Variation of metal adsorption (q, mg/g) against pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under single metal solution system.

Table 3. Estimated percentage adsorption under varied metal concentration, pH and SSR

System	Ci	SSR	% Adsorption of Mn			% Adsorption of Zn		
Single System			pH=2.5	pH=5.5	pH=8.5	pH=2.5	pH=5.5	pH=8.5
	50	10	83.1	99.9	95.7	89.0	98.6	82.3
	50	20	63.3	91.1	96.8	69.8	96.2	87.1
	100	10	74.0	84.8	91.2	80.8	92.5	96.8
	100	20	52.3	68.1	81.2	61.9	82.4	96.0
	200	10	62.5	70.8	79.3	72.7	80.8	93.4
	200	20	38.5	53.1	65.1	48.5	64.1	94.8
Binary System			pH=2.5	pH=5.5	pH=8.5	pH=2.5	pH=5.5	pH=8.5
	50	10	83.5	92.2	96.8	87.7	97.3	99.5
	50	20	62.5	78.2	93.2	68.2	88.3	99.1
	100	10	62.4	74.7	95.6	69.9	83.8	99.6
	100	20	38.4	53.6	92.1	46.4	66.7	99.3
	200	10	52.7	62.2	93.1	63.7	75.8	99.4
	200	20	32.8	40.7	88.2	37.1	58.8	99.1

promote cation exchange reactions. However, the reduced capacity at pH of 8.5 under single metal system can be related to the instability of the respective metal ions in the reacting solution at such high pH. That is to say that at pH of ≥6.5 (for Zn) and ≥8.0 (for Mn), the respective metal ion species are in hydroxide form [$Zn(OH)_2$ and $Mn(OH)_2$], which are not readily available for adsorption/exchange process, hence the reduction in capacity at pH of 8.5 for both metals under the single metal solution system.

Sorption of Zn and Mn as a function SSR: The results of assessment of the influence of quantity of sorbent (kaolinite) on the adsorption capacities of kaolinite with respect to Mn and Zn are presented in Table 3. The observed general trend is decrease in adsorption capacity with increasing SSR, which implies considerable influence of sorbent mass due to surface area effect. Increase in SSR from 10ml/g to 20ml/g is accompanied by about 20-25%, 10-20% and <5% decrease in adsorption capacities at operating pH of 2.5, 5.5 and 8.5 respectively for both Zn and Mn and under both single

and binary metal systems. However, a closer look at Table 3 shows that the influence of sorbent mass is appreciable at pH of 2.5 with decrease in adsorption capacity of >20% for both metals and under both single and binary metal systems (when SSR was increased from 10ml/g to 20 ml/g). At pH of 5.5 there are relatively lower capacity reduction of about 10-20 % for both metals while at pH of 8.5 there are much smaller influence of <10 % and <5 % capacity reduction for Mn and Zn respectively. For Zn, this can be attribute to complementary co-precipitation of hydroxides at such alkaline pH of 8.5. Furthermore the above trend is supported by graphical presentation in Fig. 4a and b above, which indicates that the estimated maximum adsorption (M, mg/g) generally increases with decreasing sorbent mass for both metals and under both single and binary systems. This implies that smaller sorbent mass get saturated faster with respect to the adsorbed metal. In summary, it can be concluded that while there is obvious decrease in adsorption capacity with increasing SSR, a situation attributed to surface area effect, the influence is appreciable only at pH of less than 6.
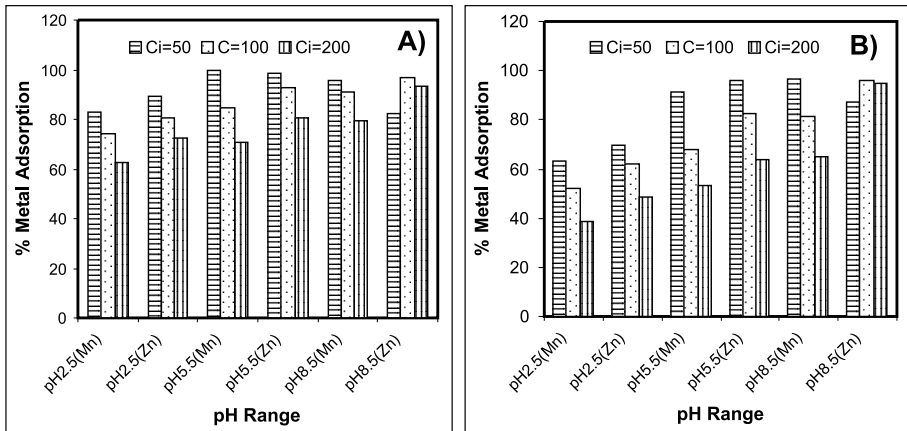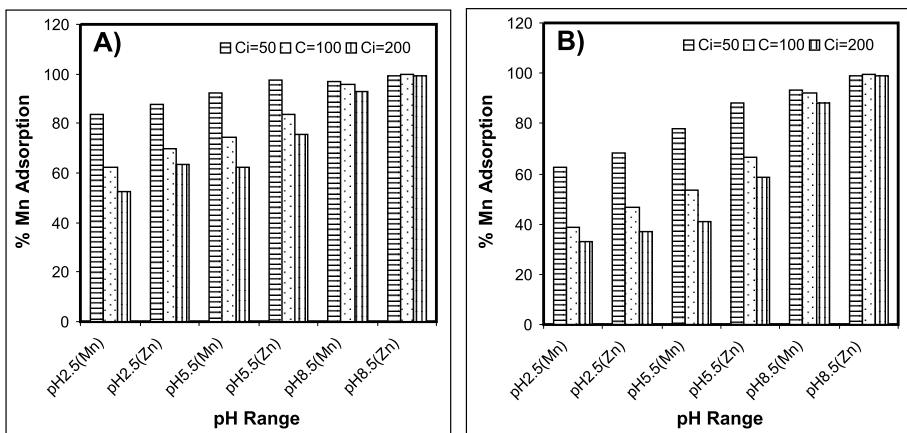
Figure 7. Variation of percentage metal adsorption with metal concentrations and pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under single metal solution system.

Effects of initial metal solution concentration:
The results presented in Table 3 also revealed the effects of initial metal concentration on the uptake or adsorption of Zn and Mn at different pH by kaolinite under both single and binary systems. From the results, it is clearly evident that adsorption capacity decreases with increasing initial metal concentrations. That is to say, higher percentage adsorptions were obtained at lower initial metal concentrations (50 mg/l) irrespective of the operating conditions under both single and binary systems (see Figure 7 and Figure 8).

On the average, the overall results show that increase in metal concentration from 50 to 100 mg/l and from 100 mg/l to 200 mg/l resulted in about 10 % reduction in adsorption capacity at pH of 2.5 and about 10-15 % reduction for pH of 5.5 under both single and binary systems.

Figure 8: Variation of percentage metal adsorption with metal concentrations and pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under binary metal solution system.

However, reduction of less than 2 % for pH of 8.5 especially under binary system is a confirmation of the fact that adsorption process at such higher pH range is a combination of exchange process and co-precipitation of metal hydroxides. Hence it can be concluded that at low concentrations metals are adsorbed by specific adsorption sites, while at higher concentrations, the specific sites are saturated and the exchange sites filled, resulting in lower effective adsorption. Nonetheless, the trend is clearly observable only for pH of 2.5 and 5.5 while at pH of 8.5 there was apparently very little or no influence on the adsorption of Zn and Mn and more especially under binary system.

Conclusions

In this study, experimental data of Zn and Mn adsorption on kaolinite at different metal concentration, varied pH and solution-solid ratio were studied. The equilibrium data correlated well with Langmuir isotherm model indicating positive influence of pH on the metal removal by kaolinite, while the estimated maximum adsorption (M, mg/g) generally increases with decreasing sorbent mass for both metals and under both single and binary systems which implies that smaller sorbent mass get saturated with respect to the adsorbed metal faster. However, increasing adsorption capacity with pH under binary system is related to the influence of silanol and aluminol groups that are less protonated with increasing pH and thus more available for the adsorption of the metal ions on one hand. On the other hand the reduced capacity at pH of 8.5 under single system can be related to the instability of the respective metal ions, whereby at pH of $\geq$6.5 (for Zn)

and $\geq$8.0 (for Mn) the respective metal ion species are in hydroxide form [$Zn(OH)_2$ and $Mn(OH)_2$] which are not readily available for adsorption/exchange process.

The overall evaluation and assessment of the data had shown that pH, solution-solid ratio, initial metal concentrations are critical factors in respect of Mn and Zn adsorption on kaolinite especially under the single metal solution system. However, in the binary metal system, physico-chemical characteristics of respective metals (i.e. ionic potential, ionic radius, ionic stability limit) seems to be exert some additional influence on the competitive preferential adsorption on metals on the sorbent kaolinite. In addition there is obvious decrease in adsorption capacity with increasing SSR, a situation attributed to surface area effect, however, this influence is appreciable only at pH of less than 6 with capacity reduction of about 10-20 % for both metals while at pH of 8.5 there is a much smaller influence of <10 % and <5 % capacity reduction for Mn and Zn respectively.

Furthermore, the higher percentage adsorptions at lower metal concentrations especially at pH of 2.5 and 5.5 under both single and binary systems imply that at low concentrations metals are adsorbed by specific adsorption sites, while at higher concentrations, the specific sites are saturated and exchange sites filled resulting in lower effective adsorption. On the average, the overall results show that increase in metal concentration from 50 to 100mg/l and from 100 to 200g/l resulted in about 10 % reduction in adsorption capacity at pH of 2.5 and about 10-15 % reduction for pH of 5.5 under both single and binary systems.

However, reduction of less than 2 % for pH of 8.5 especially under binary system is a confirmation of the fact that adsorption process at such higher pH range is a combination of exchange process and co-precipitation of metal hydroxides.

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