

Removal of water hardness causing constituents using alkali modified sugarcane bagasse and coffee husk at Jigjiga city, Ethiopia: A comparative study

Adhena Ayaliew Werkneh^{1,*}, Angaw Kelemework Abay¹, Anbisa Muleta Senbeta²

¹Department of Chemistry, College of Natural Science, Jigjiga University, PO. Box: 1020, Jigjiga, Ethiopia

²Department of Food Science and Nutrition, College of Dryland Agriculture, Jigjiga University, PO. Box: 1020, Jigjiga, Ethiopia

Email address:

adhena1988@gmail.com (A. A. Werkneh)

To cite this article:

Adhena Ayaliew Werkneh, Angaw Kelemework Abay, Anbisa Muleta Senbeta. Removal of Water Hardness Causing Constituents Using Alkali Modified Sugarcane Bagasse and Coffee Husk at Jigjiga City, Ethiopia: A Comparative Study. *International Journal of Environmental Monitoring and Analysis*. Vol. 3, No. 1, 2015, pp. 7-16. doi: 10.11648/j.ijema.20150301.12

Abstract: Alkaline modified sugarcane bagasse and coffee husk were used for the adsorption of water hardness causing constituents (Ca^{+2} and Mg^{+2}). The water hardness sample was collected using polyethylene bottle from Jigjiga city drinking water supply, Ethiopia. The adsorbents were characterized using FTIR and BET surface area techniques. The concentration of the constituents were determined using AAS Spectroscopy. It was found that, using the ABC and ACHC as an adsorbent, the maximum sorption capacity obtained for Ca and Mg hardness adsorption are 46.8 and 37.35, and 52.9 and 41.23 mg g^{-1} for ACHC and ABC respectively. Activated carbon filtration also depends on various parameters such as pH, contact time, adsorbent dose, temperature and initial Ca and Mg ion concentrations. The maximum recovery of the adsorbed calcium and magnesium was achieved in less than 200 minutes leading to 78% and 73% respectively. After treating synthetic water solution simulating an actual water stream with the alkali-modified bagasse and coffee husk, total hardness of the treated sample meets the required standard for drinking water, below 60 mg/L of CaCO_3 . Therefore, ABC is more suitable for the removal of hardness ions than ACHC from drinking water; and are considered as effective low cost adsorbents.

Keywords: Water Hardness, Activated Carbon, Bagasse, Coffee Husk

1. Introduction

Quality of water is one of the most important natural resources of the world. It plays a vital role in the development of communities; hence a reliable supply of water is essential. It needs to be maintained all the time for human and industrial use. As for human consumption, quantity and quality of drinking water have been recognized as increasingly critical issues. Addressing the deterioration of water quality in developing countries, where an estimated one billion people lack access to potable quality water, is a primary motivating factor for many community development efforts and is a key component of the Millennium Development Goals [1]. The provision of safe water to the people is an urgent development priority of any country in the world [1], [2].

Most of the water resources should be treated for purification before consumption. In some countries, groundwater is the main safe drinking water resource [1]. In

some cases, the resource does not satisfy to the desirable levels regarding their chemical properties, such as hardness, nitrate contamination, heavy metals, soluble iron, etc. [2]. Among them, water hardness can appear problematic in some cases; it can also be considered as an important aesthetic parameter. However, because public acceptance of hardness differs remarkably according to local conditions, a maximum acceptable level has not been defined. In general, water supplies with total hardness higher than 200 mg/L can be tolerated by consumers but are considered as poor resources; while values higher than 500 mg/L are not acceptable for most of the domestic consumptions [3], [4].

Recently, various methods including electro deionization process, electro membrane processes, capacitive deionization, membrane and fluidized pellet reactor, ion exchange process and adsorption have been studied for the removal of a wide variety of ionic and molecular species from various water

streams, including those responsible for hardness (e.g. Ca^{+2} and Mg^{+2} cations). Amongst the developed processes, adsorption has been widely studied for the uptake of various ionic and molecular species from water [6]-[8].

In an effort to reduce the proportion of people without sustainable access to safe drinking water, there is a need to optimize the production of activated carbon from locally available wastes and apply it for water treatment in diverse communities. This has led to the development of alternative low-cost technologies such as activated sugar cane bagasse for the treatment of drinking water in the developing world. Research has also been focused on the indigenous production of water treatment chemicals using locally available raw materials [1]. Carbon adsorption offers significant advantages including low cost, availability, profitability, ease of operation and efficiency in comparison with conventional methods especially from economically and environmentally points of view [4],[5].

In countries with poor economic base, the high cost of importing the water treatment chemicals prevents consistently good drinking water quality being achieved in many cases. The activated carbon has been widely used worldwide as an effective filtration or adsorption material for removing chemical contaminants from drinking water. In most developing countries, the activated carbon is imported at high cost, limiting the quantities of safe drinking water

available to the people. The high cost of importing the activated carbon puts a significant burden on the water treatment budget since foreign currency is scarce [6],[7]. The main aim of the study was to apply activated carbon prepared from coffee husk and bagasse wastes in drinking water treatment and assess the efficiency of the carbons in the purification of hardness of water as a function of operating parameters [3].

2. Materials and Methods

2.1. Description of the Study Area

Jigjiga is a city in eastern Ethiopia and the capital of the Somali Region of the country. The city is located in the Jigjiga Zone approximately 80 km (50 mi) east of Harar and 60 km (37 mi) west of the border with Somalia. The city has an elevation of 1,609 meters above sea level and are found with coordinates of $9^{\circ}21'N42^{\circ}48'E$. The climate of Jigjiga is a subtropical highland climate (Köppen climate classification), with the influence of mountain climate, with hot and dry summers and cold winters. The temperature range of the city was between 25 and 29 °c. As of 2008, Jigjiga has about 34.1% of the total population has access to drinking water from underground water



Figure 1.1. Map of the study area.



Figure 1.2. Shows (A) Raw sugarcane bagasse, (B) Alkali activated carbon, (C) Raw Coffee Husk.

2.2. Chemicals and Solutions

Apparatus and instruments: pH meter (MP 220, METTLER TOLEDO), FTIR spectrometer, AAS spectrophotometer (BUCK SCIENTIFIC MODEL VGP210, USA), Rotary Shaker (VRN - 480, GEMMY Orbit Shaker, Taiwan), Balance (OHAUS, E11140, Switzerland), Desiccators, Electrical mill (IKA-WERKE, M20 GMBH & CO.KG, GERMANY), Filter Paper (Whatman 542, 90 mm diameter), Sieve no of different size (IMPAOT, UK), Deionizer, hot air Oven (OV150CGENL ABWIDNES, England).

2.2.1. Reagents and Chemicals

Analytical grade CaCl_2 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ purchased from Avishkar LAB TECH CHEMICALS, LOT which were used as a model compound to stimulate the total hard water, Sulphuric acid (H_2SO_4) purchased from Reagent chemical service limited Company, Runcorn Cheshire used to activate bagasse and coffee husk, Sodium hydroxide (NaOH) from Avishkar LAB TECH CHEMICALS, LOT used to adjust the pH, HCl from Reagent chemical service limited Company, Runcorn Cheshire used for titration, Sodium Chloride (NaCl) purchased from TITAN BIOTECH LIMITED, BHIWADI which was used for titration in Sear's surface area analysis. All experiments were conducted according to the standard methods for the examination of water and wastewater [21].

2.2.2. Sampling and Sample Collections

Tap ground water samples were collected in clean 1000 ml plastic bottles. The containers were first washed with de-ionized water, and then several times with the sample water before collection in order to avoid any contamination. The samples were then carried in ice-packed coolers to the laboratory for analysis within 24 hours.

2.3. Collection and Preparation of Adsorbent

Raw Sugarcane Bagasse and coffee husk were collected from Wonji sugar factory and coffee refinery S. C in Ethiopia, which are collected as a waste. The samples were soaked for 24 hours and washed with distilled water before use in order to remove any impurities. Raw sugar cane bagasse sample was boiled for 30 min to remove remain soluble sugars. They were kept in drying oven maintained at 105°C for a period of 24 hours. The dried materials were grounded with electrical

grinder to get the desired particle size of $500\ \mu\text{m}$. Then, they were treated with concentrated sodium hydroxide, 2 M NaOH for 24 hours at room temperature with the ratio of 1:1 (base to carbon ratio) then stirred for 30 min and left for overnight. The purposes of treating carbon using 2 M NaOH were to create a suitable environment for its ring opening which increase the number of adsorption sites. Finally, the treated carbons were washed with distilled water to remove excess bases and any other soluble substances before the sample were dried in Furnace and adjusted its pH to about 6.5. These materials are referred as activated Sugarcane bagasse and coffee husk. All experiments were conducted according to the standard methods for the examination of water and wastewater.

2.4. Batch Filtration Experiments

All experiments were conducted in batch mode in 250 mL conical flasks. Several operating parameters including pH (2-10), temperature ($10-50^\circ\text{C}$), adsorbent mass (2-10 g/L), initial calcium and magnesium concentrations (40-120 mg/L) and contact time (40-120 minutes) were investigated. Optimized adsorption times for modified adsorbents were first examined by varying the contact time at room temperature, pH= 6.0 and for an adsorbent mass of 2 g per liter of solution. For this purpose, 2 g of adsorbent were added to 1 L of solution in a conical flask containing Ca^{+2} or Mg^{+2} cations at a concentration in the range of 40 to 120 mg/L. The mixture was then shaken at 200 rpm.

The removal efficiency (%R) and sorption capacity (Q_e) was determined as follows (Eq. 1 and 2):

$$R(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$Q_e (\text{mg/g}) = \frac{(C_i - C_e)}{m} V \quad (2)$$

Where, C_o and C_f are the initial and final concentration of metal in solution (mg l^{-1}), V is the volume of solution (l) and m is the mass of sorbent (g).

After investigation of the effect of the contact time and the initial ion concentration, the effects of pH and adsorbent mass were examined. The effect of temperature was then investigated in the optimal conditions for pH, adsorbent mass and contact time, for three initial concentrations of Ca^{+2} or Mg^{+2} cations (60, 120 and 180 mg/L). All the experiments had performed in duplicate and the mean values were

reported.

Analysis of the Adsorbate Solution:

Spectrophotometric measurements were carried out using Atomic Absorption spectrophotometer using calcium and magnesium hollow-cathode lamp at respective wavelengths and an air/acetylene flame with strict adherence to standard calibration guidelines.

Characterization of Adsorbents: In order to understand the mechanism of the sorption, large quantities of work was done to investigate the influence of the sorption process using different kinds of techniques. Fourier Transform Infrared (FTIR) Spectroscopy analysis was conducted at Ethiopia Pharmaceutical Factory, Addis Ababa, Ethiopia which is used to assess functional groups of the adsorbents.

Determination of BET surface area: The specific surface areas of the adsorbents were determined using the Sear's method (1956). For this 1.5 g of modified adsorbents were acidified with 0.1 M HCl to pH value of 3-3.5. The volume in the beaker was made to 150 ml with distilled water after addition of 10.0 g of NaCl. Titration was then carried out with 0.1 M of NaOH to pH value of 4.0 and then to pH value of 9.0. The volume V (ml), required to raise the pH from 4.0 to 9.0 was noted and the specific surface area was computed from the following equation [20].

$$S(\text{m}^2/\text{g}) = 32V - 25 \quad (3)$$

Determination of the zero point charge: The zero point charge was determined using 0.01 M solution of NaCl as an electrolyte and by adding 0.1 M solutions of HCl. For this purpose, the pH of eight beakers containing 50 mL of electrolyte was set to the desirable values in the range of 2 to 12. Then 2 gram of adsorbent was added into each beaker and shaken for 48 hours. After completion of the reaction, the adsorbent was filtered and the final pH of each beaker was measured. By plotting the initial pH versus the pH after 48 hours of agitation, the zero point charges of the adsorbents were determined, which were found to be 6.5 for modified bagasse and coffee husk.

2.5. Regeneration of the Spent Adsorbents

Regeneration tests for saturated modified adsorbents were carried out by adding 2 g/L of spent adsorbent in 2 M solution of NaOH. For adsorbent saturation, 2 g/L of adsorbent were let in contact with 250 mL solution containing 100 mg/L calcium or magnesium and stirred at 200 rpm until equilibrium time was reached (120 minutes). The spent of the adsorbents were filtered, washed and dried at 55 °C for 24 h. The dried spent adsorbents were let in contact of 2 N NaOH for 2 hours; then filtered, washed several times with deionized water and dried at 55 °C for 24 h. The regenerated adsorbents were then tested for the

adsorption of calcium and magnesium and the regeneration percentage were calculated based on the comparison of the removal efficiencies of fresh and regenerated adsorbents.

3. Result and Discussion

3.1. Adsorbent Characteristics

The various physical and chemical characteristics of the AC for both coffee husk and bagasse are represented in table 3.1.

Table 3.1. Physico-Chemical properties.

Parameters	ABC	ACHC
pH _{zpc}	7.58	103
BET (m ² /g)	546.6	410
Mesh size	500µm	500µm

The modified adsorbents were characterized by means of instrumental techniques called Transform Infrared spectroscopy (FTIR) and BET surface area.

The specific surface area of the adsorbents was measured using the BET technique. It showed a significantly higher specific surface area for the ABC and CHC, 546.60 and 410 m²/g respectively. The remarkable improvement of the surface area can most likely be attributed to the removal of components occupying the pores of the AC resulting in more accessible pores and consequently larger surface area.

3.1.1. Infrared Spectral Analysis

The adsorption of Ca and Mg ions on bagasse and coffee husk were also affected by other interactions between functional groups of Ca and Mg and bagasse, coffee husk in addition to electrostatic interaction. FTIR analyses were conducted in order to identify possible locations for these interactions. The result is presented in figure 3.1 (a and b). As it can be seen, the FTIR spectra of Ca and Mg ions, bagasse and coffee husk and after adsorption are discussed below.

3.1.2. FTIR Spectra of Bagasse

FTIR spectra of bagasse has a broad band centered between 3154.63 cm⁻¹ and 3334.98 cm⁻¹ (hydrogen bonded OH), the band at 2853.73 to 2954.03 cm⁻¹ (–CH₂ and –CH₃ asymmetric and symmetric stretching), the peak at 1774.54 cm⁻¹ (associated with C=O carbonyl), the peaks at 1590.34 cm⁻¹ and 1462.07 cm⁻¹ (associated with the aromatic ring of lignin) and the large peak at 1022 to 1249.89 cm⁻¹ (associated with the C-O bond bending of cellulose). FTIR spectra of SBC show peaks at 3568.37 cm⁻¹. This could be due to (N-H stretching), 1590.34 cm⁻¹ (N=N stretching), 1462.07 cm⁻¹ (aromatic C-C stretching), and 1377.20 cm⁻¹ (S-O bending).

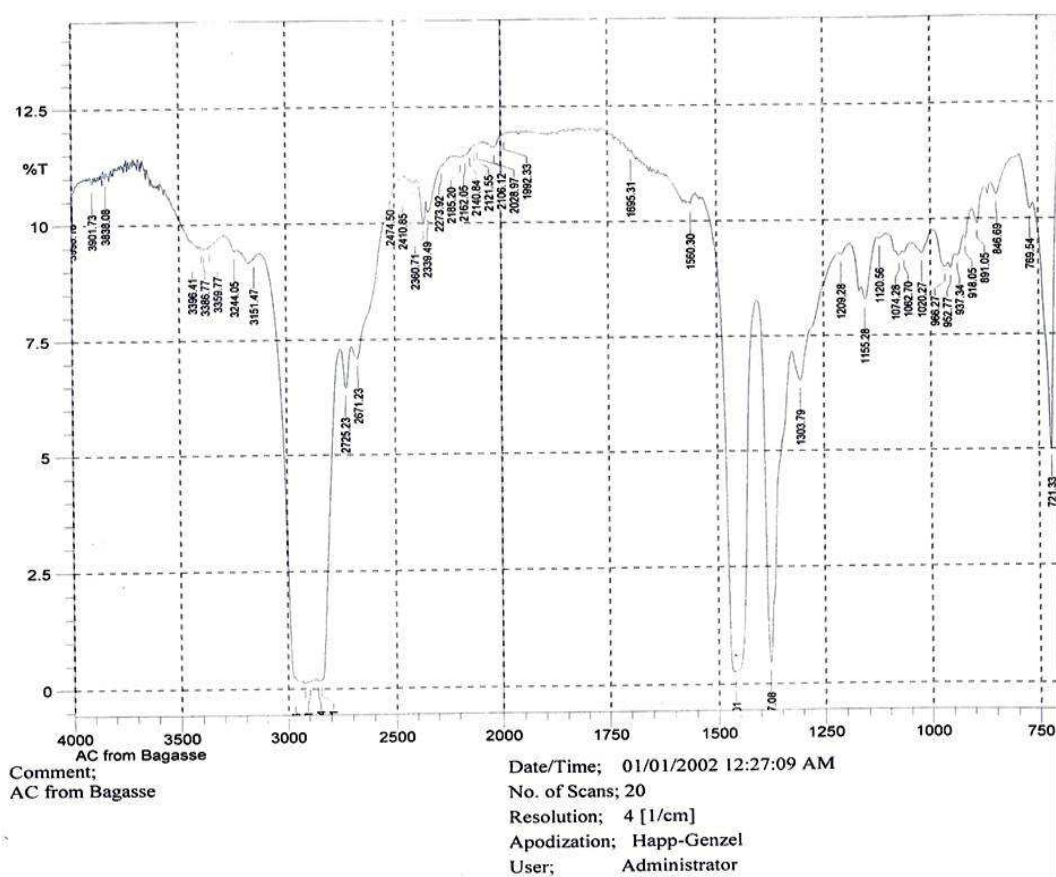


Figure 3.1. (a) FTIR spectral analysis of AC from Sugar cane bagasse.

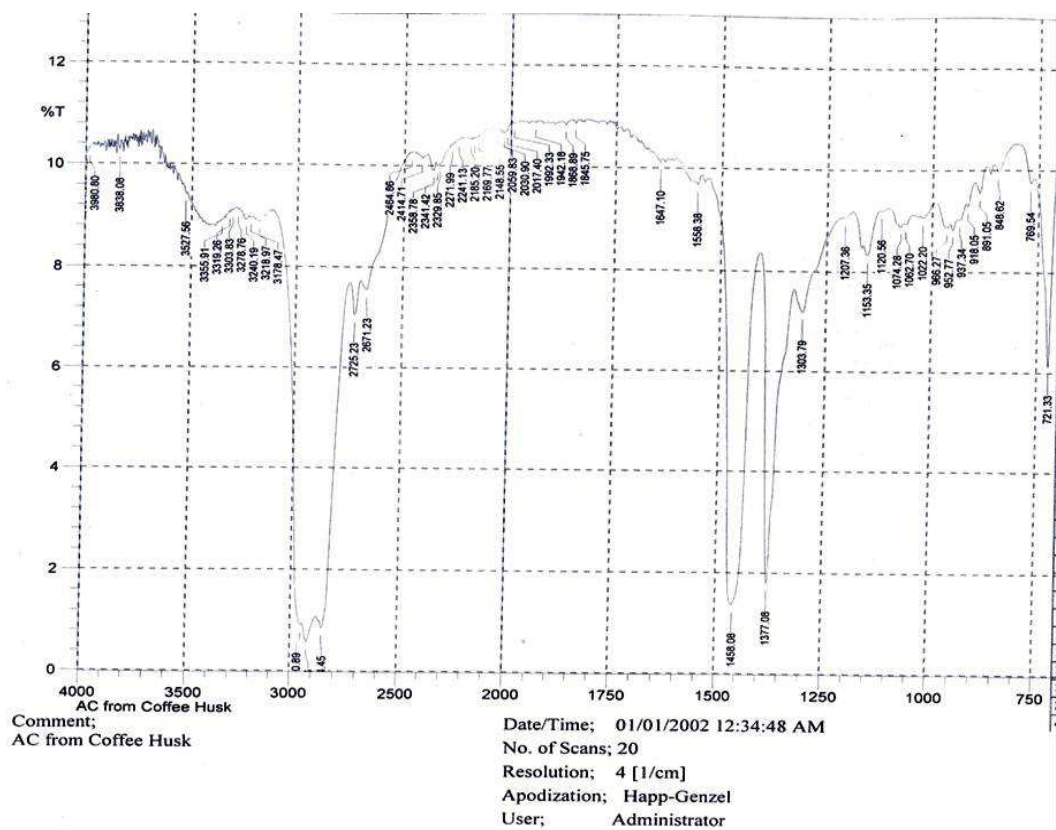


Figure 3.1. (b) FTIR spectral analysis of AC from coffee husk.

3.1.3. FTIR Spectral Analysis of Coffee Husk

The FTIR spectral analysis shows that several functional groups are available on the surface of coffee husk for binding hardness causing agents hardness causing divalent ions. The result was shown in fig 3.2 (b), Wavelengths corresponding to their respective functional groups. Therefore, the wavelengths appeared in the graph i.e. 3431, 2925, 1726, 1652 and 1450 indicates the applicability of $-\text{OH}$, $-\text{CH}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$, $-\text{COO}$ respectively. The FTIR spectra obtained for the activated coffee husk samples are shown in Fig. 1. The broad band at about 3400 cm^{-1} included many vibration modes mainly attributed to $-\text{OH}$ groups with a minor contribution of $-\text{NH}$ functional groups. The presence of methyl and methylene groups is confirmed by the two sharp peaks at 2925 cm^{-1} and 2855 cm^{-1} attributed to asymmetric and symmetric stretching of $\text{C}-\text{H}$ bonds in aliphatic chains.

The peaks located at 1737 and 1633 cm^{-1} are characteristics of carbonyl group stretching from cellulose and ketones. The presence of $-\text{OH}$ group, along with carbonyl group, confirms the presence of carboxylic acid groups in the biosorbent. The peaks at 1508 cm^{-1} are associated with the stretching in aromatic rings. The peaks observed at 1071 and 1024 cm^{-1} are due to $\text{C}-\text{H}$ and $\text{C}-\text{O}$ bonds. The $-\text{OH}$, $-\text{NH}$, carbonyl and carboxylic groups are important sorption sites.

3.2. pH Point of Zero Charge

The point of zero charge of the adsorbent ABC and ACHC were assessed from the graph of final pH versus initial pH for 0.5 g of the adsorbents. The results are presented in figure 3.2 (a and b). As shown from the graphs, the values of pH_{pzc} of an adsorbent are determined from the points where the initial pH equals the final pH. The pH_{pzc} values are 7.50 and 8.103 for ABC and ACHC respectively. As presented in the graphs it seems that, the adsorbents were negatively charged at pH greater than the pH_{pzc} and below pH_{pzc} there was a charge reversal.

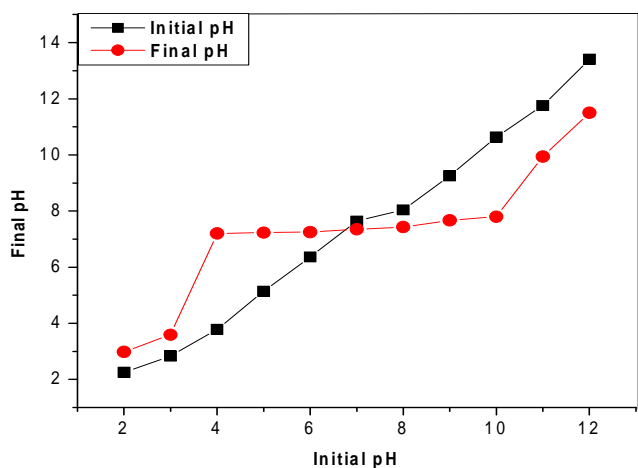


Figure 3.2. (a) pH point zero charge (pHpzc) for ABC.

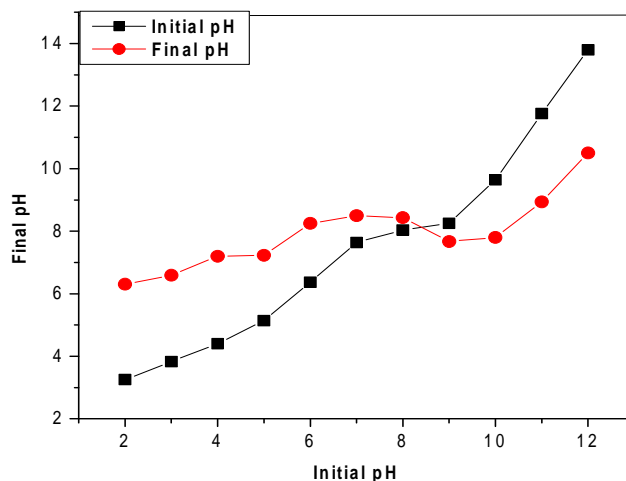


Figure 3.2. (b) pH point zero charge (pHpzc) for ACHC.

It has been reported by earlier researchers that, the pH_{pzc} of an adsorbent increases with increase in basic groups on the surface of the adsorbents [19]. This is due to that, the adsorbents have basic surfaces since the pH_{pzc} values is greater than 7.

From the results, it can be concluded that alkali modification of the adsorbent gave a negative (basic) surface charge for the adsorbent. The relationship between pH_{pzc} and adsorption capacity is that cations adsorption on any adsorbent will be expected to increase at pH value higher than the pH_{pzc} while anions adsorption will be favorable at pH values lower than the pH_{pzc} [21].

3.3. Batch Activated Carbon Filtration

In the present study, alkali treated bagasse and coffee husk are used as an adsorbent for water hardness causing constituents from aqueous solutions and polluted water. Based on the results obtained, the effects of these parameters are discussed in the subsequent sections.

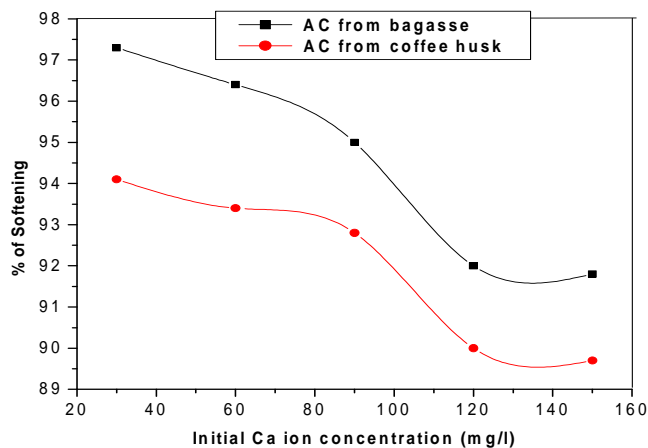


Figure 3.3. Effect of initial Ca hardness concentrations on softening efficiency (2 g adsorbent, pH 6.5, room temperature, agitation speed 200 rpm).

Effect of the contact time and initial hardness agent concentration: The effects of the initial calcium and magnesium concentrations and the contact time on the softening efficiency of ABC and ACHC are illustrated in figure 3.3. As it can be seen, adsorption efficiency was improved by increasing the contact time and decreased by increasing the initial ions concentration.

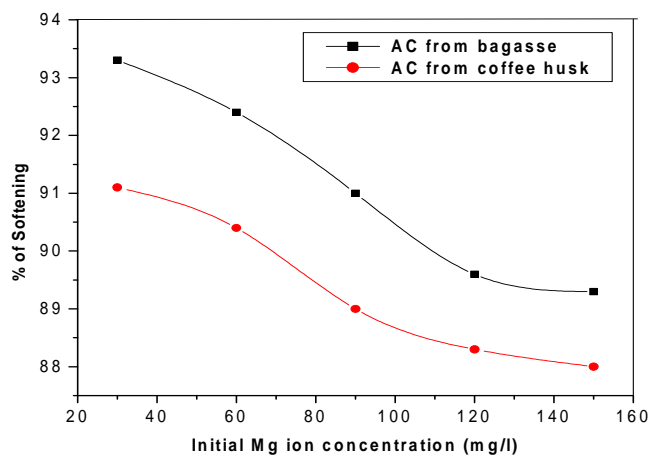


Figure 3.4. (a) Effect of initial Mg ion concentrations on softening efficiency (2 g adsorbent, pH 6.5, room temperature, agitation speed 200 rpm).

Accordingly, for an initial metal concentration of 120 mg/L, 97% and 94.1% of calcium and 90.8% and 93.3% of magnesium were adsorbed by ABC and ACHC respectively, showing for both adsorbents a higher affinity for calcium over magnesium. Furthermore, alkali modification of both adsorbents improved the adsorption capacity toward both tested cations.

The effect of contact time on Ca and Mg ions was investigated by varying the contact time (30-150 min), while other parameters were kept constant. The result is presented in figure 3.4 and 3.5. As it can be seen in the figure, softening efficiency increased with an increasing in contact time before equilibrium is reached and after equilibrium removal efficiency would be constant.

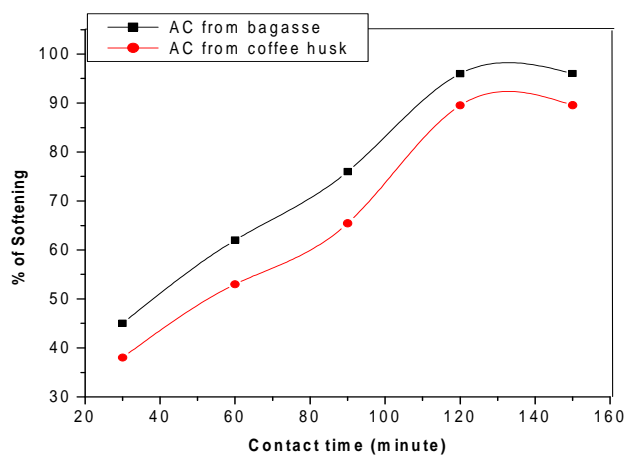


Figure 3.4. (b) Effect of contact time on softening efficiency of calcium hardness (2 g/L adsorbent, pH 6.5, room temperature, agitation speed 200 rpm and at 120 mg/l initial concentration)

The optimum time observed for removal of 96.1% and 93.4 % of Ca and Mg hardness were 120 min. There was no appreciable increase in percentage removal of total hardness after these optimum times. As shown in Figure 3.4(b) and 3.5, the adsorption process took place in two stages. The first stage was rapid. This may be due to that, at the start large number of vacant surface site may be available for adsorption process. The second stage represented a slower progressive adsorption. The reason is that, the remaining vacant surface sites may be exhausted due to repulsive forces between the solute molecules of solid and bulk phase [24],[26]. With the progressive occupation of these sites, the process becomes slower in the second stage. Moreover the initially deposited metal ions penetrate to the interior of the sorbent through intra-particle diffusion which was slower process. This was similar with the observations of other studies [21], [24,].

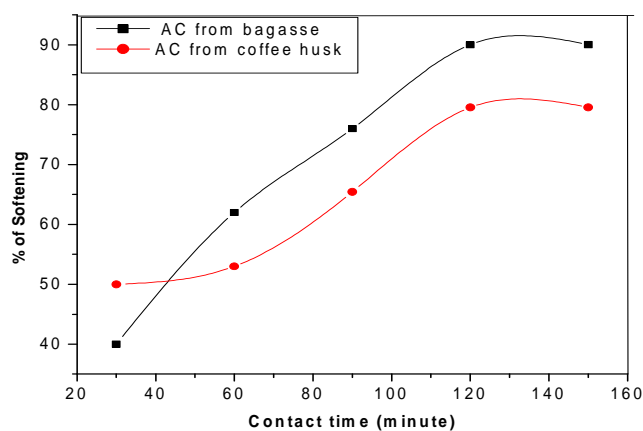


Figure 3.5. Effect contact time on softening efficiency of magnesium hardness (2 g/L adsorbent, pH 6.5, room temperature, agitation speed 200 rpm, 120 mg/l).

Surface adsorption and ion exchange can be considered as the driving forces of ion removal. While bonding of metal ions to the surface can be considered as the main mechanism responsible for metal uptake by natural pumice, in addition to surface adsorption, ion exchange can also be involved in the case of the alkali-modified pumice leading to a remarkable enhancement of the adsorption capacity [19]. Furthermore, alkali modification can contribute to the removal of impurities, which can unblock some pores improving accessibility to the active adsorption and ion exchange sites of the modified sample. Removal efficiency also showed an increase with the initial metal concentration, which can be attributed to an increase of the concentration gradient increasing the driving force [24].

Effect of the pH and the adsorbent mass: The pH of the solution should be considered as an important factor affecting metal adsorption process due to its impact on the degree of ionization of metal specie and the surface charge of the adsorbent. The effect of pH of the reaction mixture on the adsorption efficiency at various adsorbent doses was examined in order to optimize the adsorbent dosage and the pH. According to the results summarized in fig 3.6 and 3.7, the highest adsorption capacity towards Ca^{+2} and Mg^{+2} ions

was achieved at pH = 6.5 for ABC and ACHC and for all tested dosages. This optimal pH was in accordance with the zero point charge values (6.50 and 8.310 for ABC and ACHC respectively).

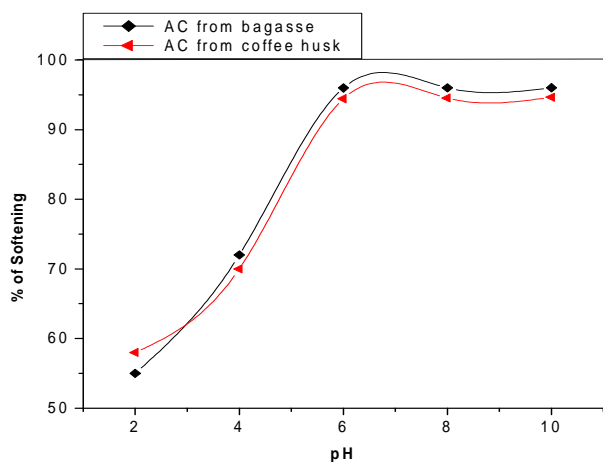


Figure 3.6. Effect of pH on softening of calcium hardness (contact time 120 min, ions concentration 120 mg/L, room temperature, 200 rpm agitation).

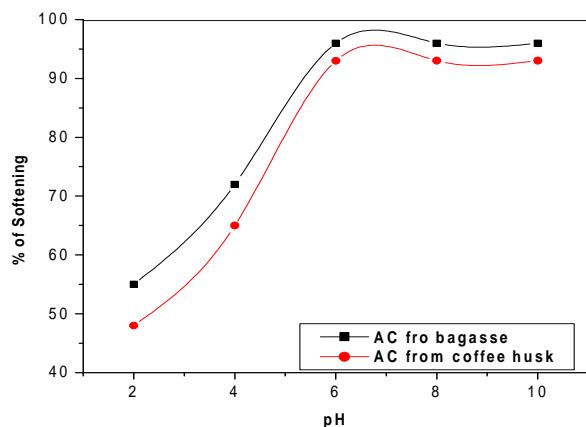


Figure 3.7. Effect of pH on softening of magnesium hardness (contact time 120 min, ions concentration 120 mg/L, room temperature, 200 rpm agitation).

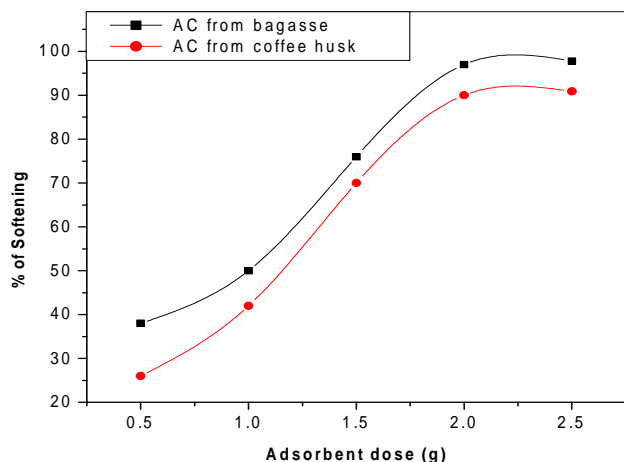


Figure 3.8. Effect of adsorbents dose on softening of calcium hardness (contact time 120 min, ions concentration 120 mg/L, room temperature, 200 rpm agitation).

The removals of water hardness causing constituents by ABC and ACHC at different dose (0.5 - 2.5 g) for the constant Ca and Mg concentration of 120 mg/l are investigated. Results are presented in figure 3.8 and 3.9. The percentage removal of Ca and Mg increases from 37.0 to 96.2% with an increase in the activated bagasse and coffee husk carbon amount from 0.5 to 2.5 g respectively. This is due to the increasing of the adsorption sites available for adsorption.

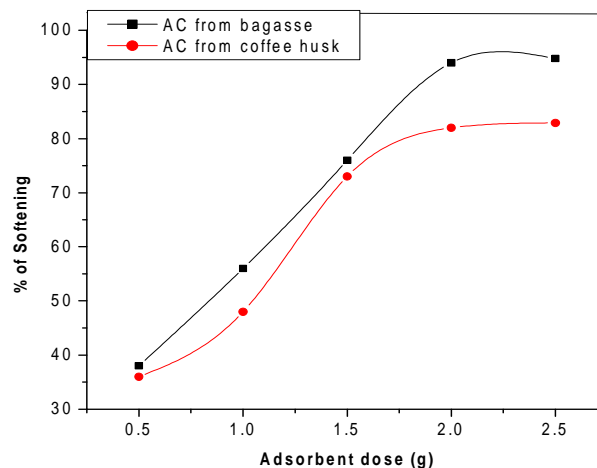


Figure 3.9. Effect of adsorbent dose on softening of magnesium hardness (contact time 120 min, ions concentration 120 mg/L, room temperature, 200 rpm agitation).

As it shows in fig 3.6 and 3.7 of the pH, 79 and 96% of calcium and 51 and 93% of magnesium were removed by 2 g/L of the ABC and ACHC adsorbents, respectively. The lower removal efficiencies observed in acidic medium (i.e. pH in the range 2-5) can be attributed to the protonation of adsorbent functional groups or competition of H^+ with metal ions to bind and occupy the active sites of the adsorbents. On the other hand, in alkaline environment (i.e. pH in the range 7-10), the formation of metal hydroxide can be considered as the main reason for decreasing metal uptake. Similar results were reported [26]. The highest removal capacity at pH=7.5, namely close to the zero point charges of both adsorbents, confirms that the studied adsorbents can be considered as promising low cost adsorbents suitable for the softening of hardness ions from drinking water.

The linear increase of the adsorption capacity for increasing adsorbent dosage indicated the accessibility of a larger number of sorption sites at higher dosage to adsorb calcium and magnesium ions. Contrarily, in the removal of calcium using raw and modified sugar cane bagasse, adsorption capacity remained constant above 100 mg adsorbent.

Effect of the temperature: The temperature effect in the range of 10 °C to 60 °C was studied and thermodynamic parameters were calculated. As shown in Fig 3.10, while the effect of temperature on magnesium adsorption seemed to be negligible, a low maximum for the adsorption of calcium was absorbed at 20 °C.

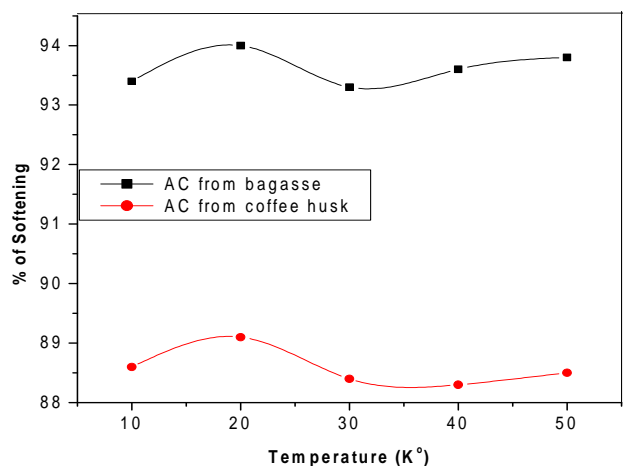


Figure 3.10. Effect of temperature on softening of Calcium hardness (contact time 120 min, ions concentration 120 mg/L, 2 g adsorbents, 200 rpm agitation).

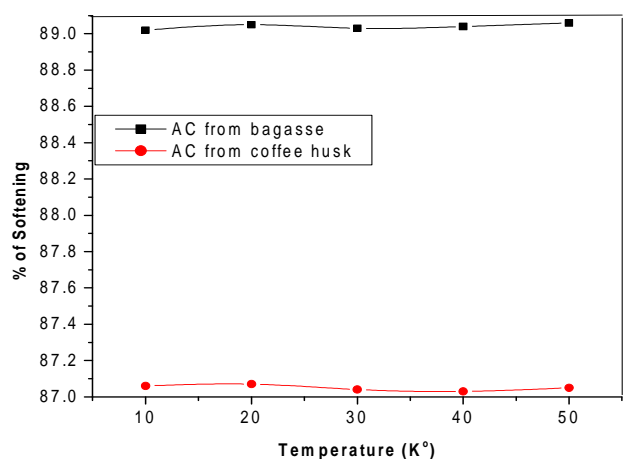


Figure 3.11. Effect of temperature on softening of magnesium hardness.

3.4. Regeneration of the Saturated Adsorbents

Regeneration experiments were conducted to study the reusability of the spent adsorbents, which is a very important parameter in terms of economic feasibility of the developed process. Regeneration using sulphuric acid solution was carried out on the spent bagasse and coffee husk samples. As it were shown in the figure below, maximum recovery of the adsorbed calcium and magnesium was achieved in less than 200 minutes leading to 78 and 73% desorption of the adsorbed calcium and magnesium at 97 and 93% of the adsorbed calcium and magnesium from ABC and ACHC respectively. Furthermore, maximum cation desorption for saturated carbon were observed after 300 min of regeneration, while only 200 min of regeneration was needed to achieve maximum cation desorption of the saturated modified adsorbent. It should be noticed that even if the modified sugar cane bagasse showed higher sorption capacity for calcium and magnesium rather than modified coffee husk, its regeneration potential was lower than that of the activated carbon from bagasse.

Generally, Ca and Mg recovery and adsorbent regeneration

under 8 cycles of adsorption and desorption (n) are presented in fig 3.12 and 3.13. As the n increased, the percentage of Ca and Mg recovered and adsorbent regeneration and also Ca and Mg removal, until 4 of these cycles slightly decreased and after that, until 8, sharply decreased. It is shown that ABC and ACHC can be reused for softening/regeneration processes; but after that, it loses its softening/regeneration ability and its performance drops down.

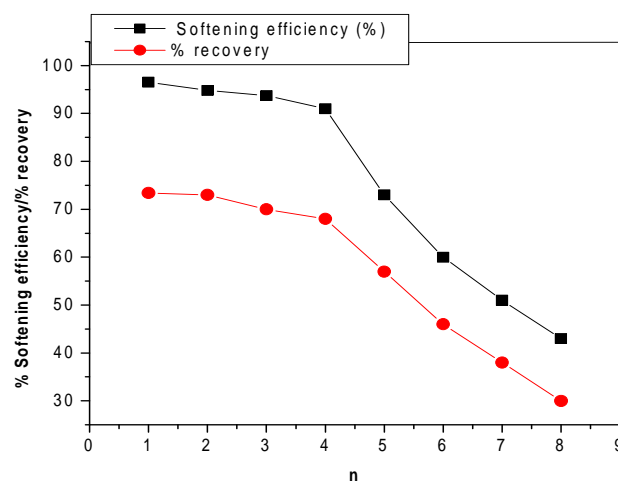


Figure 3.12. Successive softening/regeneration efficiency of Ca hardness.

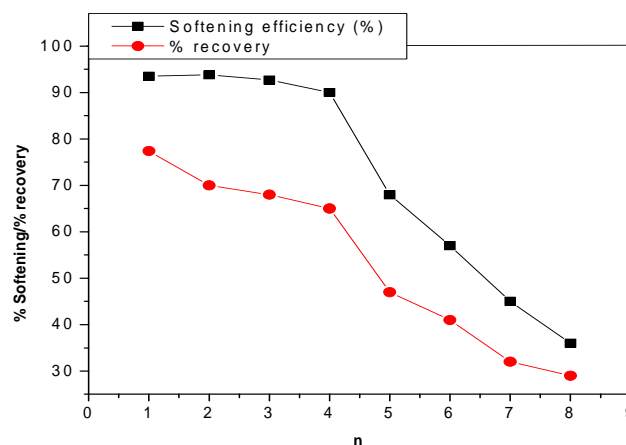


Figure 3.13. successive softening/regeneration efficiency of Mg hardness.

4. Conclusion

Softening of hard water by removing Ca^{2+} and Mg^{2+} cations was studied using alkali-modified sugar cane bagasse and coffee husk as adsorbents. Increasing the mass of adsorbent, the contact time and decreasing the initial ions concentration leads to an increase of cations removal. The studied adsorbents showed a higher selectivity for calcium adsorption if compared to magnesium in ABC than ACHC. Both adsorbents are efficient to adsorb water hardness causing constituents; but, ABC is more critical than ACHC. After treating synthetic water solution simulating an actual water stream with the alkali modified activated bagasse and activated coffee husk, total hardness of the treated sample met the required standard for drinking water.

Acknowledgement

This paper was sponsored by Jigjiga University under Research and Community Service Directorate as part of the 2014 funded proposal. I am grateful to Haramaya University and Ethiopian pharmaceutical factory for their cooperation in AAS and FTIR analysis and characterization respectively.

References

- [1] AWWA, Standard Methods for the Examination of Water and Wastewater, 20th ed., Washington, DC, 2005.
- [2] O.K. Jinior, L.V.A. Gurgel, L.F. Gil, Removal of Ca(II) and Mg(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD), *Carbohydr. Polym.* 79 (2010) 184–191.
- [3] A. Zuorro, R. Lavecchia, S. Natali, Magnetically modified agro-industrial wastes as efficient and easily recoverable adsorbents for water treatment; *chemical engineering transactions* Vol. 38, 2014.
- [4] Ami Cobb, Low-Tech Coconut Shell Activated Charcoal Production, *International Journal for Service Learning in Engineering* Vol. 7, No. 1, pp 93-104, (2012).
- [5] D. Bruggen, C. Vandecasteele, Removal of pollutants from surface water and groundwater by nano filtration: Overview of possible applications in the drinking water industry, *Environ. Pollut.* 122 (2003) 435–445.
- [6] M.R. Teixeira, M.J. Rosa, The impact of the water background inorganic matrix on the natural organic matter removal by nanofiltration, *J. Membr. Sci.* 279 (2006) 513–520.
- [7] M. Yan, D. Wang, J. Ni, J. Qu, Y. Yan, C.W.K. Chow, Effect of polyaluminum chloride on enhanced softening for the typical organic-polluted high hardness North-China surface waters, *Sep. Purif. Technol.* 62 (2008) 401–406.
- [8] K. Suzuki, Y. Tanaka, T. Osada, M. Waki, Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration, *Water Res.* 36 (2002) pp 2991–2998.
- [9] A. Dimirkou, M.K. Doula, Use of clinoptilolite and an Fe-overexchanged clinoptilolite in Zn^{2+} and Mn^{2+} removal from drinking water, *Desalination*. 224 (2008) 280–292.
- [10] R. Sheikholeslami, Composite scale formation and assessment by the theoretical Scaling Potential Index (SPI) proposed previously for a single salt, *Desalination* 278 (2011) 259–267.
- [11] L. Fu, J. Wang, Y. Su, Removal of low concentrations of hardness ions from aqueous solutions using electrodeionization process, *Sep. Purif. Technol.* 68 (2009) 390–396.
- [12] J.S. Park, J.H. Song, K.H. Yeon, S.H. Moon, Removal of hardness ions from tap water using electromembrane processes, *Desalination* 202 (2007) 1–8.
- [13] S.J. Seo, H. Jeon, J.K. Lee, G.Y. Kim, D. Park, H. Nojima, J. Lee, S.H. Moon, Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, *Water Res.* 44 (2010) 2267–2275.
- [14] C.W. Li, J.C. Liao, Y.C. Lin, Integrating a membrane and a fluidized pellet reactor for removing hardness: effects of NOM and phosphate, *Desalination* 175 (2005) 279–288.
- [15] J.N. Apell, T.H. Boyer, Combined ion exchange treatment for removal of dissolved organic matter and hardness, *Water Res.* 44 (2010) 2419–2430.
- [16] H. Faghihian, M.G. Maragheh, H. Kazemian, The use of clinoptilolite and its sodium form for removal of radioactive caesium, and strontium from nuclear wastewater and Pb^{++} , Ni^{++} , Cd^{++} , Ba^{++} from municipal wastewater, *Appl. Radiat. Isot.* 4 (1999) pp 655–661.
- [17] H. Kazemian, H. Modarres, H.G. Mobtaker, Evaluating the performance of an Iranian natural clinoptilolite and its synthetic zeolite P for removal of Cerium and Thorium from nuclear wastewaters, *J. Radioanal. Nucl. Chem.* 258 (2003) 551–556.
- [18] Seifi *et al.* Adsorption of BTEX on surfactant modified granulated natural zeolite nanoparticles: parameters optimizing by applying Taguchi experimental design method, *Clean-Soil, Air, Water*, 39 (2011) pp 939–948.
- [19] Sepehr *et al.* (2013) Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary systems, *Applied Surface Science*, pp 295–305, Vol. 03 (42)
- [20] N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, Biosorption of heavy metals from aqueous solutions by chemically modified orange peel, *J. Hazard. Mater.* 185 (2011) 49–54.
- [21] B. Ersoy, A. Sariisik, S. Dikmen, G. Sariisik, Characterization of acidic pumice and determination of its electrokinetic properties in water, *Powder Technol.* 197 (2010) 129–135.
- [22] B. Ozturk, Y. Yildirim, Investigation of sorption capacity of pumice for SO_2 capture, *Process Saf. Environ. Prot.* 86 (2008) 31–36.
- [23] M.R. Panuccio, A. Sorgona, M. Rizzo, G. Cacco, Cadmium adsorption on vermiculite, zeolite and pumice: Batch experimental studies, *J. Environ. Manage.* 90 (2009) 364–374.
- [24] F. Akbal, Sorption of phenol and 4-chlorophenol onto pumice treated with cationic surfactant, *J. Environ. Manage.* 74 (2005) 239–244.
- [25] H. Kazemian, M.H. Mallah, Elimination of Cd^{2+} and Mn^{2+} from Wastewaters Using Natural Clinoptilolite and Synthetic Zeolite-P, *Iran. J. Chem. Chem. Eng.* 25 (2006) 91–94.
- [26] F. Gode, E. Moral, Column study on the adsorption of Cr(III) and Cr(VI) using Pumice, Yarıkkaya brown coal, Chelex-100 and Lewatit MP 62, *Bioresour. Technol.* 99 (2008) 1981–1991.