



# **Point Zero Charge Determination and Fluoride Adsorption on Natural Red Ash (Metal Oxide)**

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## **Authors' contributions**

*This work was carried out in collaboration between both authors. Author LAD designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author DAC managed the analyses of the study and managed the literature searches. Both authors read and approved the final manuscript.*

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## **ABSTRACT**

The PZC is essential parameter for the characterization of certain materials used for the treatment of organic or inorganic wastes in the environment, particularly from waste water and industrial sludge. Potentiometric titration and batch experimentation method was used to determine PZC value and type of adsorption isotherm behavior observed. Red ash is the natural metal oxides collected from the rift valley of Ethiopia which have PZC values of 3.35 for 0.5g, 1g and 1.5g adsorbent dose studied. On the adsorbent surface, monolayer and homogeneous adsorption process of fluoride observed. Therefore, based on the interest of the researcher and the adjustment of the pH of red ash solution might used for the treatment of ionic wastes.

**Keywords:** Red ash; PZC; adsorption; fluoride; potentiometric titration; isotherm model and batch experimentation.

## **1. INTRODUCTION**

The point of zero charge is a fundamental description of a mineral surface, and is more or less the point where the total concentration of

surface anionic sites is equal to the total concentration of surface cationic sites, and most (but not all) of the sites are as the neutral hydroxide.

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The surface of solids, principally, of the mineral (hydr) oxides, is charged in electrolytic solutions, and this charge depends on the pH of the solution. The pH at the charge takes a zero value is defined as PZC [1,2]. At this pH, the charge of positive charge surface sites equal to that of negative ones. It is very important parameter to characterize the protonation-deprotonation behavior of various type of solids i.e. Inorganic Colloids, organic Colloids, microbes and Mineral surfaces. Mainly that of (hydr) oxides, in aqueous suspensions, the determination of point of zero charge assists to know whether solids act as (CEC) exchange of cation or (AEC) exchange of anion at specific pH above or below the PZC. It is used to characterize materials used for adsorbent in various processes [3,4,5].

There are few methods used to determination PZC of solid material such as potentiometric titration (pt), salt addition method or immersion methods (SA or IT) .mass titration (MT), potentiometric mass titration (PMT), differential mass titration (DMT),and Zeta potential technique (is electric point of material). In this experiment, we have used potentiometric titration method and Batch experimentation method. Particularly, in Ethiopian Rift Valley most people faces serious public fluorosis problem due to exposures of fluoride from drinking water and different food chains. These study open new insight for our society how they treat fluoride contaminated water bodies before use for different purpose using locally available red ash. The objective of this study is (1) To determine the point zero charge of metal oxides (red ash) and (2) To determine the adsorption behavior of red ash using common isotherm models.

Generally we can calculate the value of  $x$  at equilibrium in batch experiment, using the following equation [6].

$$X = \left( \frac{C_i - C_f}{X_{mass}} \right) (\text{volume of solution}) \quad (1)$$

Where  $X$  is the fluoride concentration on red ash at equilibrium.

$C_f$  is the fluoride concentration in solution at equilibrium.

$C_i$  is the intial concentration of fluoride before adsorption process.

$X_{mass}$  mass of red ash used for the adsorption process.

Different scholars conduct research about the point zero charge of soil with different measurement methods [7], electro coagulation precipitate from iron anode point zero charge [8],

comparison of different methodology using standard substrate goethite and pyrolusite [9], the point zero charge of maple saw dust, wood ash, peat moss, compost and alge [10] vermicompost, oxides, hydroxides, organic and inorganic colloids and mineral surfaces.

## 2. MATERIALS AND METHODS

### 2.1 Materials

#### 2.1.1 Equipments

Polyethylene plastic bags were used for collecting red ash samples. Mortar and pestle were used for grinding and homogenizing the samples. Weighing balance (Sartorius Group, Model VIC 303, USA), with precision of 0.001 g was used for weighing of samples. Muffle furnace (Audiotronics, Wagtech International Ltd., UK) was used for fusion of samples within nickel crucibles (50 mL). A pH/ISE meter (Orion model, EA 940 Expandable Ion Analyzer, USA) equipped with combination fluoride ion selective electrode (Orion Model 96-09, USA) was employed for the determination of fluoride in the samples and standards solutions. A pH meter (HANNA instrument, HI 9025, Malaysia) equipped with glass electrode was used to measure the pH values of sample solutions. Borosilicate volumetric flasks (1000 mL) were used for preparation of 8 M NaOH solution. Hot plate with magnetic stirrer was used for dissolution of soluble fluoride in the sample and fusion cake. Measuring cylinders (Duran, Germany), pipettes (Pyrex, USA); micropipettes (0.5-10.5  $\mu\text{L}$ , 1-100  $\mu\text{L}$ , 100-1000  $\mu\text{L}$  Dragonmed, Shangai, China) were use during measuring of different volumes of samples solutions and fluoride standard solutions. 50 mL plastic centrifuge tubes were used for the storage of sample solutions. Plastic funnels were also used for sample filtration. Different types of volumetric flasks (50, 100, 500 and 1,000 mL) and 50 mL plastic beakers were used sample and standard preparation during the determination of fluoride.

#### 2.1.2 Chemicals and reagents

The analytical grade reagents were used in the analysis. De-ionized water was used throughout the experiment. Nitric acid (69%, Research Lab Fine Chemical Industries, Mumbai, India) was used for cleaning purpose and sodium fluoride (99%, Analar, NaF, BDH Chemicals Ltd, England) used to prepare standard solutions.

The pH standard buffers (pH of 4, 7 and 10) were used for pH calibration purpose. Sodium chloride (Fisher Scientific UK), glacial acetic acid (100%, Sigma-Aldrich Laborchemikalien, Germany), trisodium citrate (BDH Laboratory Supplies, poole, England), and EDTA (Scharlau Chemie S.A., Barcelona, Spain) were used to prepare Total Ionic Strength Adjustment Buffer (TISAB) solution. Sodium hydroxide (Scharlau Chemie S.A., Sentmenat, Spain) solution was used to dissolve samples homogeneously before alkali fusion and also used to adjust the pH of TISAB solution to pH of 5.3. Hydrochloric acid (36%, Fisher Scientific UK Limited) was used for neutralization of dissolved fusion cake. TISAB was prepared by dissolving 58 g sodium chloride, 57 mL glacial acetic acid, 7 g of trisodium citrate and 2 g EDTA in 500 mL de-ionized water into 1000 mL beaker and its pH was adjusted to 5.3 with 5 M sodium hydroxide. The solution was then transferred to 1000 mL volumetric flask and diluted to the mark with de-ionized water.

## 2.2 Methods

### 2.2.1 Potentiometric titration

Red ash (0.5 g, 1 g & 1.5 g) in an electrolytic solution containing 0.1 N  $\text{NaNO}_3$  in 50 ml of distilled water was added to carry out three potentiometric titration. The experiment was performed under  $\text{N}_2$  gas and the suspension was equilibrated for about one hour's to reach an equilibrium pH value. Then small amount of 1N NaOH was added to make the pH around 10 and initial pH was recorded after 15-20 minute.

Then the solid suspension was titrated with 0.1N  $\text{HNO}_3$ , using 665 dosimat. The pH of each suspension was measured with 1 minute time interval using a digital pH meter standardized by buffers.

### 2.2.2 Batch experimentation

Five polyethylene volumetric flasks with a volume of 250 ml was prepared and added 0.5g of red ash in each flask and 5ppm, 10ppm, 15ppm, 20ppm and 25ppm fluoride concentration was also prepared and added to the corresponding flasks. Then it was equilibrated for about one hour. Then, after equilibrium established the fluoride concentration was measured using pH/ISE meters. Deionized water was used throughout the experimentation.

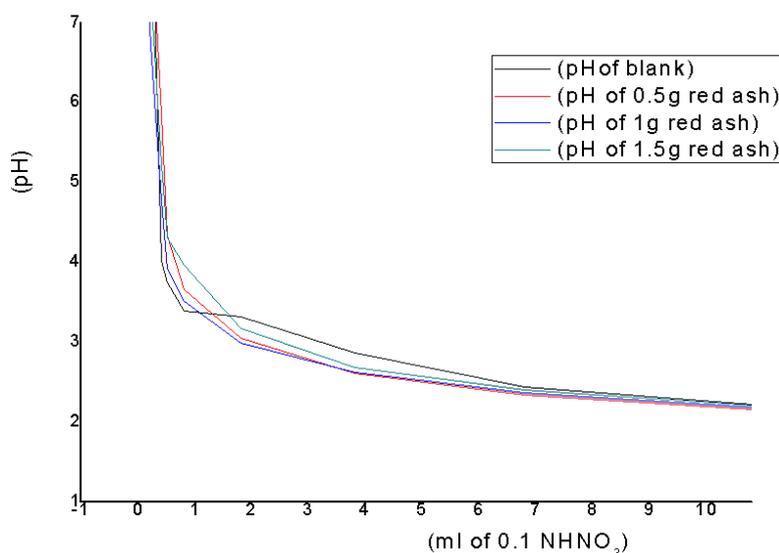
## 3. RESULTS AND DISCUSSION

As indicated in the curve (volume of 0.1 N  $\text{HNO}_3$  against pH of solution), the point zero charge of red ash was determined with three different mass of adsorbent and 0.1 N  $\text{HNO}_3$  as titrant. This experiment results with a value of 3.35 point zero charge pH values of 0.5g, 1g and 1.5g adsorbent dose. The PZC result is comparable with different scholars reported for various materials and season i.e. [1] using different methods on oxisol (3.4-4.4) and ultisol (2.3-3.7), [4] reported hydroxide/oxihydroides (3.6) which is predominantly positively charged surface, [3] reported the point zero charge of different organic materials which is predominantly cationic surface.

The point zero charge of red ash exists in acidic range which show that the surface can be used for the treatments of anionic effluent/waste sludge from the environment (soil and water) and industrial wastes. In general, the solution of red ash at pH values below  $\text{pH}_{\text{PZC}}$  is AEC, above the  $\text{pH}_{\text{PZC}}$  CEC and at  $\text{pH}_{\text{PZC}}$  both AEC and CEC sorption occurs simultaneously. Fig. 1 also indicates the adsorption capacity in relation to adsorbent dose.

**Table 1. Potentiometric titration data for red ash with 0.1N  $\text{HNO}_3$**

Blank		0.5 g Red Ash		1 g Red Ash		1.5 g Red Ash	
ml of 0.1M $\text{HNO}_3$	pH	ml of 0.1M $\text{HNO}_3$	pH	ml of 0.1M $\text{HNO}_3$	pH	ml of 0.1M $\text{HNO}_3$	pH
0	10.48	0	9.68	0	9.3	0	9.13
0.209	9.10	0.218	8.34	0.264	6.72	0.247	7.40
0.405	4.01	0.390	5.84	0.399	4.77	0.388	5.22
0.505	3.74	0.533	4.33	0.553	3.92	0.538	4.31
0.801	3.39	0.801	3.66	0.829	3.51	0.837	3.97
1.805	3.32	1.802	3.04	1.853	2.99	1.852	3.17
3.801	2.86	3.857	2.61	3.812	2.62	3.852	2.68
6.801	2.44	6.806	2.34	6.854	2.36	6.852	2.4
10.808	2.22	10.827	2.16	10.812	2.18	10.588	2.2



**Fig. 1. Potentiometric titration curve of blank and (0.5g, 1g and 1.5g) of red ash with the titrant (volume from 0 ml-10.8 ml) of 0.1N HNO<sub>3</sub>**

Determination of isotherm model

$$X = \left( \frac{C_i - C_f}{X_{mass}} \right) \text{volume of solution}$$

$$X_1 = \frac{(5 - 2.85) \text{ mg/L}}{0.5 \text{ g}} (0.25 \text{ l}) = 1.075 \text{ mg/g,}$$

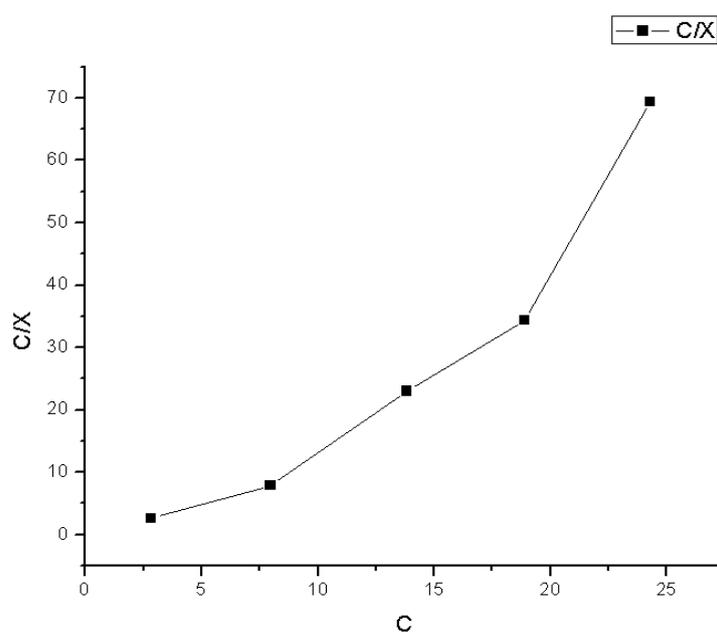
$$X_2 = \frac{(10 - 7.97) \text{ mg/L}}{0.5 \text{ g}} (0.25 \text{ l}) = 1.015 \text{ mg/g}$$

$$X_3 = \frac{(15 - 13.8) \text{ mg/L}}{0.5 \text{ g}} (0.25 \text{ l}) = 0.6 \text{ mg/g,}$$

$$X_4 = \frac{(20 - 18.9) \text{ mg}}{0.5 \text{ g}} (0.25 \text{ L}) = 0.55 \text{ mg/g}$$

$$X_5 = \frac{(25 - 24.3) \text{ mg}}{0.5 \text{ g}} (0.25 \text{ L}) = 0.35 \text{ mg/g}$$

X<sub>mass</sub> = 0.5g red ash and volume of solution 0.25 L in which batch experiment was done.



**Fig. 2. Sorption process of fluoride on the surface of red ash**  
 $C/X = 2.97326C - 12.87134$ ,  $R^2 = 0.87439$ , indicates good fitting which is an important isotherm model to discuss the results

**Table 2. Fluoride adsorption on red ash surface at equilibrium in the batch experiment**

X (mg/g)	C (ppm)	C/X (g/L)
1.075	2.85	2.65
1.015	7.97	7.85
0.6	13.8	23
0.55	18.9	34.36
0.35	24.3	69.43

This result fits the Langmuir isotherm model. As indicated in the Fig. 2, the adsorbent surface used in the study is homogenous and monolayer adsorption of fluoride observed in this research conducted. There is no transmigration between the fluoride ions on the red ash which strengthen the report done by [11]. Once the maximum adsorption of fluoride on the surface of red ash occurred at equilibrium and no further adsorption favored in the system. However, fluoride desorption favored instead of adsorption after equilibrium established. In general the adsorption process of fluoride is influenced by contact time, initial dose of fluoride and the pH as indicated by [12].

#### 4. CONCLUSION

The point zero charge of red ash is 3.35 for the mass of 0.5g, 1g and 1.5g adsorbent dose in the study. Therefore, Red ash below the pH of 3.35 is used for fluoride mitigation from different water body. The adsorption process forms homogenous monolayer of fluoride on red ash surface. Natural red ash is anion exchanger and it can be also cationic exchanger through the adjustment of the pH of the given adsorbent. Researchers may use red ash as ionic substrate removal from waste water/industrial sludge.

#### DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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