


Thermal activation, characterization and performance evaluation of Ethiopian bentonite for sodium removal

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ABSTRACT

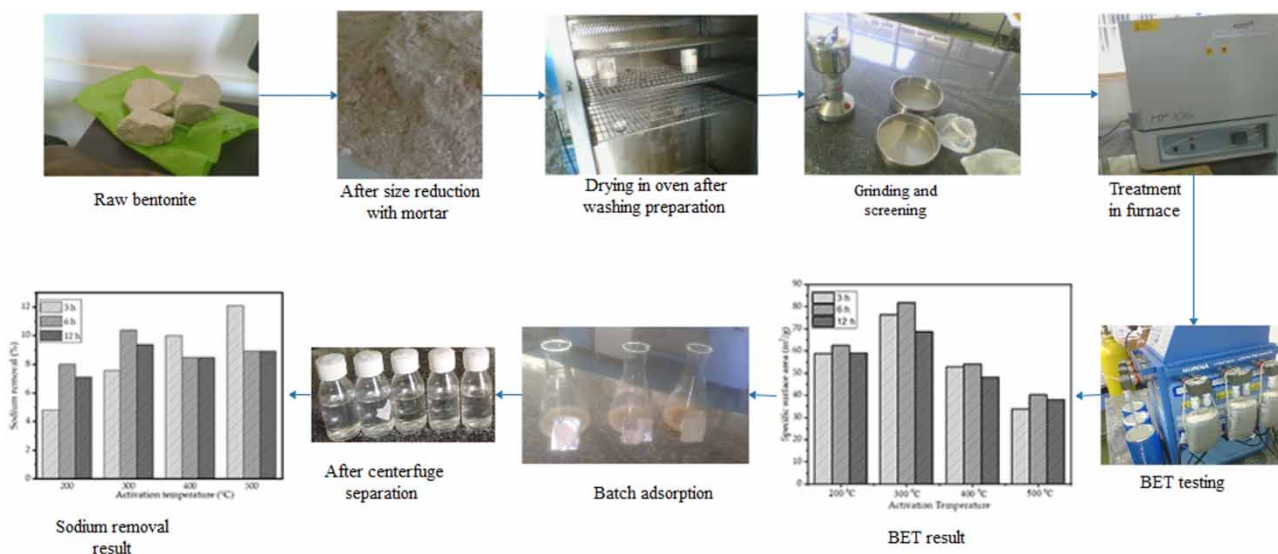
Bentonite is one of the clay materials that have important characteristics and is applicable to construction and for different industrial uses. Treatment of this material to enhance some of its physicochemical properties to suit the desired applicability has been a focus research area. In this work, natural bentonite from Warseisso, Afar region, Ethiopia was activated with thermal treatment. The raw and treated bentonites were then characterized using SEM, FTIR, XRD, BET, and cation exchange capacity. The effects of activation parameters (time and temperature) on its physicochemical properties and its performance for the removal of sodium ions from water were investigated. Bentonite activated for 6 h at 300 °C showed a maximum specific surface area of 81.74 m²/g while the raw one showed 57.6 m²/g. However, the cation exchange capacity value of the raw bentonite was found to be 82.1 meq/100 g while the value was reduced to 67.2 meq/100 g for treated bentonite with high specific surface area. To check the performance of the activated bentonite for desalination application, batch adsorption of sodium from synthetically produced sodium chloride solution was made. A sodium removal performance of 10% was achieved with treated bentonite at the maximum specific surface area.

Key words: adsorption, bentonite, sodium, specific surface area, thermal activation

HIGHLIGHTS

- Warseisso bentonite was activated at different time periods and temperatures.
- Raw and activated bentonites are characterized by SEM, BET, XRD, FTIR and CEC.
- Activated bentonite was applied for sodium removal from a synthetic solution.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Bentonite is natural clay with a very high montmorillonite content, and it is classified as a 2:1 family of phyllosilicate (Al-Ani & Sarapaa 2008). It is formed as a unit crystal lattice from one octahedral sheet sandwiched between two silica tetrahedral sheets. An interlayer between the crystal lattices of bentonite comprises cations and water molecules (Carlson 2004). This interlayer can also change in size through expansion or contraction by retaining the integrity of two-dimensional crystals by absorbing and losing water. These important characteristics make bentonite useful for different applications, such as cosmetics, adhesives, thickeners, paint and paper (Allo & Murray 2004), adsorbent (Pandey 2017), catalysis (Garrido-Ramírez *et al.* 2010) oil bleaching, beer and wine clarifications (Eisenhour & Brown 2009), etc. Industries using bentonite and the amount of usage have expanded significantly during the 20th century (Eisenhour & Brown 2009). The increase in bentonite demands resulted in searching for new bentonite source explorations around the world (Harvey & Murray 1997). The world bentonite production increased from about 10 million tons in 2001 to 21 million in 2019 (Bernhardt & Reilly 2019). The top producers according to Bernhardt & Reilly (2019) are China, USA, Turkey, Greece and India in descending order. Ethiopian geological survey report shows Ethiopian Rift Valley, specifically Afar depression of Ethiopia, have sizable bentonite reserves (Tessema 2010). However, the properties of this bentonite and its applications for water desalination were barely investigated.

Access to safe and clean water is one of the challenges of our society today. About 97% of the planet's water body is seawater and unsuitable for direct human consumption (Ahuja 2009). Moreover, out of the 3% fresh water, two-thirds of it are present in the form of ice and is not accessible for use (Ahuja 2009). The remaining one-third of freshwater is getting diminished due to various reasons such as an increase in freshwater salinity. Dissolved salts drained from natural and human salt consumption outlets are one of the causes for an increase in freshwater salinity (Ahuja 2009; Van Weert *et al.* 2009). Moreover, intensive water evaporation from freshwater bodies (Pérez & Chebude 2017) and transportation of salt deposits from weathering of salt rock and natural salt marshes (Velmurugan *et al.* 2020) are also some of the causes of water salinity. The use of saline water for irrigation increases the salinity of the agricultural soil and results in reduction in agricultural productivity causing food insecurity (Van Weert *et al.* 2009; Wang *et al.* 2021). More than 50% of the irrigated land on the globe and 10–20 million hectares of land per year are deteriorated due to salinity created by inappropriate irrigation (Panta *et al.* 2014; Kumar *et al.* 2018). On the other hand, following an increase in population size and improvement in living standards in most of the world, the need for freshwater has been significantly increasing (FAO 2017; Kumar *et al.* 2018; Islam & Karim 2019). Therefore, the use of desalination for reduction of water salinity to fulfill the need for fresh water is an important task for many countries.

Different desalination techniques have been identified to circumvent the water salinity problem out of which thermal and membrane methods are widely commercialized (Abdel-Fatah & Al Bazedi 2020). However, these techniques have some

drawbacks such as high energy and advanced technology requirements, and therefore are not widely practiced (Miller 2003; Alnajdi *et al.* 2020). Its application has been restricted to some countries that have sufficient energy resources and are technologically developed. Adsorption and ion exchange techniques are the desalination processes that have recently been under consideration (Baltrėnas & Baltrėnaitė 2020; Song & Li 2021).

Bentonite-based adsorptions for the removal of various water pollutants such as metal pollutants have been widely investigated (Uddin 2017; Chen *et al.* 2018). To use bentonite for adsorption, enhancing the properties such as surface area and cation exchange capacity (CEC) has been accepted as a very essential activity (Sarikaya *et al.* 2000; Alemdaroglu *et al.* 2003). Therefore, activation has been utilized to improve physical and chemical characteristics of bentonite. Chemical and thermal activation methods have been used for bentonite property enhancement (Barakan & Aghazadeh 2021). In our earlier work, the performance of acid-treated bentonite for the removal of sodium from water was reported (Musie & Gonfa 2022). Chemical activation methods using acid or alkali may leave chemical residue and cause environmental problems (Barakan & Aghazadeh 2021). Thermal treatment method is considered as a cost-effective approach for improving the properties of bentonite (Gan *et al.* 2009; Yin *et al.* 2017). Hence, thermal treatment was used to modify bentonite obtained from local deposits and to investigate the performance of both raw and treated bentonites for the removal of sodium from water. The effects of thermal treatment on the morphological and physicochemical properties of bentonite were studied. The effects of activation temperature and time on surface morphology, specific surface areas, surface charge or functional group, crystal properties, cation exchange properties and sodium removal performance were studied.

2. MATERIALS AND METHODS

2.1. Materials

Raw bentonite was collected from the Warseisso deposit of the Afar region, Ethiopia. Methylene blue (15% loss on drying) and pellets of sodium chloride (99%) were obtained from Sigma-Aldrich. The chemicals were of analytical grade and used without further purification.

2.2. Bentonite preparation

The raw bentonite was dried at 105 °C for 4 h in an oven (TD-1315, UK) and the bentonite was then ground into powder using mortar and pestle. The sample was then washed with distilled water to get rid of water-soluble impurities by settling and decantation. Then, the sample was dried for 18 h at 105 °C in the oven. After allowing the sample to cool, it was grounded by using a grinder (RRH-1000, China) and sieved by passing through a mesh of size 75 µm and stored. One hundred g of the finely grounded bentonite samples were then put in crucibles and thermally treated in a muffle furnace (MV-106, UK) at pre-adjusted temperatures of 200, 300, 400 and 500 °C for treatment times of 3, 6 and 12 h. After treatment for a specified period in the furnace, the samples were removed and allowed to cool to room temperature in a desiccator and then used in characterization and for sodium removal from water.

2.3. Characterization of bentonite

Surface morphologies and specific surface area of the bentonite samples were analyzed using a field emission scanning electron microscopy (SEM, Inspect F50) and Brunauer–Emmett–Teller (HORIBA, SA-9600 series) specific surface area analyzer, respectively. Fourier-transform infrared spectroscopy (Thermo scientific FTIR, IS50) and X-ray diffraction (XRD) (Shimadzu, XRD-7000) were also used to investigate the effects of thermal treatment on functional group and crystalline structure of raw and thermally treated bentonite.

2.4. Cation exchange capacity

CEC is one of the basic properties of clay minerals (Drever 1982; Wilson 1994; Al-Ani & Sarapaa 2008). Bentonite clay with a high CEC is required for adsorption of cations from water in addition to other requirements such as its selectivity and regenerability (Bertagnolli *et al.* 2011). CEC of the current bentonite was determined using the methylene blue test method using the French Standardization Association (AFNOR) standard (Chiappone *et al.* 2004). Methylene blue in aqueous solution is a cationic

dye ($C_{16}H_{18}N_3S^+$) that adsorbs negatively charged clay surfaces (Chen *et al.* 1999). The total volume of methylene blue solution consumed to complete the titration was used to calculate the CEC as shown in the following equation (Rihayat *et al.* 2018):

$$CEC = \frac{V_{MB} * N_{MB}}{m_c} \quad (1)$$

where CEC is the cation exchange capacity (meq/100 g), m_c is the mass of clay sample (g), V_{MB} is the amount of methylene blue added to the clay sample (mL) and N_{MB} is the normality of the methylene blue solution (meq/L).

2.5. Sodium removal studies

To evaluate the performance of treated bentonite, batch adsorption was conducted in 250-mL flasks with 0.04 L of salt solution and 0.5 g of adsorbent at pH of 10. The pH of solution was adjusted by adding 0.1 M NaOH and H_2SO_4 . Aqueous sodium solution with a concentration of 2,196 mg/L was prepared by adding sodium chloride to distilled water. The salt solution was mixed with the specified adsorbent before running in a shaker at 120 rpm, for 180 min at room temperature. Then, a Flame photometer (KRUSS, FP8400, Germany) was used to measure sodium concentration in the solutions after separating the liquid part by centrifugation (Pro-analytical C2004, UK). Percent sodium removal (R) was then calculated by using Equation (2) for performance evaluation by using initial and final sodium concentrations:

$$R = \frac{(C_o - C_f)}{C_o} \times 100\% \quad (2)$$

where C_o and C_f are the sodium concentrations (mg/L) before and after adsorption.

3. RESULTS AND DISCUSSION

3.1. Surface morphology

The SEM images of raw and bentonite thermally treated at different temperatures are shown in Figure 1. Aggregated flakes of closely packed particles are easily visible in raw bentonite as shown in Figure 1(a). However, when it is treated, the surface of bentonite was changed from dense and smooth aggregate to partially broken and cotton-like flake surfaces, shown in Figure 1(b)–1(e). The effects of changing temperature and heating time were not significant and no significant changes were observed as activation temperature and time increased. Thermal treatment removes free water and structural water from the center of bentonite crystal to create pores on the surface at an early stage of heating. However, further increases in activation temperature and time may create structural collapse and may reduce the surface area of the bentonite. This trend was also observed in previous works (Bertagnolli *et al.* 2011; Chen *et al.* 2018).

3.2. Specific surface area

Thermal treatments play an important role in bentonite-specific surface area, CEC, particle size and surface acidity (Hussin *et al.* 2011). Hence, in this work, the effects of the treatment temperature and time on bentonite-specific surface area are depicted in Figure 2. The specific surface area of the raw bentonite is 57.6 m²/g. Bentonite activations were carried out at treatment times of 3, 6 and 12 h and treatment temperatures varied at 200, 300, 400 and 500 °C. The specific surface area increases as activation temperature increases from 200 to 600 °C; however, further increase in temperature results in reduction of the surface area. Similarly, an increase in activation time from 3 to 6 h results in increases in specific surface area; however, further increase in activation time results in reduction of the surface area. The trend of increase and then decrease in the specific surface area on increasing activation temperature is in agreement with previously reported works even though the values may differ (Sarıkaya *et al.* 2000; Moghadamzadeh *et al.* 2013; Toor *et al.* 2015). The differences in the values would be due to the difference in chemical constituent of the bentonite. The initially observed increase in the surface area with the temperature is due to the removal of volatile organic compounds and hydrated water molecules attached to the surface of bentonite material. However, calcination at a higher temperature resulted in a dehydroxylation point where physicochemical properties of the bentonite get altered and a collapse of interlayer spacing occurs (Toor *et al.* 2015). Treatment of bentonite at this condition is not recommended since it creates an irreversible crystal structure and leads to surface area reduction. A maximum of 81.7 m²/g was observed for activated bentonite at 300 °C temperature and 6 h. This is higher

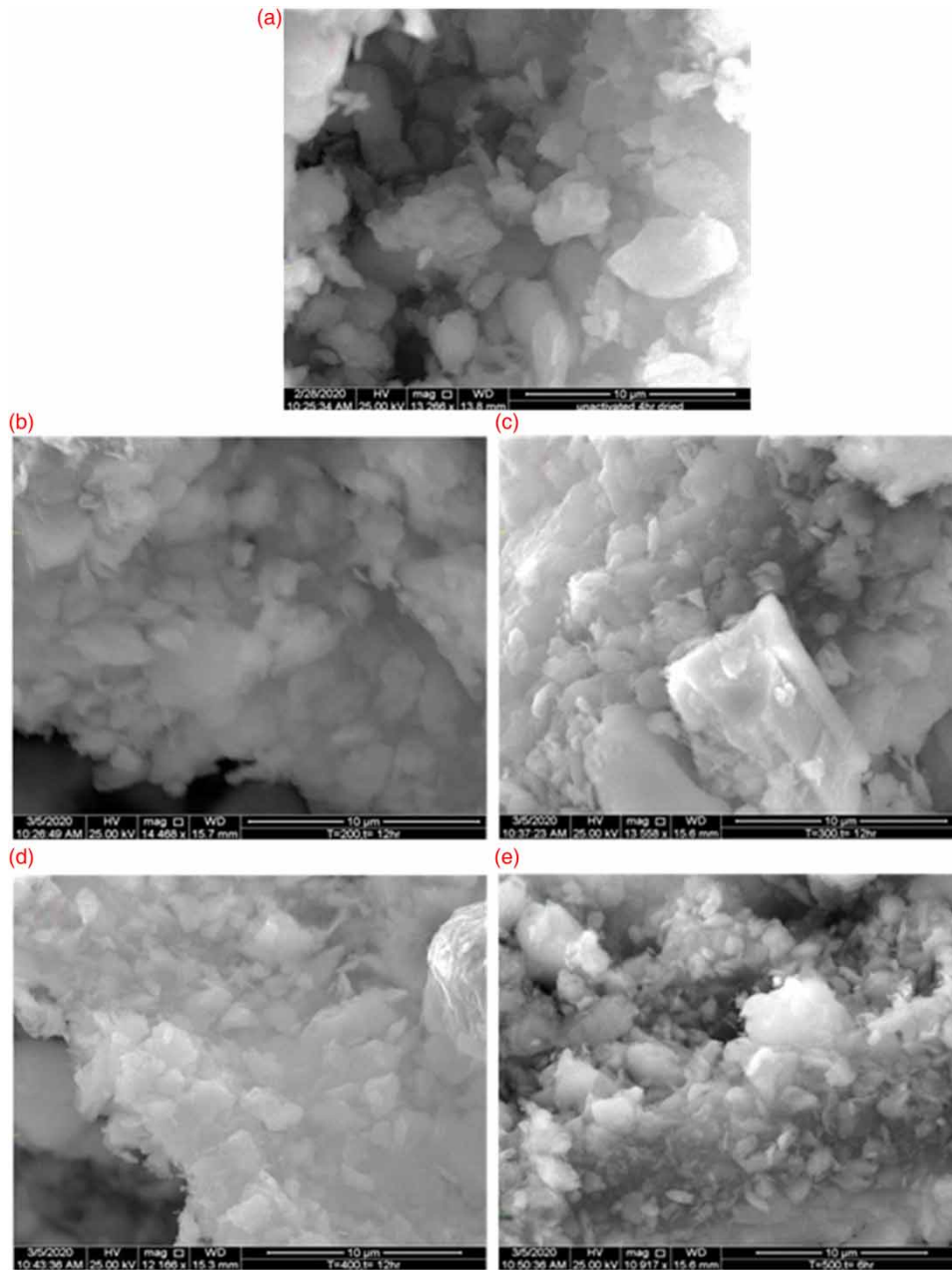


Figure 1 | SEM images of (a) raw bentonite, and bentonites treated at (b) 200 °C for 12 h; (c) 300 °C for 12 h; (d) 400 °C for 12 h and (e) 500 °C for 6 h.

than the value ($46.11 \text{ m}^2/\text{g}$) reported for Brazilian bentonite activated at 500 °C (Bertagnolli *et al.* 2011). Further comparison of the maximum specific surface area to different works from different countries was made and the result is shown in Table 1. The result shows the current bentonite is better than most of the bentonite used for comparison. The specific surface area of the current bentonite is also comparable with the value reported for bentonite obtained from Kutahya, Turkey. The variation in specific areas observed for bentonite obtained from different countries would be mostly related to the chemical constituents of bentonite from different geographical sites and activation conditions as well.

3.3. FTIR analysis

FTIR spectrum is an important characterization parameter used to indicate the changes in important functional groups in the bentonite structure before and after thermal treatment. The spectrum of raw and thermally activated bentonite at 300 °C for

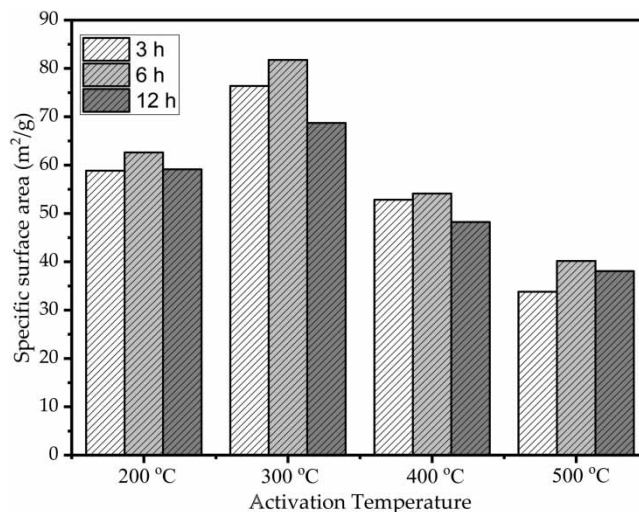


Figure 2 | Effects of activation temperature and time on specific surface area of bentonite.

Table 1 | Comparison of bentonite surface area at different activation temperatures

Source	Specific surface area (m ² /g)		Temperature (°C)	References
	Raw	Activated		
Turkey (Kutahya)	42.0	89.0	500	Sarikaya <i>et al.</i> (2000)
Turkey (Ankara)	44.0	105.0	300	Bayram <i>et al.</i> (2010)
Iran	45.0	48.0	150	Moghadamzadeh <i>et al.</i> (2013)
Australia	25.7	33.2	100	Toor <i>et al.</i> (2015)
China (Zhengzhou)	12.9	56.1	400	Chen <i>et al.</i> (2018)
Ethiopia (Warseisso)	57.5	81.7	300	This work

6 h is shown in Figure 3. The peak in wavenumber regions of 1,200–400 cm⁻¹ indicates the dominance of the montmorillonite group in the bentonite structure confirming bentonite property (Balci 2018). The absorption bands caused by stretching vibrations of OH groups in montmorillonite and in water molecules were observed at wavenumbers of 3,610 and 3,394 cm⁻¹, respectively. The band observed at 1,033 cm⁻¹ relates to Si–O stretching and the one observed at 1,635 cm⁻¹ is for OH deformation of water (Toor *et al.* 2015). These two regions showed variations in thermal treatment as water is more affected on dehydration. Very weak spectra observed at 432 and 509 cm⁻¹ bands suggest the presence of Si–O bending and Al–O stretching vibration. However, the band shown at wavenumber 787 cm⁻¹ indicates Si–O bending in quartz (Toor *et al.* 2015). Similar observations were reported in previous works (Toor *et al.* 2015; Balci 2018).

3.4. XRD analysis

The spectra of XRD for the raw and thermally activated are shown in Figure 4. The crystalline structure of the bentonite was more or less preserved after the thermal treatment. The X-ray spectrum shows peaks at 2θ of 5.66° to 7.3, 13.7, 19.78, 35 and 61.8° confirming the presence of montmorillonite in the bentonite structure (Zhirong *et al.* 2011). The X-ray pattern also indicates the presence of other mineral crystals at different 2θ pick positions: cristobalite (22°), hematite (23.8°), feldspar (27.8°) and quartz (21, 26.6 and 41.9°) are some of the observed crystals. Similar observations were reported by previous research works (Steudel *et al.* 2009; Tomic *et al.* 2011).

Thermal activation is observed to increase the intensity of quartz peak due to the removal of impurities and removal of water from the bentonite structure. This indicates that quartz cannot be eliminated from clay by thermal activation. Previous works also reported the enhancement of this spectrum after thermal treatment (Amari *et al.* 2018). The decreased peak of

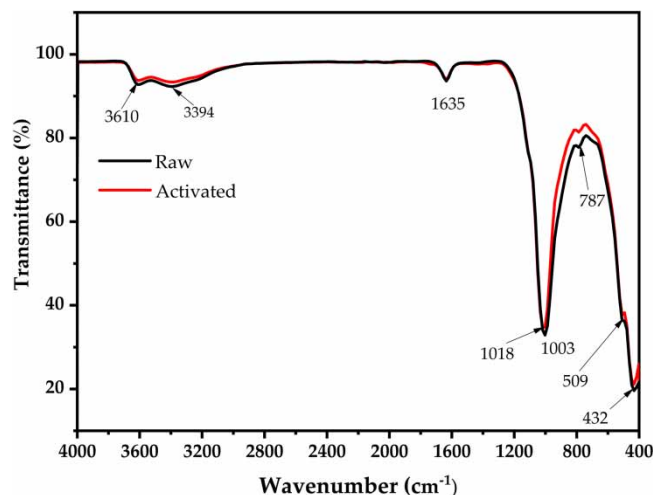


Figure 3 | FTIR spectra of raw bentonite and thermally activated bentonite for 6 h at 300 °C.

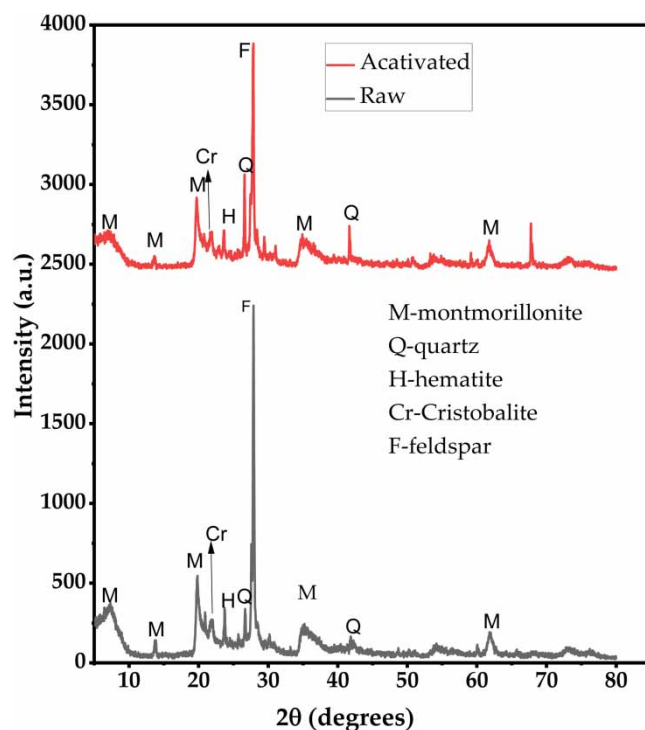


Figure 4 | XRD spectra of raw bentonite and thermally activated bentonite for 6 h at 300 °C.

montmorillonite observed at 2θ of 5.66 in the thermally activated sample is due to dehydration in the interlayer of the montmorillonite (Sarikaya *et al.* 2000).

3.5. Cation exchange capacity

The CEC values for raw and thermally activated bentonite at various temperatures for 6 h are determined and shown in Figure 5. Previous works reported the CEC of raw bentonite obtained from different deposits. Wilson (1994) reported the CEC of raw bentonite can be in the range of 80–150 meq/100 g, whereas the value reported by Drever (1982) was 60–150 meq/100 g. The CEC value of the current raw bentonite is 82.1 meq/100 g which is in the range of the value reported by

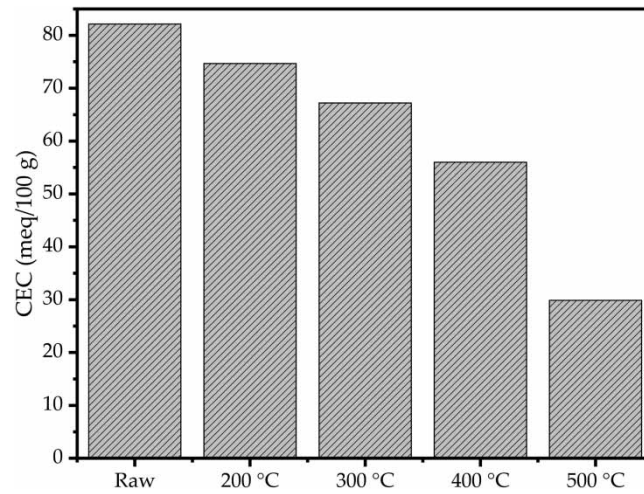


Figure 5 | CEC of raw bentonite and bentonite thermal activated for 6 h.

previous works. Commercial-grade bentonites have CEC values of typically between 40 and 120 meq/100 g (Inglethorpe *et al.* 1993). Therefore, the Warseisso bentonite is in the range of both raw and commercial-grade bentonite.

The CEC of thermally activated bentonite decreased continuously irrespective of the changes in specific surface area. The CEC showed a reduction with increasing temperature due to dehydration and dehydroxylation of bentonite (Sarikaya *et al.* 2000). Comparing the CECs and specific surface areas of the samples activated at different conditions, the one that showed the largest specific surface area and fairly good CEC may be selected for further performance study.

Bentonite activated at 200 °C showed higher CEC, however, lower specific surface area. For thermal treatment at the temperature of 400 °C and above, both the surface area and CEC were observed to be low for consideration. Hence, bentonite activated at a temperature of 300 °C for 6 h was selected for adsorption performance studies.

3.6. Sodium removal studies

The thermally activated bentonite was studied for the removal of sodium ions from an aqueous solution using batch adsorption. The batch adsorption was conducted for an initial sodium concentration of 2,196 mg/L by adding 0.5 g of adsorbent to 0.04 L of salt solution (solid-to-liquid ratio of 1.0 g/80 mL), adsorption time of 3 h and at pH of 10. The effect of activation time and activation temperature on the sodium removal performance of bentonite is shown in Figure 6. The sodium removal

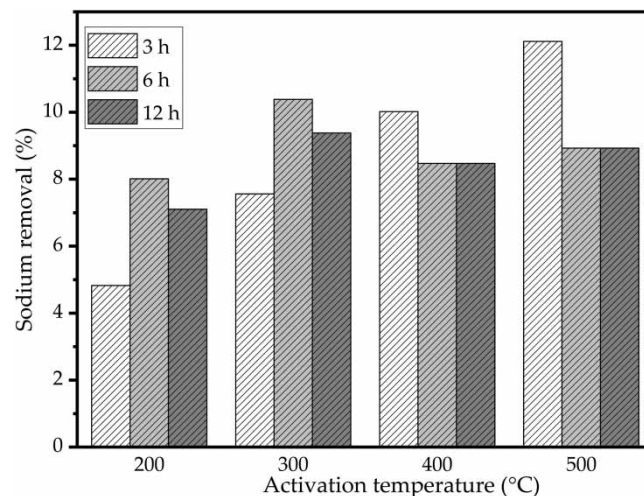


Figure 6 | Percentage removal of sodium with bentonite activated at different treatment times and temperatures.

percentage for bentonite activated for 3 h increases with activation temperature. For bentonite activated for 6 and 12 h, the trend in sodium removal follows the trend observed for the specific surface area shown in Figure 2. Although 6-h time activation showed high specific area in all temperatures as shown in Figure 2, it provides high sodium removal percentage only for bentonite activated at 300 °C. The maximum sodium removal performance of 12% was achieved with bentonite activated at 500 °C for 3 h. The maximum removal performance observed is slightly higher when compared to the percent removal value (10%) observed for bentonite with highest specific surface areas (activated at 300 °C for 6 h). Exposing bentonite to a temperature of more than 300 °C and a time of more than 6 h not only reduces the specific surface area and CEC but also reduces sodium removal performance of bentonite. This shows the performance of the bentonite for removal of sodium from water depends both on specific surface area and CEC which in turn depends on activation temperature and activation time.

The performance studies for removal of sodium from water using bentonite were not widely reported. Al-Essa (2018) used raw and HCl-treated bentonite for removal of sodium from an aqueous solution with an initial sodium concentration of 297.9 mg/L and a solid-to-liquid ratio of 1.0 g/10 mL. The sodium removal percentages of the raw and HCl-treated bentonite were 37 and 60%. The differences between the reported and the current sodium removal performances could be due to the initial sodium concentration and the solid-to-liquid ratios. In the current work, the initial sodium concentration was 2,196 mg/L which is much higher than the value reported by previous work. The solid-to-liquid ratio of the current work is 1.0 g/80 mL while the value used by previously reported work was 1.0 g/10 mL. In our previous work (Musie & Gonfa 2022), it was managed to remove 18% sodium from an aqueous solution with similar initial sodium concentration and solid-to-liquid ratio with sulfuric acid-treated bentonite.

4. CONCLUSIONS

In this work, natural bentonite was activated using thermal treatment. Both the raw and thermally treated bentonite samples were characterized by using SEM, FTIR, XRD, BET and CEC. The effects of time and temperature as activation parameters showed a positive response on the specific surface area initially, and their effects become negative as the values of these parameters exceed the temperature of 300 °C and activation time of 6 h. Also, the performance of the activated bentonite for desalination was checked using a synthetic salt solution and found to follow the specific area. Bentonite treatment at high temperatures (more than 300 °C) or prolonged time (more than 6 h) showed reduced specific surface area and also reduced sodium removal. Therefore, the 300 °C temperature of activation for 6 h time exposure was selected for a maximum surface area and also good at desalination potential on Warseisso bentonite. The second option would be heating at 500 °C for a short period of time (3 h). The third option suitable may be 400 °C at 3 h; otherwise it is advisable to use the adsorbents treated at 300 °C at 12 h; 500 °C at 6 h; 400 °C at 6 h and 200 °C at 6 h time of activation in descending order for sodium removal.

ACKNOWLEDGEMENTS

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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