

## DETERMINATION OF $Zn^{2+}$ ION ADSORPTION CAPACITY OF MONTMORILLONITE CLAY

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**ABSTRACT:** Drinking water contaminated with heavy metals is a serious problem in Sri Lanka in the recent years. Therefore to provide safe drinking water, it is compulsory to remove heavy metals and we should have to use water filters. montmorillonite, which is a mineral from the smectite group and considered as a great candidate as an adsorbent material for heavy metal ions such as  $Zn^{2+}$  in aqueous solution due to its typically elevated surface area, high availability and low cost. In this study, removal of heavy metals from water was investigated by studying adsorption of them onto montmorillonite clay material. Properties of the clay have been stabilized by a thermal treatment. The montmorillonite clay material was characterized by applying different techniques of Fourier transformation infrared spectroscopy and also the surface properties of the clay material, Scanning electron microscopy were also used to study the morphology of the samples. The obtained results showed that the raw clay has a maximum removal efficiency of 97.84 %. Among the heat treated samples, the sample heat treated at 400 °C showed a maximum removal efficiency of 96.72 %. Further, the removal efficiency continuously decreased with the increasing treatment temperature above 400 °C.

**Keywords:** Adsorption, Montmorillonite, Heavy Metals

### INTRODUCTION

Water intended for human consumption is universally expected to be absence of turbidity, color, odors and disagreeable or detectable tastes. Currently, Sri Lanka faces lot of challenges to provide safe drinking water mainly due to high hardness and heavy metal contamination in drinking water [1]. The removal of pollutants from water is an important process and is becoming more important with the rapid growth of industries, municipal waste and agricultural runoff. It is critical due to discharge of heavy metals to water systems, which supply water intended for domestic use that causes serious environmental and health problems [2]. Zinc is a heavy metal and exists as  $Zn^{2+}$  ions [2]. Heavy metal Zn should be removed from drinking water when present in excess of WHO Limit of 5ppm (5mg/l) [3].

Due to high cost and lack of expected filtering function in existing filtering materials, considerable attention has recently been devoted to study of different types of locally available, low cost raw materials as adsorbing materials for water filters. One of such kind of material is montmorillonite clay. Clay minerals are readily available, inexpensive materials and can offer a cost-effective alternative to existing adsorbents. Porous structure and high surface area of the clay provide benefits in the adsorption of heavy metals [4]. However, in general, most of the clay minerals tend to have a negative charge resulting from the substitution of silica cation ( $Si^{4+}$ ) by aluminum cation ( $Al^{3+}$ ) in the clay sheet structure. This phenomenon (referred to as isomorphous substitution) produces the capacity in clay sheets

to hold positive charges. Therefore clay can be used as effective adsorbent for removal of heavy metals with positive charge such as  $Zn^{2+}$  [5].

The present study deals with the development of montmorillonite clay as a filtering material for water filters to remove heavy metal ions. In order to improve the stability of the clay, a heat treatment was introduced by heating clay samples in the temperature range 350 - 550 °C. The effect of heat treatment was evaluated by studying  $Zn^{2+}$  removal efficiency of montmorillonite clay treated at different temperatures.

## 2. METHODOLOGY

Montmorillonite clay material from Mannar district, Sri Lanka was selected to be used as an adsorbent. The clay material was washed thoroughly with distilled water, until visible pieces of plant materials and sand particles vanish. Then the sample was completely dispersed in water for a sufficient time. Thereafter, the clay fraction was separated by using standard centrifuging at 1000 rpm for 20 min. Heat treatment of 6g of montmorillonite clay was heat treated in a crucible using a muffle furnace in temperature range of 350 - 550 °C for 1 hour (Carbolite CWF 1300). All the heat treated samples were crushed to powder form and weighed. The heat treated clay samples were characterized by different techniques. Surface morphology of the adsorbent was studied by Scanning Electron Microscopy (SEM) (EVO LS 15) together with Energy Dispersive X-ray (EDX) spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) analysis (Nicolet 6700) was used to determine the functional groups present in samples.

Analytical grade metal salt  $ZnCl_2$  was used without further purification. Stock solution (1000 mg/l) of Zn (II) was prepared in distilled water. The stock solution was diluted as required to obtain standard solution containing 10 ppm (10 mg/l). Adsorption measurements were made by a batch technique at room temperature ( $25 \pm 1^\circ C$ ). The batch mode was selected because of its simplicity and reliability. In all experiments 0.1 g of montmorillonite clay material were weighed in a bottle flask (50 ml capacity). The required volume (20 ml) of the adsorptive compound solution ( $ZnCl_2$  - 10ppm) was added at 25 °C. The solutions were then stirred vigorously for 30 minutes.

The agitation speed was kept constant for each sample to ensure equal mixing. After completion of a pre-selected stirred time, the suspensions were allowed to settle for two hours to reach the equilibrium. After equilibration, the solutions were centrifuged, then the supernatant solution from suspended particles was used to analyze the trace metal by Atomic Absorption Spectrophotometer (AAS). Also initial 10 mg/l (10ppm)  $ZnCl_2$  solution was

analyzed by atomic absorption spectrophotometer (Analytik jena). The amount adsorbed was determined by analyzing the metal content before and after each experiment.

### 3. RESULTS AND DISCUSSION

#### 3.1. Scanning Electron Microscope Analysis

Results of the SEM Analysis for montmorillonite clay showed in figure A, B, C and D. A,C- Layered structure of raw clay sample, B,D- structure of heat treated (400°C) clay sample. The SEM images reveal that after the heat treatment, the amount of flakes on the clay surface has been increased. Also the surface area of the clay material has been increased.

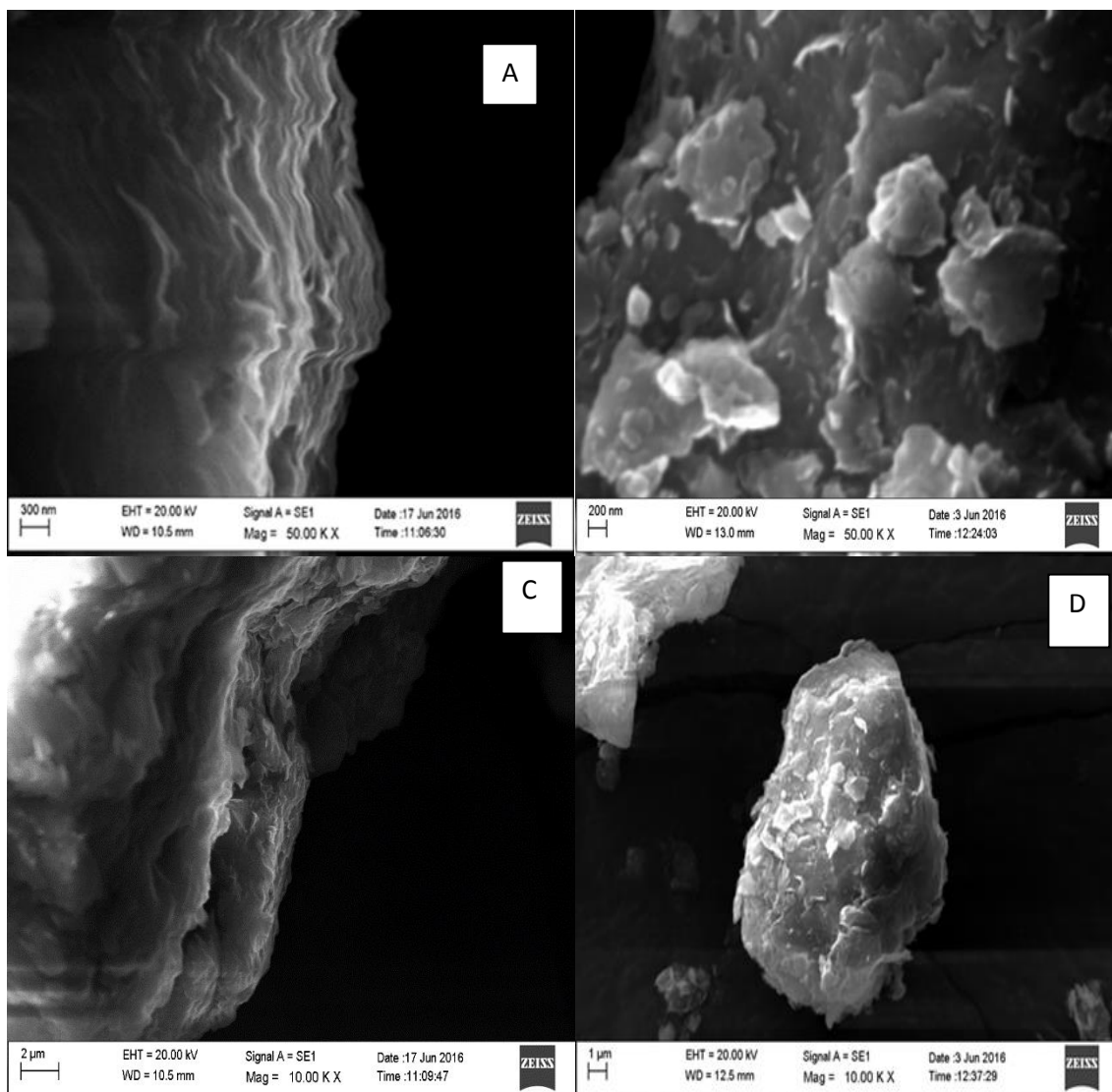


Figure 1: SEM images of raw and heat treated (400°C) montmorillonite clay

Results of the EDX Analysis for montmorillonite clay showed in figure 2. It indicates that after the adsorption procedure zinc ion has been intercalated to the clay surface.

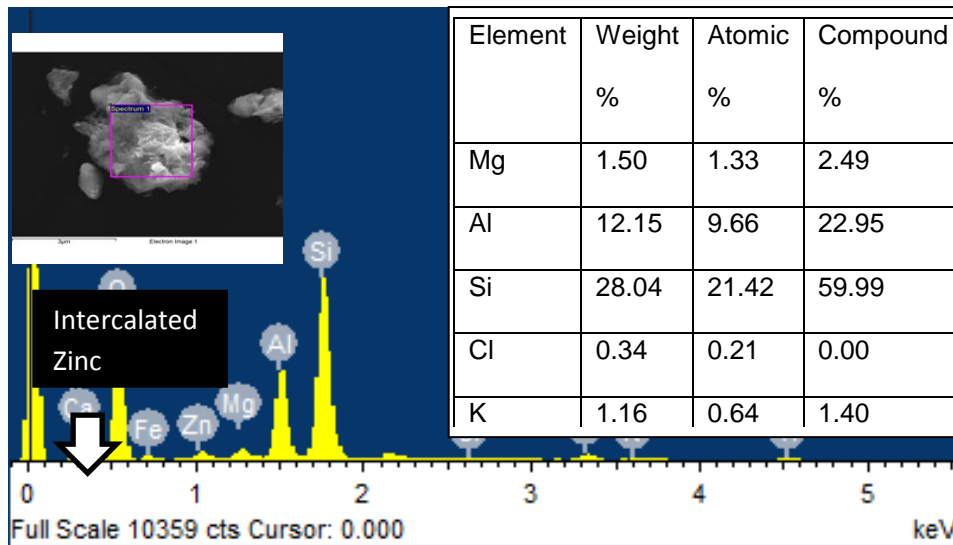


Figure 2: Energy dispersive x-ray spectroscopy for Zinc ion adsorbed clay

The results of the FTIR analysis for raw and heat treated montmorillonite clays are shown in figure 3 and 4, respectively. According to the literature [6], FTIR absorption peaks of montmorillonite clay were identified and almost all the FTIR absorption peaks of raw and heat treated montmorillonite were according to the reference with closely related wave numbers. Therefore it can predict that the heat treatment will not affect functional groups or bonds in the material. But with the increasing of treatment temperature, the intensity of the absorption peaks decreased. Especially the absorption peaks of second order HOH bending and vibration of OH decrease of OH groups in clay layers with increasing temperature.

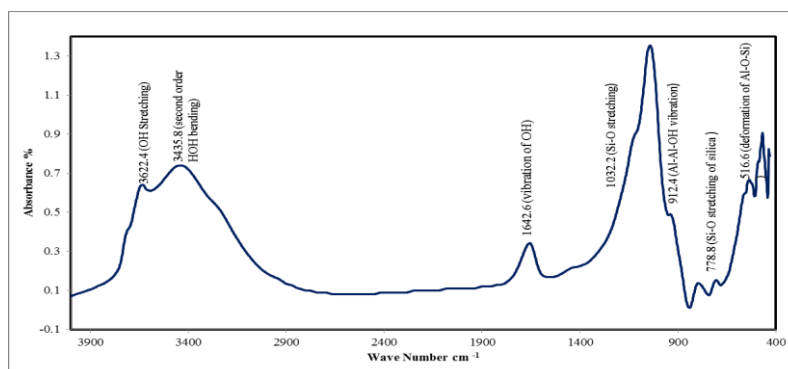


Figure 3: FTIR analysis for the raw sample of Montmorillonite

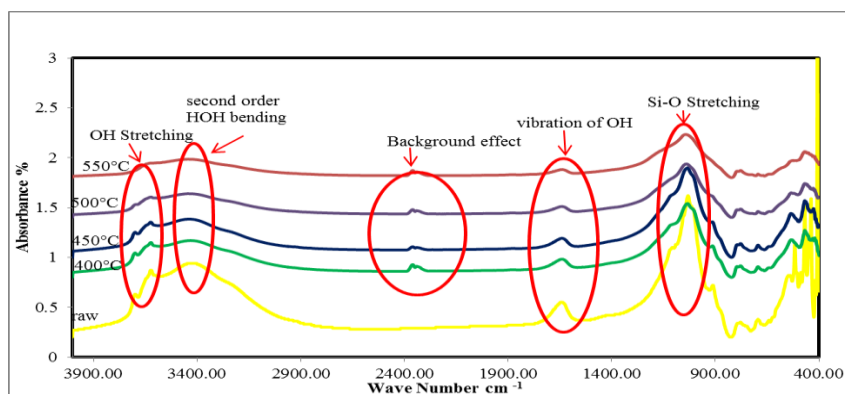


Figure 4: FTIR analysis summary of Montmorillonite clay

Zn<sup>2+</sup> ion adsorption capacity of raw and heat treated montmorillonite were determined by AAS. Table 1 shows the measured final concentrations of Zn<sup>2+</sup> ions (in ppm) present in the adsorptive solutions. The percentage removal of Zn<sup>2+</sup> ions (%) are given by adsorbent and Zn<sup>2+</sup> ion concentration on adsorbent (mg of metal ion/g of adsorbent).

Table 1: Percentage removal of Zn<sup>2+</sup> ions (%) by adsorbent and Zn<sup>2+</sup> ion concentration on adsorbent (mg of metal ion/g of adsorbent)

Sample	Raw Clay 150°C	Heat treated clay-350°C	Heat treated clay-400°C	Heat treated clay-450°C	Heat treated clay-500°C	Heat treated clay-550°C
Initial concentration of Zn <sup>2+</sup> (ppm)	10.0000	10.0000	10.0000	10.0000	10.0000	10.0000
Final concentration of Zn <sup>2+</sup> (ppm)	0.2159	0.3839	0.3277	0.7914	1.2970	1.3400
Percentage removal (%)	97.84	96.16	96.72	92.08	87.03	86.60
Zn <sup>2+</sup> concentration on adsorbent (mg)	1.95	1.92	1.93	1.84	1.74	1.73

of metal /of adsorbent)						
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At temperature 150° C, the purified and vacuum dried raw montmorillonite clay sample indicates the maximum percentage removal of Zn<sup>2+</sup> ion with the value of 97.84 % by adsorption.

Figure 5 shows the percentage removal of Zn<sup>2+</sup> ion by heat treated Montmorillonite Clay, sample heat treated at 400°C, showed the maximum percentage removal of 96.72%. With further increase of treatment temperature gradually decreased the percentage removal. But removal efficiency of all heat treated samples was less than the raw clay sample.

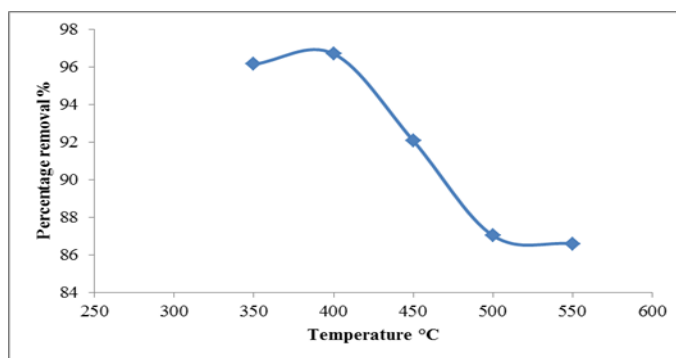


Figure 5: Percentage removal of Zn<sup>2+</sup> ion by heat treated Montmorillonite Clay

Even though raw clay has high removal efficiency of heavy metals from water, it cannot directly use for purification applications because of some practical issues such as the risk of clay material can also be dissolved and added into drinking water.

Therefore before applying to the water purification applications, the raw clay should be subjected to a thermal treatment, which will not affects or alters the structure or properties of the raw clay to stabilize the material. With high temperature heating water removed by evaporation and all the organic material that incorporated with the clay material can be removed as carbon dioxide. Therefore dehydroxylation can occur [7]. So most probably heat treatment up to 400°C will be more effective for Montmorillonite clay to be used as effective adsorbent.

Figure 6 shows the Zn<sup>2+</sup> ion concentration on heat treated Montmorillonite clay (mg of metal ion/g of adsorbent). Sample heat treated at 400°C showed the maximum value of 1.93 (mg of metal ion/g of adsorbent) and with increasing treatment temperature, Zn<sup>2+</sup> ion concentration on clay sample gradually decreased. Zn<sup>2+</sup> ion concentration on clay sample of all heat treated samples was less than the raw clay sample.

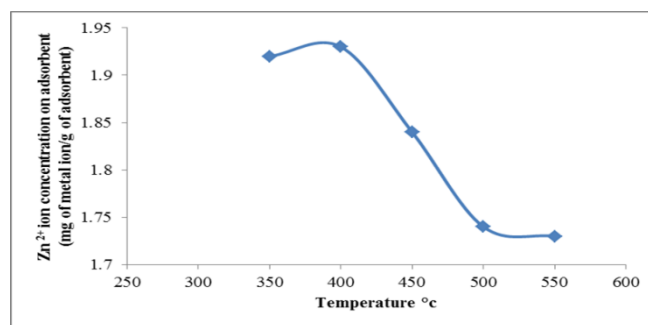


Figure 6: Zn<sup>2+</sup> ion concentration on heat treated Montmorillonite clay (mg of metal ion/g of adsorbent)

#### 4. CONCLUSION

Montmorillonite clay is a potential and promising adsorbent for removal of heavy metals from aqueous solution due to their structure and high cation exchange capacity. Atomic absorption results indicate that raw montmorillonite clay with maximum removal efficiency of 97.84% found to be effective, low cost and locally available raw material for water purification applications to remove heavy metals from drinking water. But due to some practical issues such as dissolution of clay material in drinking water due to instability of clay, raw clay cannot be directly used and heat treatment was introduced to stabilize the clay. The clay heat treated at 400°C shows the removal efficiency of 96.72% and represents a cheap and viable option for the removal of low concentration metal ions from the polluted water.

#### 5. REFERENCES

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