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Cost-effective and non-toxic method to modify clay to increase the hardness adsorption capacity of clay

Bingun T Perera[1], RMH Rajapaksha[2], RCW Arachchige[3], IRM Kottegoda[4]
[1, 3] Materials Technology Section, Industrial Technology Institute, Colombo 07, Sri Lanka
[1, 2] Department of Chemistry, Faculty of Science, University of Kelaniya, Dalugama, Kelaniya, Sri Lanka

Abstract
Hardness of the drinking water has been considered as one of the major causes of Chronic Kidney Disease of unknown etiology (CKDu) in the Northern part of Sri Lanka. The present study was ultimately aimed at removing the water hardness using clay as a cheap renewable adsorbent. The hardness adsorption capacity of raw clay was increased by treating clay with $NaCl_{(aq)}$. The present methodology was proposed due to low toxicity, low cost, and high commercial availability of clay and NaCl. Clay samples were collected from Deniyaya Sri Lanka. The particle size reduction of clay was achieved by treating raw clay with $NaCl_{(aq)}$ at different durations at 303K temperature. During the study, adsorption of Ca^{2+} and Mg^{2+} (the water hardness) was analyzed using EDTA titration following the standard APHA method protocols. The highest adsorption was observed at 33 hours of treatment. XRD spectrum of raw clay showed a sharp strong diffraction peak of the sample at $2\theta = 22.45°$ which is a characteristic peak of Kaolinite-2M with 97.1% abundance. XRD spectrum of treated clay showed considerable changes that the clay consisted of kaolinite (44%) and Orthoclase (56%). It was noted that with the increasing of treating time, although the particle size decreased, after some point small clay particles tend to aggregate again reducing cation adsorption capacity. Treated clay enabled to reduce the total hardness by 96% of the tested water obtained from CKDu prevalent area.

Keywords: Adsorbent, capacity, chronic kidney disease, XRD, hardness of water

1. Introduction

Chronic Kidney Disease of Unknown Etiology (CKDu) is an evolving health problem in some low and middle-income nations such as El Salvador, Egypt, Cuba, Sri Lanka, Bangladesh, and India [1]. In Sri Lanka, Anuradhapura and Polonnaruwa districts along, there are around 33000 CKDu patients identified in the last decade. In Sri Lanka, the North Central Province (NCP) is an endemic area for CKDu [2]. Some areas outside the NCP, but geographically adjacent were later identified as having a similarly high prevalence of CKDu. District such as Anuradhapura (Divisional Secretary Division (DSD-all), Polonnaruwa (DSD-all), Kurunegala (DSD-Polpithigama and Giribawa), Ampara (DSD-Dehiattakandiya), Trincomele (DSD- Padavi Siripura), Badulla (DSD- Mahiyanganaya and Redeemaliyadda), Mullaitivu (DSD-Welioya), Vavuniya (DSDVavuniya and Vavuniya South) and Matale (DSD- Wilgamuwa) are at a high risk of CKDu [2]. CKDu's risk factors are being male farmers, using agrochemicals (pesticides and fertilizers), living in a hot environment, drinking hard water, and having a family history of CKD [3,4].

CKDu is characterized by a gradual decrement of glomerular filtration rate (GFR) over time due to structural and functional defects of the kidney [5]. Morphology changes in kidneys are often referred to as tubulointerstitial nephritis or tubulointerstitial disease, but major glomerular lesions are often found, such as global glomerulosclerosis and signs of glomerular ischemia [6]. Interstitial fibrosis can be observed even at the initial stage of CKDu. Fibrosis in arteries also observed in some patients [7]. When a biopsy of CKDu patients was observed under an electron microscope, interstitial inflammation was localized to fibrotic areas, glomerular basement membrane thickening, and cell debris were recorded between capillaries of the Bowman capsule [8].

Given its unknown origin, CKDu has spurred a variety of investigative efforts in recent years. Several research studies have been completed to identify risk factors. But, up to the present date, no specific reason has been proven scientifically to be the exact cause [9]. Hypnotized causative agents of CKDu are pesticides, heavy metals, water hardness, fluoride ion, and cyanobacterial toxins [10].

Water hardness has gained special attention as surface and groundwater samples from CKDu affected areas have shown elevated levels of hardness [11–13]. The primary causes of water hardness are soluble polyvalent metallic ions from carbonate stones, sedimentary rock as well as soil drainage. Calcium and magnesium, the two main ions are available in many frequently found sedimentary rocks such as limestone and chalk. Even though the body can regulate the blood calcium level to some extent, the high calcium concertation itself can damage the kidney over a long time, but high blood calcium can lead to nephrocalcinosis and such an effect is not observed in CKDu patient's kidney biopsies [7]. According to Rajapakse S, water hardness increment results in increased nephrotoxicity by fluoride ions [2]. The absence of CKDu in fluoride-rich areas indicates that fluoride ion alone cannot cause CKDu and a combination of high water hardness and high fluoride level is more significant [14], therefore the development of a proper technique hardness removal has utmost important.

The national response to the prevention of CKDu is mainly

focused on providing the affected populations with clean water. Methods such as rainwater harvesting systems, reverse osmosis (RO) systems, and electrocoagulation-based systems have been introduced for water supply at the village level. Individual water filter units at the household level are also common [15]. The main limitation of the above-mentioned techniques is the high implementation and maintenance costs associated with them and indicate the need for a cost-effective method to clean water. Clay-based filters provide a low-cost alternative.

Clay, a small particle, found naturally on the surface of the earth composed mainly of silica, alumina, water, and weathered rock [16]. Clay particles show its use as an effective adsorbent to metal ions present in aqueous solution for more than a decade now [17]. The use of clays as adsorbents has advantages over commercially available adsorbents in terms of low-cost, abundant quality, high specific surface area, excellent adsorption properties, non-toxic nature, and great ion-exchange potential [18]. The adsorption of metal ions by clay minerals requires a number of complex adsorption processes, such as direct bonding between metal cations and the surface of clay minerals, surface complexation and exchange of ions, etc. [17]. Even though clay as bulk is non-polar, Brocken edges and defects give their surface negative charge and cation holding ability [19]. Metal adsorption properties of clay can be further improved by different modifications for treatments [20].

2. Materials and methods

2.1 Initial characterization of raw materials (clay)

The X-ray diffraction patterns of clay were obtained by using the X-Ray Diffractometer (XRD ULTIMA 4 RIGAKU). The sample was ground to a fine homogenous powder, and then it was loaded into a sample holder to obtain a smooth, flat surface. Parameters were set as (scan range (2θ range) = 0 - 120^0, Width = 0.1, Scanning rate = 2θ min^{-1}).

Scanning Electron Microscope (SEM LEO 1420VP) was used to study surface morphology. A small amount of each clay samples was attached to the sample holder using carbon tape. Finally, samples were gold-sputtered and observed in the SEM with different magnifications.

Particle Size Analyzer wet dispersion (PSA FRITSCH ANALYSETTE 22 Nanotec) was used to measure the particle size of clay samples in different stages of treatment.

Fourier Transformation Infrared Spectroscopy (FTIR) (BRUKER TENSOR27) analysis was done to observe the chemical properties of the sample.

2.2 Treatment of raw clay

The raw clay was sieved with 250-micron mesh. Sieved clay (100.0g) was treated with $NaCl_{(aq)}$ (1.5 M, 150.0 mL) for 15, 30, 45, 60 hours at 303 K temperature. During the treatment period, the samples were not agitated. After the relevant time of treatment, the excess solution was discarded and washed with distilled water. In the end, clay samples were dried in the air.

2.3 Study the adsorption capacity of treated clay

The adsorption of the hardness of natural hard water was carried out by hardness analysis with standard APHA method protocols. The hardness was calculated as mg $CaCO_3$/L. Total hardness, Temporary hardness, and Permanent hardness were calculated for raw water from CKDu prevalent area. The hardness reduction was calculated using the APHA method. Each sample was equilibrated 1.5 hours on a shaker with 10.00g of clay sample and 50.0 mL of each ion solution. EDTA $_{(aq)}$ solution was standardized with standard $CaCO_{3(aq)}$ solution.

2.4 Characterization of treated clay

Clay, treated with $NaCl_{(aq)}$(1.5 M) was observed under Scanning Electron Microscope (SEM) to obtain microgram scans, and samples were subjected to X-Ray Diffractometer (XRD) and Fourier Transformation Infrared Spectroscopy analysis. And also the particle size was analyzed using PSA.

3. Results and discussion

3.1 Clay characterization with XRD

Figure.1 shows the X-ray diffraction (XRD) patterns of natural (Unmodified) clay and treated (Modified) clay. It can be seen that natural clay has a sharp and strong diffraction peak at 2θ =22.45^0 which is the (002θ) characteristic peak of Kaolinite-2M. When the XRD spectrum of treated clay samples is compared with original spectra (see Figure.1), a clear deviation from the original spectra can be seen. This indicates changes in the crystalline structure (lattice parameters) of treated clay. Peaks of the two spectra have somewhat similar shapes, but they were different with respect to theta values and intensities. The strongest observed peak (at 2θ = 12.350) belong to Kaolinite and indicate sharp and strong diffraction. The treated clay mineral is less ordered than the raw clay. It is indicated by the shapes of peaks in the XRD range 35^0- 40^0 (2θ).

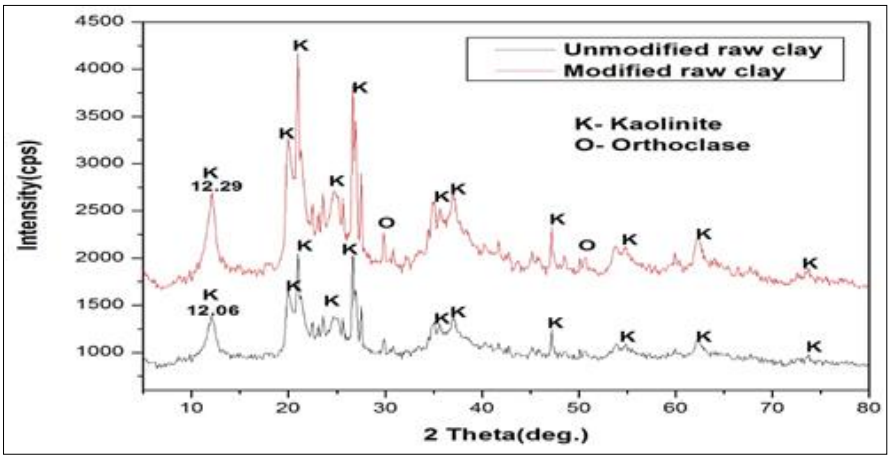

Fig 1: Comparison between XRD patterns of raw clay and treated clay.

When analyzing the results, it is clear that when treated with NaCl, the crystallinity and the interlayer structure of the clay material is altered. The untreated samples had a Kaolinite-2M percentage of 97.1% (see Figure 2). In treated clay, there were 44.6% and 55.2% of Kaolinite and Orthoclase respectively. A clear comparison between the composition of raw clay and treated clay is given in Figure.2.

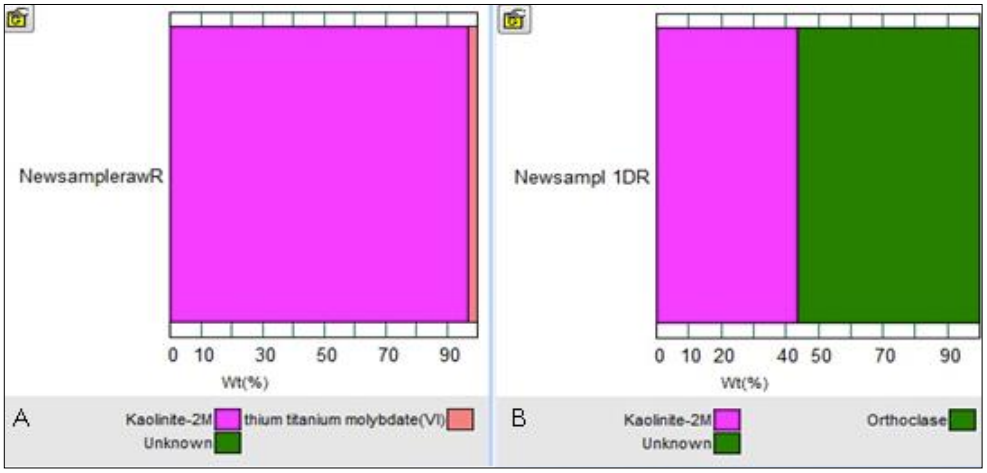

Fig 2: Composition of raw clay (A) and treated clay (B)

3.2 Fourier-Transform Infrared spectroscopy (FTIR) analysis

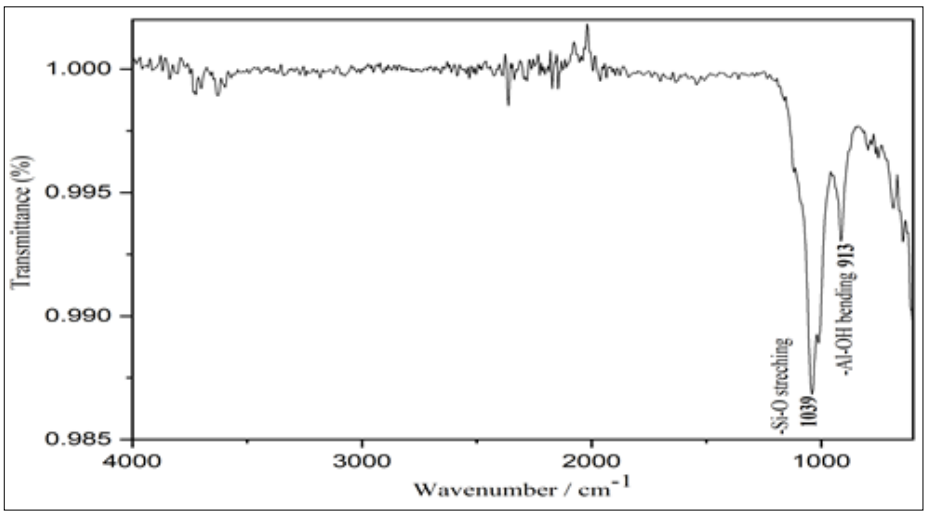

Fig 3: FTIR spectrum of raw clay (Unmodified) sample

The characteristic absorption bands in Fourier transform infrared (FTIR) spectrum fingerprint region was used for the identification and characterization of raw and treated clay samples (see Figure 3). Clay has characteristic absorption bands at 1040-1035 $cm^{-1}$and 900-920 cm^{-1} for in-plane stretching of Si-O bond and stretching of Al-OH bond respectively. These peaks can be clearly seen in both the raw and treated clay (see Figure 4) samples with similar frequencies and shapes.

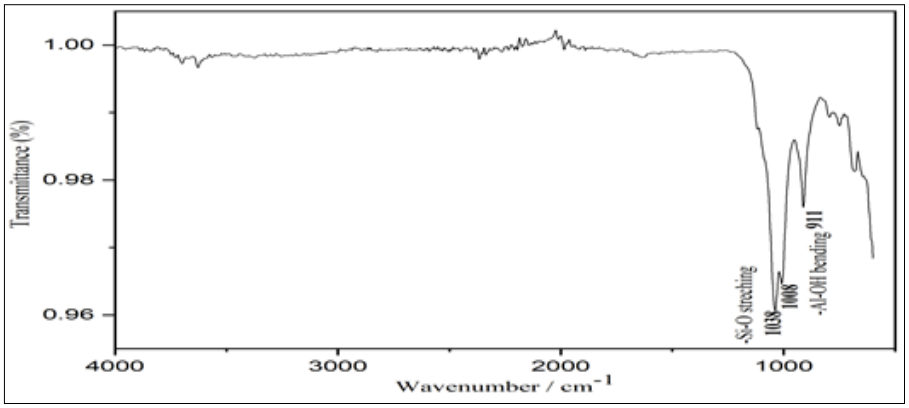

Fig 4: FTIR spectrum of treated clay (Modified) sample

An additional absorption band at 701-755 cm^{-1} is associated with surface hydroxyls. These three IR absorption bands of the clay are widely used in the study of adsorption and interface reactions. When analyzing two spectrums, all of the above-mentioned peaks can be clearly seen. In comparison, the frequencies of peaks haven't changed a significant amount, but their intensities were mildly different.

3.3 Particle Size Analysis (PSA)

PSA results clearly indicate that the particle size decreases linearly with the increase of treatment time (see Figure 5). Usually, a decrease of particle size results in an increase of effective cation binding surface area of cation exchange materials such as clay but sometimes this may be problematic as decreased particle size may cause increased bleeding of filter media.

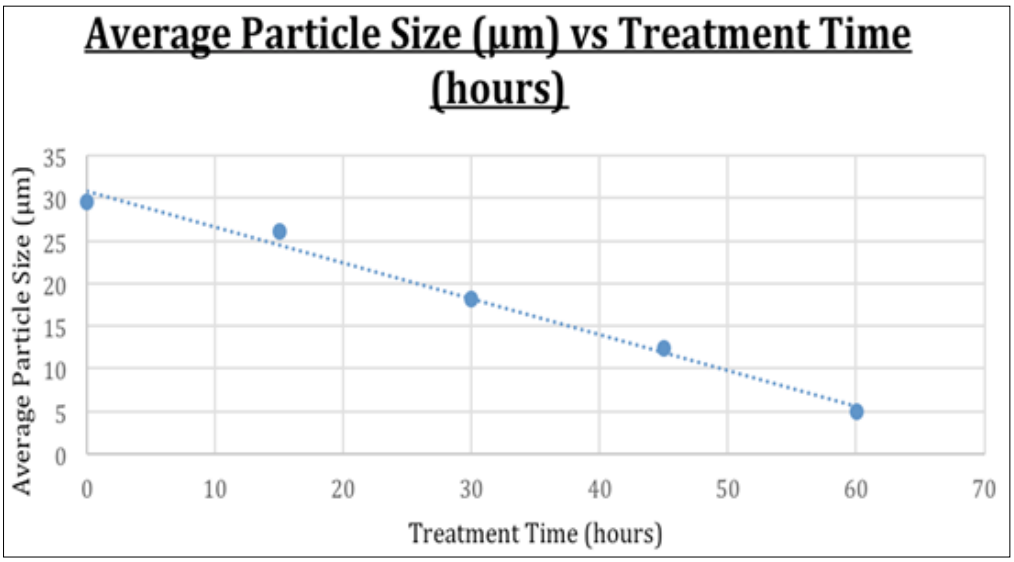

Fig 5: Particle size variation with treated time with NaCl solution

3.4 Scanning Electron Microscope (SEM) analysis

According to the SEM results (see Figure 6 - 9), Clay particles tend to be more porous and reduced in particle size after 15 hours of treatment. With 30 hours treatment, the particle porosity further increased and particle sizes were further reduced and thus increasing the surface area of the material. By the 60 hours treatment, particles tend to be aggregate with each other and it shows that overtreatment can decrease the surface area of the material. This can clearly be seen in adsorption data as adsorption of Ca^{2+} and Mg^{2+} ions were decreased with over treatment of clay.

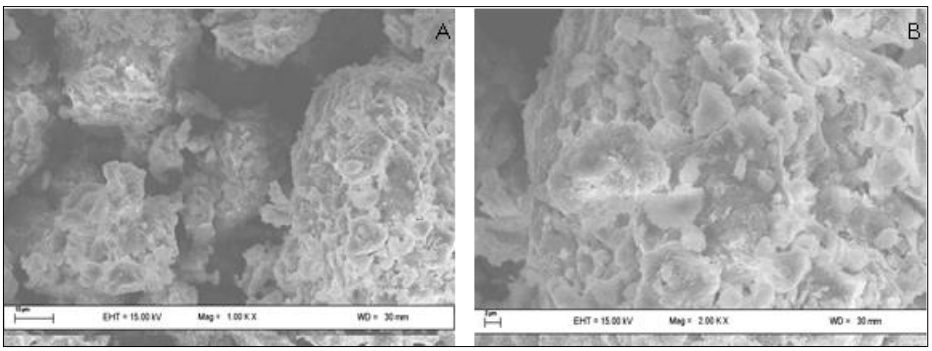

Fig 6: SEM images of raw clay sample (A) 1.0k (B) 2.0k

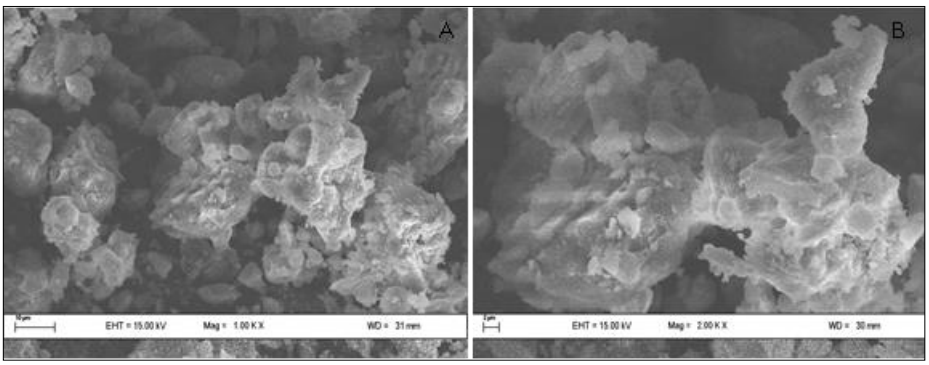

Fig 7: SEM image of clay sample treated for15 hours (A) 1.0k (B) 2.0k

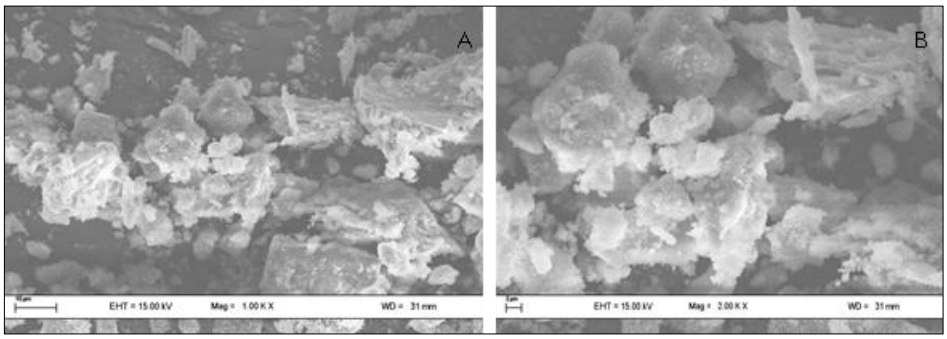

Fig 8: SEM image of clay sample treated for 30 hours (A) 1.0k (B) 2.0k

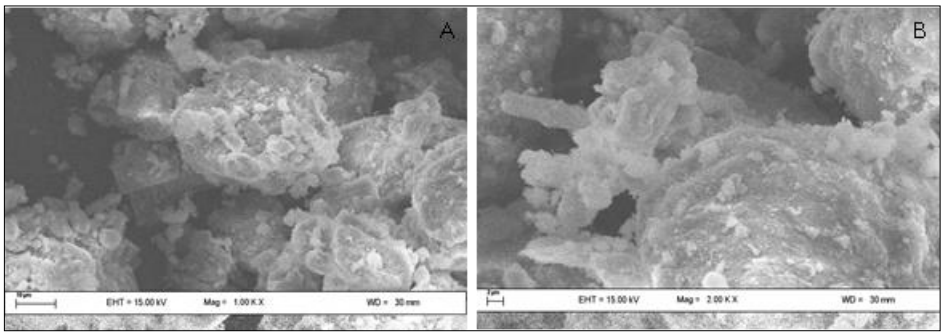

Fig 9: SEM image of clay sample treated for 60 hours (A) 1.0k (B) 2.0k

3.5 Adsorption of Ca^{2+} and Mg^{2+} ions in the water by raw clay and treated clay

When it considers the adsorption capacity of the clay, the adsorption capacity of Ca^{2+} and Mg^{2+} ions increase with the treatment time up to 33 hours. When treatment time increase beyond 33 hours, the adsorption capacity tends to decrease (see Figure 10)

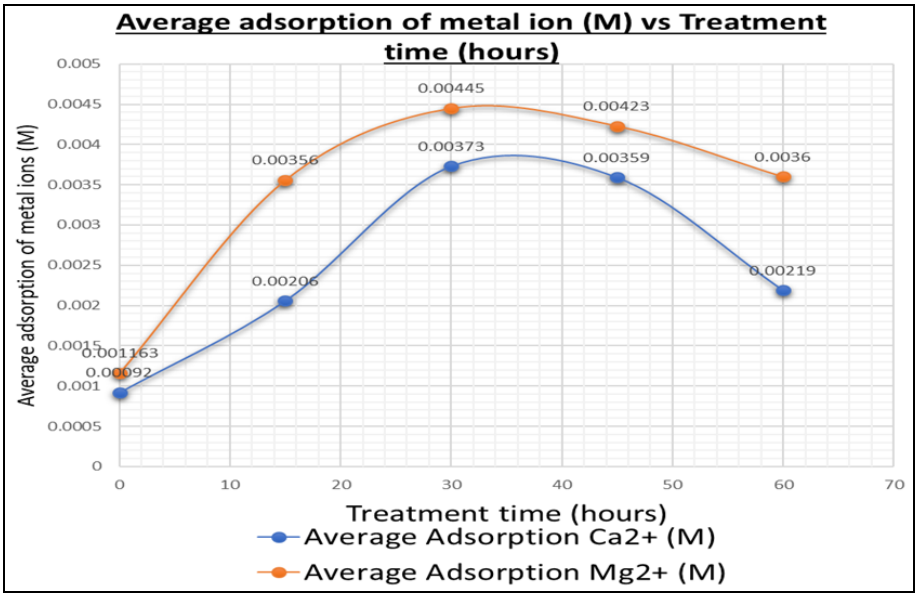

Fig 10: Adsorption of Metal ions (Ca^{2+}, Mg^{2+}) with the treatment time for clay.

This adsorption results coincide with SEM image analysis. According to SEM microgram results, up to 30 hours of treatment, the particle size of clay material gets decrease and more porous. After the 30 hours of treatment clay particles tend to be aggregated with each other decreasing the surface area and porosity of the clay material. PSA results show a continuous reduction of particle size up to 60 hours of treatment. This can be a result of the wet dispersion method of particle size analyzer. In the particle size analyzing procedure in the instrument, the aggregated clay particles can become fine smaller particles. It shows that overtime treatment of clay may decrease the cation adsorption capacity.

In summary, the treatment process had improved the particle size quality, particle porosity, and adsorption capacity of Ca^{2+} and Mg^{2+} ions by 318.48% and 285.21% increase when treated with optimum treatment time.

3.6 Adsorption of Hardness of raw hard water from CKDu prevalent area

Total hardness of the water = 310.14 mg $CaCO_3$/L

Permanent hardness of the water = 155.07 mg $CaCO_3$/L

Temporary hardness of the water = 155.07 mg $CaCO_3$/L
Total hardness of the filtered water with 30 hours treated clay material = 12.406 mg $CaCO_3$/L
Total hardness reduction = 96%

7. Conclusions

According to the Particle size analyzing results, the particle size decreased linearly with the increase of treatment time with $NaCl_{(aq)}$. Scanning electron microscopic analysis shows that beyond the 33 hours of treatment, particles tend to aggregate each other and reduce the porosity and surface area of the material. When the treatment time increases up to 33 hours, it shows adsorption results allowing more adsorption sites for Mg^{2+} and Ca^{2+} ions. According to the XRD data the $NaCl_{(aq)}$ treatment lead to a specific modification leading to the increased absorption capacity of Ca^{2+} and Mg^{2+} ions. More studies can be carried out regarding the reduction of cation adsorption capacity in muddy agricultural lands due to particle size reduction of soil.

8. Acknowledgment

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