Kane Harlow

Environmental Monitoring and Control

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About the Book

Environmental Monitoring evaluates the quality of the environment along with the impact of human activities on it. The increasing environmental degradation has fueled the research in this field. It includes the monitoring of air, water, soil, etc. This book attempts to understand the multiple branches that fall under the discipline of environmental monitoring and how such concepts have practical applications. It elucidates the concepts and innovative models around prospective developments with respect to this field. This book will serve as a reference to a broad spectrum of readers including environmentalists, ecologists, researchers, professionals and students associated with this field at various levels.

About the Editor

Kane Harlow holds a master's and doctoral degree in environmental science from a public research university in United Kingdom. He has worked extensively in the field of sustainable development in various domains (life science, environment, etc.). His academic and research interests lie in sustainable agricultural design. Harlow has been the recipient of several awards and research grants in his career of over two decades. He has more than 150 articles and journal papers in the field of environmental science to his credit.

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Edited by Kane Harlow

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PREFACE

This book has been an outcome of determined endeavour from a group of educationists in the field. The primary objective was to involve a broad spectrum of professionals from diverse cultural background involved in the field for developing new researches. The book not only targets students but also scholars pursuing higher research for further enhancement of the theoretical and practical applications of the subject.

Environmental Monitoring evaluates the quality of the environment along with the impact of human activities on it. The increasing environmental degradation has fueled the research in this field. It includes the monitoring of air, water, soil, etc. This book attempts to understand the multiple branches that fall under the discipline of environmental monitoring and how such concepts have practical applications. It elucidates the concepts and innovative models around prospective developments with respect to this field. This book will serve as a reference to a broad spectrum of readers including environmentalists, ecologists, researchers, professionals and students associated with this field at various levels.

It was an honour to edit such a profound book and also a challenging task to compile and examine all the relevant data for accuracy and originality. I wish to acknowledge the efforts of the contributors for submitting such brilliant and diverse chapters in the field and for endlessly working for the completion of the book. Last, but not the least; I thank my family for being a constant source of support in all my research endeavours.

Editor

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

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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

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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°21′N42°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

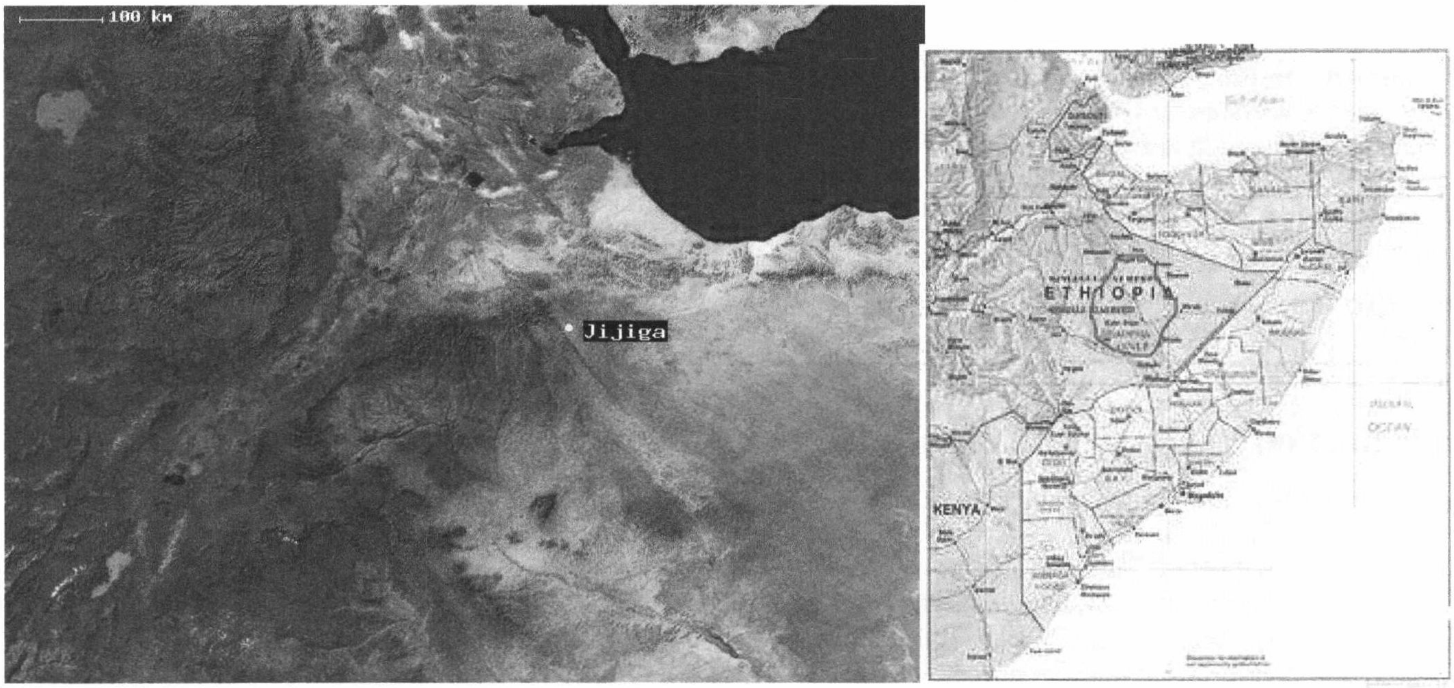

Figure 1.1. *Map of the study area.*

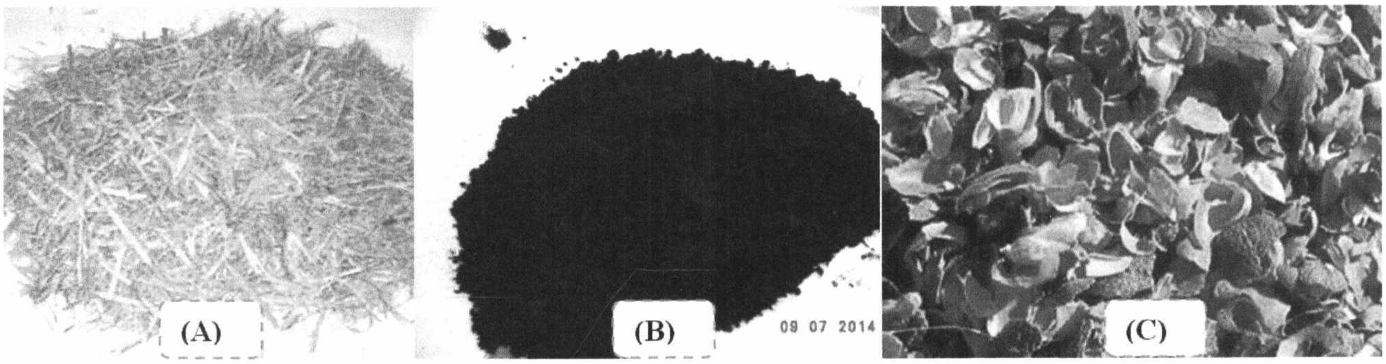

Figure 1.2. *Shows (A) Raw sugarcane bagasse, (B) Alkali activated carbon, (C) Raw Coffee Husk.*

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 $MgSO_4 . 7H_2O$ 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) purchazed 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 μm. 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 °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 (Qe) was determined as follows (Eq. 1 and 2):

$$R(\%)=[(Ci-Ce)/Ci]\times 100 \quad (1)$$

$$Q_e\,(mg/g) = [(Ci-Ce)/m]V \quad (2)$$

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 asses 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].

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

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
pHzpc	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 m^2/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}($-CH_2$ and $-CH_3$ 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).

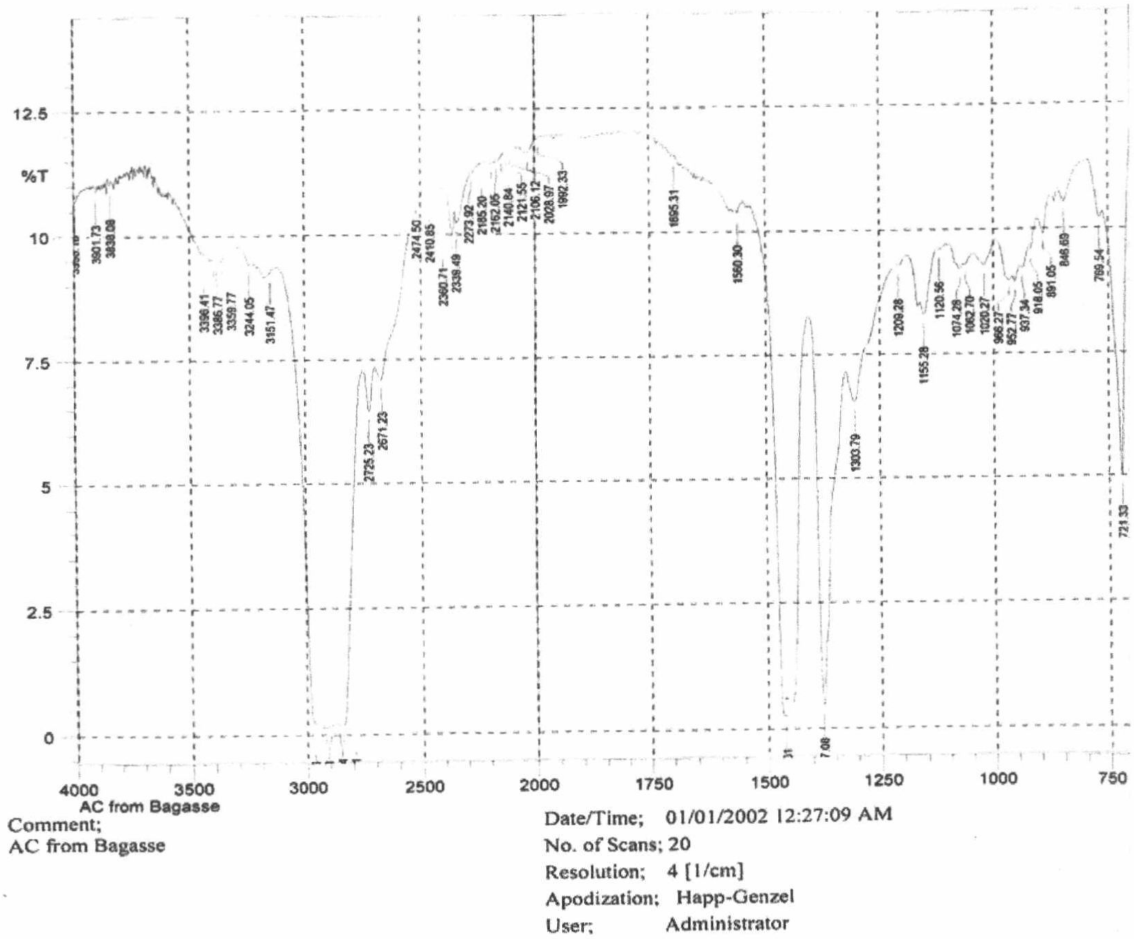

Figure 3.1. (a) *FTIR spectral analysis of AC from Sugar cane bagasse.*

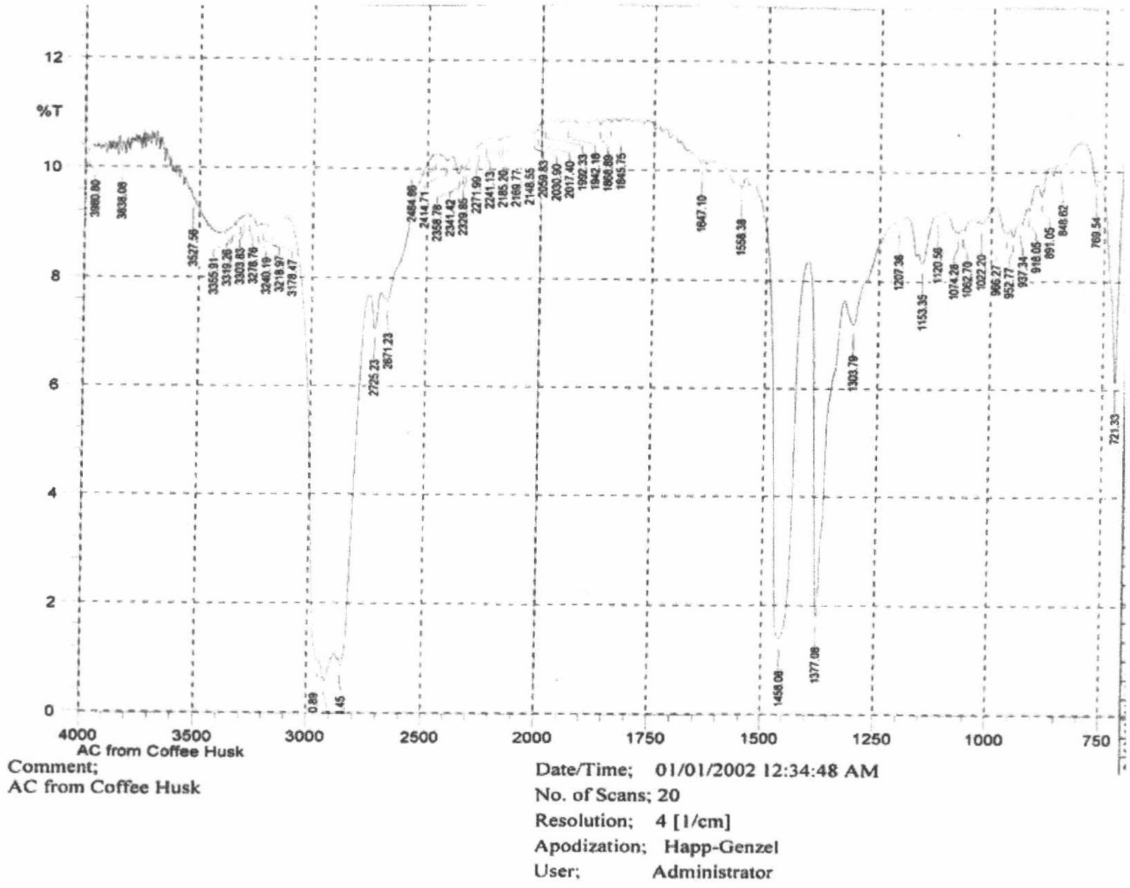

Figure 3.1. (b) *FTIR spectral analysis of AC from coffee husk.*

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 –OH, -CH, C=O, C=C, -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 -OH groups with a minor contribution of -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 C- 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 -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 C-H and C-O bonds. The -OH, -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 pHpzc of an adsorbent are determined from the points where the initial pH equals the final pH. The pHpzc 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 pHpzc and below pHpzc there was a charge reversal.

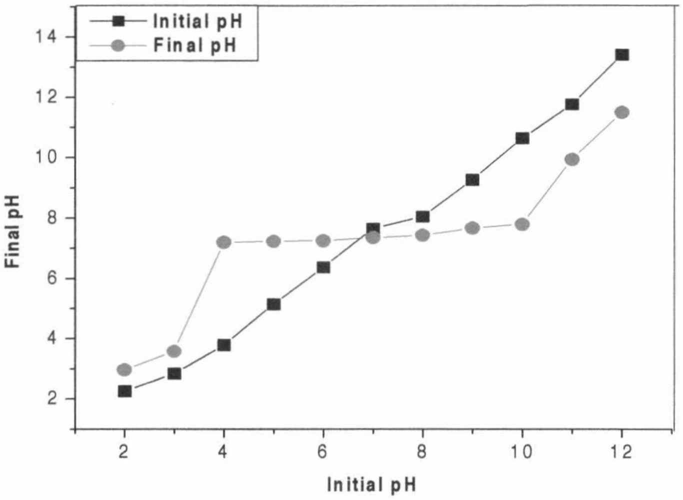

Figure 3.2. (a) pH point zero charge (pHpzc) for ABC.

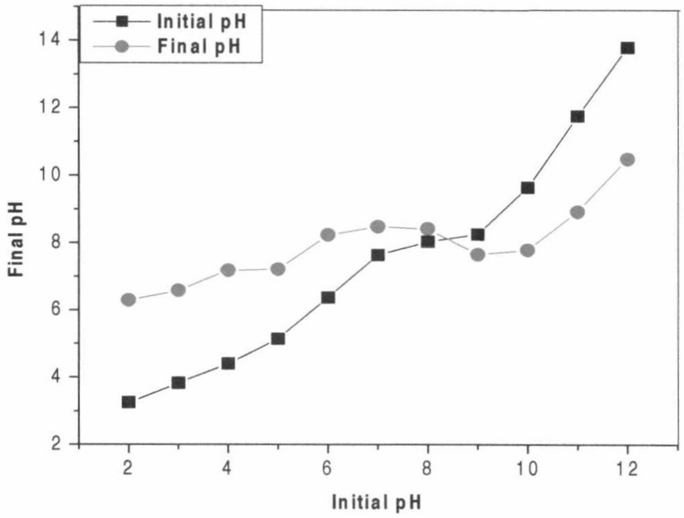

Figure 3.2. (b) pH point zero charge (pHpzc) for ACHC.

It has been reported by earlier researchers that, the pHpzc 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 pHpzc 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 pHpzc and adsorption capacity is that cations adsorption on any adsorbent will be expected to increase at pH value higher than the pHpzc while anions adsorption will be favorable at pH values lower than the pHpzc [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.

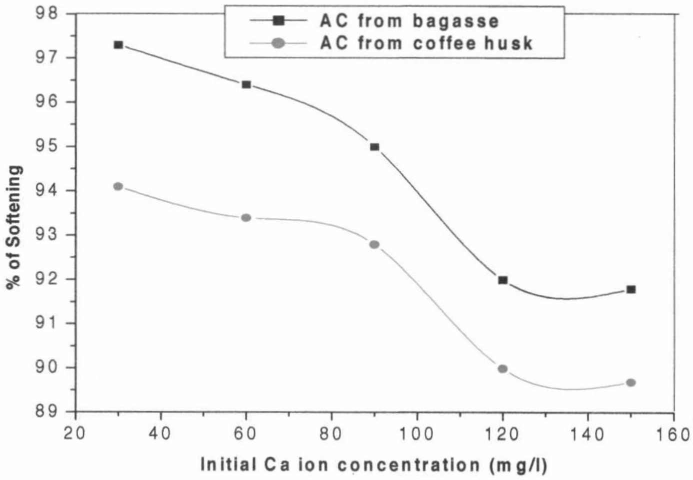

Figure 3.3. Effect of initial Ca hardness concentrations on softening efficiency (2 g adsorbent, pH 6.5, room temperature, agitation speed 200 rpm.