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## Suitability of Two Methods for Determination of Point of Zero Charge (PZC) of Adsorbents in Soils

Michael K. Miyittah<sup>a</sup>, Francis W. Tsyawo<sup>a</sup>, Kingsley K. Kumah<sup>a</sup>, Craig D. Stanley<sup>b</sup>, and Jack E. Rechig<sup>lb</sup>

<sup>a</sup>University of Cape Coast, Department of Environmental Sciences, Cape Coast, Ghana; <sup>b</sup>University of Florida, Soil and Water Science Department, Gulf Coast Research and Education Center, Wimauma, Florida, USA

### ABSTRACT

The points of zero charge (PZC) of manganese oxide (MnO<sub>2</sub>), titanium dioxide (TiO<sub>2</sub>), aluminum (Al) laterite, ferruginous (Fe) laterite, aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and a commercial activated carbon sample (AC001) were determined using acid-base potentiometric (PT) and mass titration (MT). The MT technique has been used extensively for carbonaceous materials but less for soils. In addition, little work has been done on the PZC of these metal oxides and carbon materials under similar experimental conditions concurrently. Our aim is to buttress the ease of MT usage over PT in routine laboratory analysis. The experimental PZC measured by acid-base potentiometric and mass titrations respectively were 4.97 and 4.11 for MnO<sub>2</sub>; 5.38 and 5.74 for TiO<sub>2</sub>; 4.19 and 4.08 for Al laterite; and 4.45 and 4.10 for Fe laterite. For Al<sub>2</sub>O<sub>3</sub> and activated carbon, mass titration gave 7.53 and 8.41 respectively. Calculated standard deviations between the means of PT and MT were less than 1, and Student's *t*-test at 95% confidence interval (CI) gave a *P* value of 0.135, suggesting that there is no significant difference between PT and MT and buttressing the reliability of the experimental procedures. In routine laboratory work, mass titration should be preferred for PZC measurement of (hydr)oxides and soil materials because it saves time.

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Acid-base potentiometric titration; adsorbent; mass titration; point of zero charge (PZC)

## Introduction

The pH of a suspension medium at which colloidal particles have no surface charge, the point of zero charge (PZC), is useful in understanding adsorption processes in environmental media. The determination and precision of surface characterization of ion-exchanging colloidal particles based on the PZC is critical for effective adsorption of contaminants.

Methods such as potentiometric titration (Van Raij and Peech 1972; Uehara and Gillman 1981), electrokinetic and electroacoustic mobility (Appel et al. 2003), and a number of techniques including mass titration (Noh and Schwarz 1989), ion adsorption (Balistreiri and Murray 1982), and scanning force microscopy (Eggleston and Jordan 1998) have been employed to measure the PZC of colloidal materials. In the operation of these techniques, their accuracy, cost, and simplicity are also weighed. For instance, a zeta potentiometer is expensive, although PZC values obtained are highly accurate. The acid-base potentiometric (PT) and mass titration (MT) methods are less expensive and may be suitable for repetitive laboratory work.

The PT measures surface charge (due to H<sup>+</sup>/OH<sup>-</sup> ion adsorption) as a function of pH at different electrolyte concentrations. The PZC is located at the point where charge is independent of electrolyte strength (Van Raij and Peech 1972) and coinciding with the pH at which surface charge is zero in cases of nonspecific ion adsorption. On the other hand, PZC measured by MT denotes the

point of equilibrium between protonation and deprotonation of surface sites predicated on the buffering behavior of colloidal particles (Noh and Schwarz 1989).

Despite the extensive studies on the PZC and surface charging characteristics of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and titanium dioxide ( $\text{TiO}_2$ ), their exact PZCs have not been established. Numerous authors (Bund and Thiemiig 2007; Ghosh et al. 2008; Li and Xu 2008; Kosma et al. 2009; Zhou et al. 2009) have reported different PZC and isoelectric point values (9.5, 7.9, 6.2, 8.5, 6.1 respectively) for  $\text{Al}_2\text{O}_3$  of distinct sources. Further, Kosmulski (2004) showed that PZC values reported for  $\text{TiO}_2$  between 1995 and 2003 ranged within 2.3–7.2. More recent studies (Lakshminarasimhan, Kim, and Choi 2008; Zhang et al. 2009) also showed different isoelectric point (IEP) values (6.9 and 4.8 respectively) for synthetic  $\text{TiO}_2$  (anatase). Limited PZC/IEP data, however, are available on laterite soils. Maiti et al. (2007) used laterites as adsorbent for removal of at least 94% arsenite, in which case the PZC of laterite was found to be 7.49. Sarkar et al. (2006) and Vithanage et al. (2012) have also measured widely varying PZC values (3.98 and 8.72 respectively) for laterite soils.

Noh and Schwarz (1989) used MT for materials that exhibit ion-exchange properties. Previous studies have shown that there is a correlation between ion-exchange capacity and net surface charge (Anderson 1975). Soils have been known to possess electrical surface charges and the mechanism by which soils developed surface charges has been an active area of research in recent years. The presence of surface charge controls a wide range of physicochemical reactions in soils, particularly the retention of exchangeable cations and anions (Gillman 2007).

However, MT has been used extensively for routine laboratory work for PZC determination of activated carbon but little information is available for soils, although the original method included metal hydr/(ox)ides, which are abundant in soils. The main advantages of the MT appear to be simple data of pH vs mass content and that it does not need addition of acid or a base to the system in evaluating the surface charge. This simple approach may save time for routine laboratory determination of PZC. Further, little information is available regarding using the methods under similar experimental conditions and concurrently with PT and for using MT for soils samples. The objectives of the study were the following: (1) to determine the PZC of manganese oxide ( $\text{MnO}_2$ ),  $\text{TiO}_2$ , aluminum (Al) and iron (Fe) laterites (soils from Ghana),  $\text{Al}_2\text{O}_3$ , and a commercial activated carbon sample based on acid-base potentiometric and mass titration data; and (2) to suggest the relative application of the two techniques for routine laboratory work.

## Materials and methods

### Samples

The  $\text{Al}_2\text{O}_3$  (neutral, activity grade I) and  $\text{TiO}_2$  (minimum purity 99.45%) were commercial samples from Woelm Pharma GnbH and Co. (Eschwege, Germany) and British Drug House (BDH) Chemicals Ltd. (Poole, UK) respectively. Manganese oxide and laterite samples were obtained from Nsuta mines (Tarkwa, Western Region, Ghana) and Bensworth Brick Factory (Cape Coast, Central Region, Ghana) respectively. To obtain uniformity of results, all samples were sieved using 250-micron mesh to obtain uniform particle sizes. The pH of the samples was determined in 1:2 solid/solution ratio (Miyittah and Inubushi 2003).

The elemental compositions of the samples were analyzed by means of instrumental neutron activation analysis. The overall advantage of the method using neutron activation analysis has been enumerated by other researchers (Kucera 2001; Tandoh et al. 2009). However, a short description of the procedure is discussed here. In brief, samples were analyzed at Ghana Atomic Energy Commission for the determination of elemental concentrations. The samples were crushed into finer particles suitable for irradiation. About 100 mg of samples were weighed into ultraclean polyethylene films. The samples were wrapped and heat sealed, then packed into 7.0-mL volume polyethylene irradiation vials, which were capped and heat sealed. Standard reference materials

obtained from US National Institute of Standard and Technology were treated in the same way as the samples for quality assurance and quality control. The samples were irradiated in the inner irradiation site of the Ghana Research Reactor 1 facility operating at half power (15 kW) at a neutron flux of  $5.0 \times 10^{11}$  neutrons/cm<sup>2</sup> s. The scheme and characterization of the irradiation was chosen based on the sample matrix and the half-life of the elements of interest. Counting of induced radioactivity was performed by PC-based gamma-ray spectrometry. The gamma-ray product radionuclides were qualitatively identified by the energies emitted and then quantitatively analyzed by converting the counts area under the photo peaks using MAESTRO-32 software analysis package.

Specific surface area was determined by the Blaine test and then converted to the Brunauer-Emmett-Teller (BET) equivalent (Brunauer, Emmett, and Teller 1938; Potgieter and Strydom 1996). In brief, samples were ground into fine particles after passing through a sieve of 0.251  $\mu$ m mesh in order to obtain uniform size and porosity. A sample mass of 2.75 g was weighed and then poured into the test cell, and standard reference material number 114 was treated in a similar manner for quality control and quality assurance. A fixed volume of air is allowed to pass through a sample bed of defined porosity at a decreasing rate, which is controlled and measured by the movement of oil in a manometer. The time required for the movement of oil is measured. The specific surface area is calculated in square meters per kilogram by multiplying values in cm<sup>2</sup>/g by a factor of 0.1. A more detailed description of the actual computation is given by Iyer and Stanmore (1995).

### ***Acid-base potentiometric titration***

The acid-base potentiometric titration method used was described by Uehara and Gillman (1981). Briefly, a colloidal material of 4 g was weighed into 20 ml of 0.002 M potassium chloride (KCl) electrolyte and was equilibrated for more than 18 h through horizontal shaking. The initial pHs of suspensions were varied using 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) while the blank suspensions contained no acid or base.

The pH of suspensions was measured after each subsequent addition and equilibration with 0.1 M (1 ml) KCl and 2 M (0.5 ml) KCl. The amount of potential-determining ions (H<sup>+</sup>/OH<sup>-</sup>) adsorbed is estimated as the pH difference between the blank and acid/base titrated suspensions at each different KCl concentrations.

### ***Mass titration***

The mass titrations procedure as carried out in this study have been outlined by Noh and Schwarz (1989). The advantage of the titration method is that the procedure is simple and requires only a pH meter. The equilibrium experimental setups were conducted at room temperature ( $25 \pm 2$  °C) with 0.01 M KCl as background electrolyte to mimic soil solution composition and to control solution ionic strength. In brief, the experiments were carried out using an increasing mass of the colloidal materials, which were added to a known volume of the electrolyte solution in a centrifuge tube and allowed to equilibrate. A previous study using 24 h equilibration time suggested that an equilibration of about 14 h is enough to achieve optimal mixing and sorption of ions into colloidal materials. A known volume of nitrogen gas was also allowed to pass through the reacting solutions to prevent anaerobic conditions. The pH of each solution was measured and the value of PZC was determined on the curve of pH vs percentage mass to volume ratio of colloidal suspensions.

## **Results and discussion**

### ***Physical properties and elemental composition***

The physical properties and elemental composition of the samples are presented in Table 1. The laterite soils, MnO<sub>2</sub> and TiO<sub>2</sub>, are acidic with pH values < 6 whereas the activated carbon is alkaline.

**Table 1.** Some physical properties and elemental composition of samples.

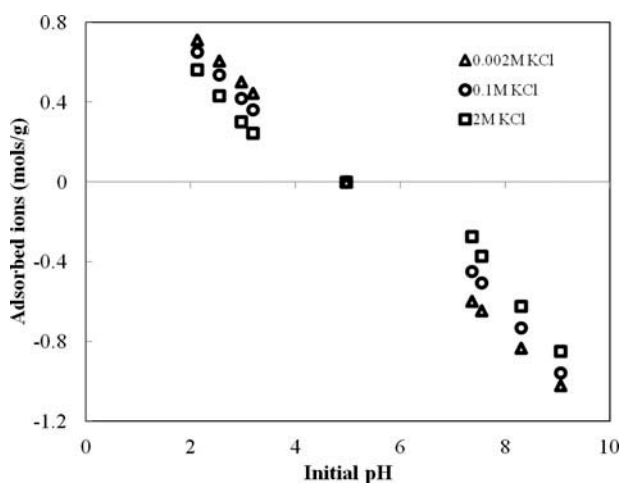
Parameter (units)	Value					
	MnO <sub>2</sub>	TiO <sub>2</sub>	Al laterite	Fe laterite	Al <sub>2</sub> O <sub>3</sub>	Activated carbon
pH (1:2)	4.48	5.93	4.42	4.49	7.00	8.26
BET surface area <sup>a</sup> (m <sup>2</sup> /g)	339.99	NA	319.99	299.46	294.24	NA
Elemental composition (%)						
Fe	0.0002	0.0002	11.0670	81.4213	0.0005	—
Al	0.8124	0.5955	70.3810	7.1811	96.8130	—
Si	0.0002	0.0005	0.0008	0.0025	0.0019	—
Ti	3.1759	97.3534	1.2553	0.2767	0.0517	—
Mg	—	0.2046	4.2318	0.5872	2.1054	—
Cu	0.1413	0.0120	0.0006	0.0011	0.0001	—
V	0.0489	0.0066	0.0301	0.0173	0.0016	—
Mn	95.6002	0.0054	0.0367	0.0233	0.0003	—
Ca	1.1530	0.1520	0.3720	0.1490	0.0300	—
Na	0.1350	0.0117	0.0330	0.0257	0.0510	—
K	0.0087	0.0033	0.0410	0.6375	—	—

<sup>a</sup>Calculated from Blaine surface area (Potgieter and Strydom 1996). BET: Brunauer-Emmett-Teller (Brunauer, Emmett, Teller 1938). Note. NA, not available.

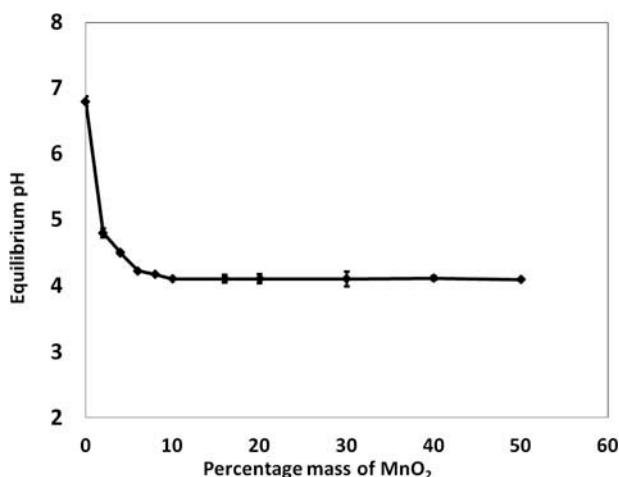
Also, Al<sub>2</sub>O<sub>3</sub> has a neutral pH, as indicated by the producer. The samples (oxides and Al/Fe laterites) have specific surface areas ranging from 294 to 339 m<sup>2</sup>/g, and comparatively have values greater than some tropical and subtropical soils (Maiti et al. 2007; Zhang et al. 2011). In addition, elemental analyses show relatively greater composition of major cations with respect to oxides and laterites.

### PZC of MnO<sub>2</sub>

The results of potentiometric and mass titration methods for MnO<sub>2</sub> are shown in Figures 1 and 2 respectively. The graph of amount of H<sup>+</sup>/OH<sup>-</sup> adsorbed versus pH showed a common intersection point (CIP) for the three KCl concentrations and the corresponding pH (4.97) of this point is the PZC of MnO<sub>2</sub>. On the other hand, the curve of pH against percentage mass fractions of MnO<sub>2</sub> sample for mass titration leveled off at an equilibrium pH of 4.11 to give the PZC. Despite a relatively greater PT experimental value, both results are consistent with the range (4.0–5.3) reported in literature (Kosmulski 2009a). Tan et al. (2008) reported that MnO<sub>2</sub> mostly has very low PZC.



**Figure 1.** Amount of H<sup>+</sup>/OH<sup>-</sup> adsorbed as a function of the pH of MnO<sub>2</sub> in different KCl electrolytes at room temperature (25 ± 2 °C); PZC = 4.97.

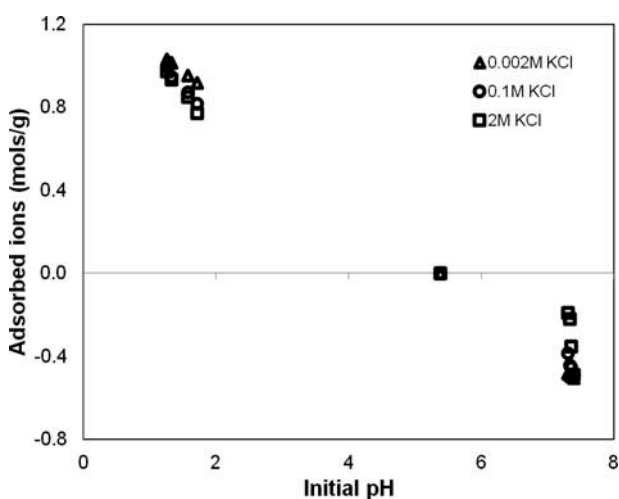


**Figure 2.** Effect of percentage mass of MnO<sub>2</sub> on the equilibrium pH of suspension at 25 ± 2 °C (PZC = 4.11). Error bars indicate standard deviation of the mean (±SD), with some bars not visible on the graph.

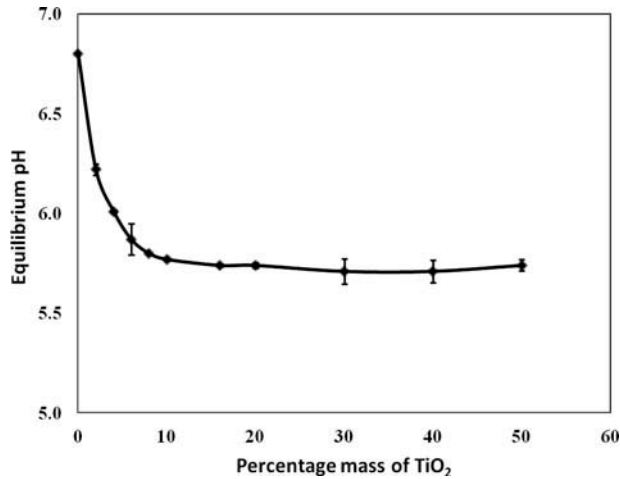
### PZC of TiO<sub>2</sub>

Figure 3 shows the PT data for TiO<sub>2</sub> suspensions. The experimental PZC of TiO<sub>2</sub> is 5.38, the pH at which no ions (including H<sup>+</sup>/OH<sup>-</sup>) are adsorbed. This data support the findings of Fedkin et al. (2003). On the other hand, the MT (Figure 4) PZC is 5.74, comparatively greater than the value measured by PT in this study. The two values lie within the range (5.8 ± 0.59) of recommended PZC values compiled for Aldrich rutile (Kosmulski 2009b) but are greater than the value (5.1) reported by Zhou et al. (2009) and less than IEP (6.2) reported by Preocanin and Kallay (2006) for a commercial sample. The differences may arise from factors including the nature of the samples, aging, sample preparation, purity, experimental protocols, and the data analysis, which are known to significantly influence the PZC of metal (hydr)oxides (Mustafa et al. 2002).

In Figure 3, the clustering of adsorption data points at very low (1–2) and high pH (7–8) may be indicative of the greater stability and stronger buffering capacity of TiO<sub>2</sub> colloids at the respective pH of suspension.



**Figure 3.** Amount of H<sup>+</sup>/OH<sup>-</sup> adsorbed as a function of the pH of TiO<sub>2</sub> in different KCl electrolytes at room temperature (25 ± 2 °C); PZC = 5.38.

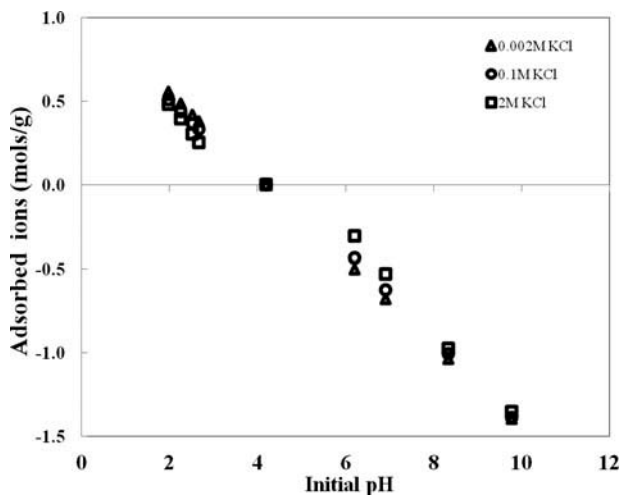


**Figure 4.** Effect of percentage mass of TiO<sub>2</sub> added on the equilibrium pH of suspension at room temperature  $25 \pm 2$  °C; PZC = 5.74. Error bars indicate standard deviation ( $\pm$ SD) of the mean, with some of the bars not visible on the graph.

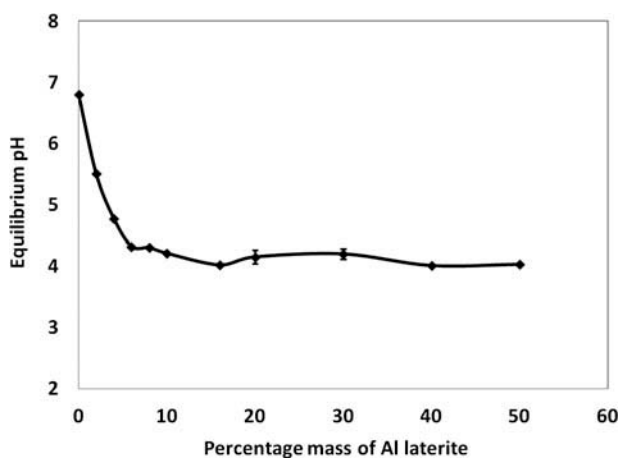
The MT data (Figure 4) show a relatively constant equilibrium pH after 10% mass of the colloids. The resistance to change in pH is due to the buffering behavior of variable charge colloids in electrolyte suspension (Noh and Schwarz 1989): Increased amounts of the colloidal material provides a greater buffering capacity due to increased frequency of adsorption sites to adsorb protons that would otherwise lower the suspension pH at PZC.

### PZC of Al laterite

The values in Figures 5 and 6 show PT and MT data for Al laterite. The results of the PT showed PZC at 4.19 (Figure 5). The MT data (Figure 6) show fluctuating equilibrium pH about a mean of 4.08, representing the PZC at mass ratios greater than 10%. The fluctuation of the equilibrium pH could be due to exchange of protons and anions on the surface by the presence of residual and legacy



**Figure 5.** Amount of H<sup>+</sup>/OH<sup>-</sup> adsorbed as a function of the pH of aluminum laterite in different KCl electrolytes at  $25 \pm 2$  °C; PZC = 4.19.

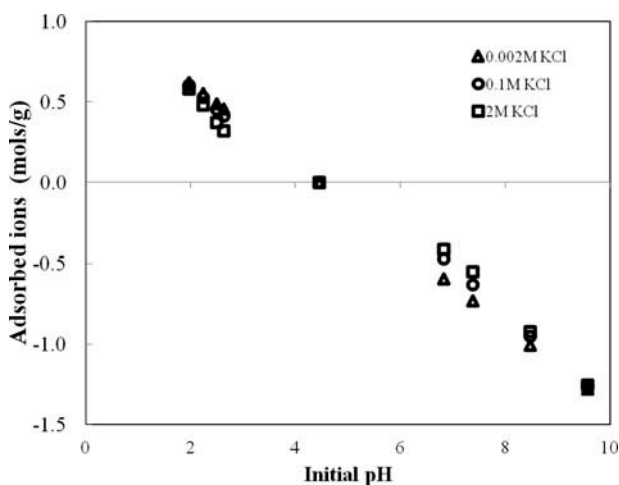


**Figure 6.** Influence of percentage mass of aluminum laterite on the equilibrium pH of suspension in KCl electrolyte at  $25 \pm 2$  °C; PZC = 4.08. Error bars indicate standard deviation of the mean ( $\pm$ SD), with some of the bars not visible on the graph.

functional groups on the surface of the laterite. The experimental PZC values are, however, very close and comparable to the value (3.98) reported by Sarkar et al. (2006), but dropped widely below values (7.49 and 8.72 respectively) suggested by Maiti et al. (2007) and Vithanage et al. (2012).

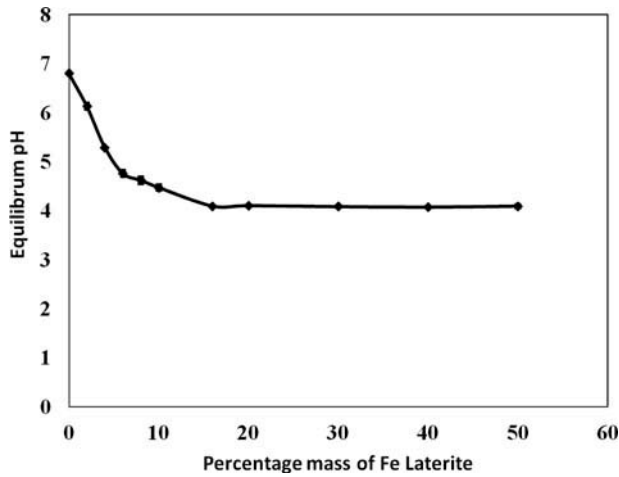
### PZC of Fe laterite

Acid-base potentiometric titration data show PZC of Fe laterite coinciding at 4.45 (Figure 7) and the MT PZC is 4.10 (Figure 8). The PZC values are slightly greater than Al laterite PZC indicated earlier. Stable pH was reached at about 16% mass/suspension volume loading of Fe laterite in contradiction with the case of  $\text{TiO}_2$ . This disagrees with the original studies by Noh and Schwarz (1989) that showed 10% mass of colloid is sufficient to stabilize the equilibrium pH. The explanation may be that Fe laterite elemental contents may induce differential functional groups of significant charges and



**Figure 7.** Influence of varying pH values at different KCl concentrations on the number of moles per gram of  $\text{H}^+$ / $\text{OH}^-$  adsorbed onto Fe laterite at  $25 \pm 2$  °C; PZC = 4.45.



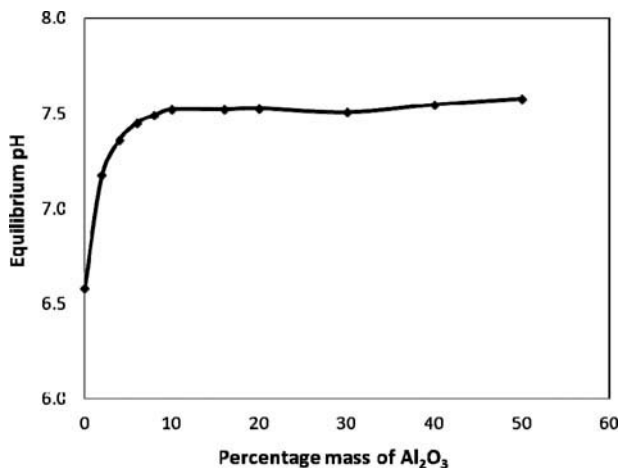


**Figure 8.** Equilibrium pH of Fe laterite / 0.1 M aqueous KCl suspension as a function of the percentage mass of colloid loaded at  $25 \pm 2$  °C; PZC = 4.10. Error bars indicate standard deviation ( $\pm$ SD) of the mean, but some of the bars not visible on the graph.

thus a greater mass portion is required to offer the number of surface adsorption sites that will protonate excess  $H^+$  and stabilize the suspension pH. The fluctuating equilibrium pH of Fe laterite may also be due to presence of other functional groups induced from weathering of parent materials forming the laterite.

### **PZC of $Al_2O_3$**

The MT data for  $Al_2O_3$  (Figure 9) shows PZC of 7.53. The value lies within the range of 5.49–9.6 reported by Kosmulski (2009a). The experimental PZC is much closer to the value (7.2) reported by Todorovic, Milonjic, and Dondur (2004) and falls outside the range of values (8.5–9.2) reported by Goldberg et al. (2005).



**Figure 9.** Influence of percentage mass of  $Al_2O_3$  colloids on the equilibrium pH of suspension at room temperature ( $25 \pm 2$  °C); PZC = 7.53. Error bars indicate standard deviation ( $\pm$ SD) of the mean, but bars are not visible on the graph.

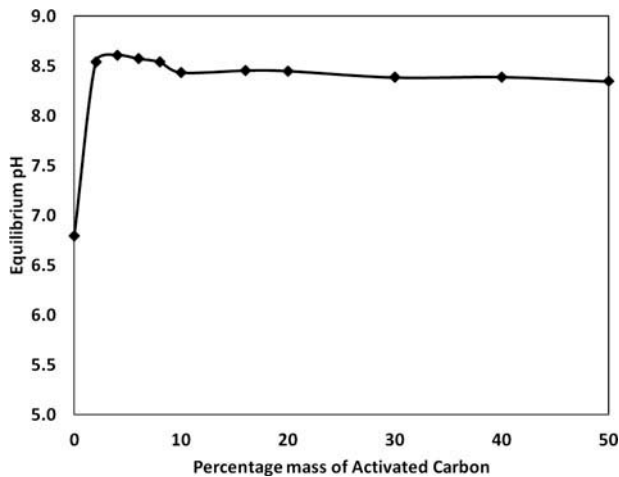
### PZC of activated carbon (AC001)

The mass titration of activated carbon gave PZC value of 8.41 (Figure 10). The methods and conditions of preparation as well as the materials used influence the PZC and adsorption behavior of activated carbons (Ekpete and Horsfall 2011). Thus diverse PZC values are reported in literature for various activated carbons. In addition, activated carbons also have different kinds of surface functional groups (carboxyl, hydroxyl, pyridine, pyridine-N-oxide, etc.) that significantly influence surface charging. For example, the MT curve shows greater initial equilibrium pH of suspensions between 2% and 10% mass of activated carbon, suggesting degrees of surface charges to overcome before reaching equilibrium. The MT equilibrium pH therefore may suggest protonation and deprotonation of surface sites relative to different functional groups in the presence of electrolytes.

### Comparison of the two methods

The summary of PZC data obtained by the two techniques (Table 2) shows mean PZC values with relatively small standard deviations for the samples. The standard deviations are comparably less than those found in literature (0.42–1.17) for  $\text{TiO}_2$  (Kosmulski 2009b), thus reflecting greater similarity between the two methods under similar conditions. In addition, statistical analysis using Student's t-test at 95% CI gave a *P* value of 0.135 (data not shown), suggesting clearly that there is no significant difference between the two methods and thus buttressing the reliability of the MT procedure.

The intent of different electrolyte concentrations used was to mimic natural aqueous systems but the background ionic strength for MT may be too high. Preocanin and Kallay (1998) stated that the PZC equals the IEP only at low electrolyte concentrations. Steric competition for surface sites due to greater ionic concentrations shifts the equilibrium towards deprotonation of surface sites. This may



**Figure 10.** Influence of percentage mass of activated carbon on the equilibrium pH of suspension at room temperature ( $25 \pm 2^\circ\text{C}$ ); PZC = 8.41. Error bars indicate standard deviation ( $\pm\text{SD}$ ) of the mean, but bars are not visible on the graph. SD, standard deviation.

**Table 2.** PZC of adsorbents measured by two techniques in KCl electrolyte at  $25 \pm 2^\circ\text{C}$ .

Sample	PT PZC	MT PZC	PT $[\text{H}^+] \ 10^{-6} \ \text{M}$	MT $[\text{H}^+] \ 10^{-6} \ \text{M}$	$[\text{H}^+] \ \text{Difference} / 10^{-6} \ \text{M}$	Mean PZC ( $\pm\text{SD}$ )
$\text{MnO}_2$	4.970	4.110	10.7	77.624	$6.69 \times 10^{-5}$	$4.540 \pm 0.61$
$\text{TiO}_2$	5.380	5.740	4.17	1.819	$2.35 \times 10^{-6}$	$5.560 \pm 0.25$
Al laterite	4.190	4.080	6.46	83.170	$1.86 \times 10^{-5}$	$4.140 \pm 0.08$
Fe laterite	4.450	4.100	3.55	79.432	$4.40 \times 10^{-5}$	$4.280 \pm 0.25$
$\text{Al}_2\text{O}_3$	ND	7.530	—	0.029	—	—
Activated carbon	ND	8.410	—	0.004	—	—

Notes. PT, potentiometric titration; MT, mass titration; ND, not determined; SD, standard deviation.

explain why only TiO<sub>2</sub> with probably extensive numbers of adsorption sites has greater MT than PT experimental PZC value, because a greater amount of H<sup>+</sup> that may lower the equilibrium pH has been protonated. Conversely, lower proton adsorption capacities of MnO<sub>2</sub>, Al, and Fe laterites mean that all available surface sites were saturated by electrolyte ions and protons in solution lowered the pH at PZC. The natural pH values of the materials therefore lie between the equilibrium pH at 0% mass/suspension volume ratios and the PZC of the materials. Also, the samples except TiO<sub>2</sub> are natural samples, which may have different types of functional groups that influence the PZC and adsorption behavior of the respective materials.

The general explanation is that the MT is very responsive to electrolyte concentration, because extra colloidal mass added to the solution tended to stabilize the pH. Similar to PT, MT accuracy has also been considered very dependent on the purity (acidic or basic traces) of samples (Kosmulski 2009a); although the fraction of impurities can be easily determined (Preocanin and Kallay 1998). Mass titrations are easier and simpler because only one electrolyte concentration datum is required to reach equilibrium point for PZC. Mass titration would be preferred for routine laboratory PZC measurement because rapid equilibrium stabilization may be reached if the sample is relatively free of acidic or basic functional groups.

## Conclusions

The suitability of mass titration of colloidal suspensions for PZC determination of metal oxides and soils was shown. Experimental PZC values based on acid-base potentiometric and mass titrations are similar with standard deviations of less than one. This indicates that the techniques are similar and valid for (hydr)oxides, soil materials, and activated carbons. However, the mass titration procedure is simpler and would be rapid in stabilization curves if the sample is devoid of several acidic or basic functional groups, obviating the need for expensive zeta potentiometer measurements in routine laboratory PZC determination. Further studies with other oxides and soils relative to geologic conditions may be important to ascertain the environmental and agronomic significance of several soil types.

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