International Research Journal of Environment Sciences ISSN 2319–1414
Vol. **6(2),** 44-54, February **(2017)** *Int. Res. J. Environment Sci.*

Investigation on the removal of Mn(II) ions from synthetic wastewater by using a novel biocarbon

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Available online at: www.isca.in, www.isca.me
Received 30th December 2016, revised 4th February 2017, accepted 14th February 2017

Abstract

The pollution of heavy metals has extended worldwide deliberation due to their toxicity, non-degradability and accumulation in the living organisms. Therefore, treatment of wastewater contaminated by heavy metals is an important environmental concern. Manganese is the second most abundant metal in nature. In a lower concentration, Mn (II) ions and Mn (VII) ions have many valuable functions in biological systems of humans and plants. However, they become toxic at higher concentration. According to WHO, 0.05 mg/L is the maximum concentration dose of manganese admissible in drinking water. Thus, the removal of Manganese from water is imperative. In the present research work, removal of manganese (II) ions from synthetic wastewater by biocarbon generated from Acalypha indicaplant leaves was investigated by batch adsorption technique. The biocarbon was characterized using FTIR, XRD and SEM analysis. The results suggest that, the adsorption process was relatively fast and equilibrium was established at the time of 150 min. The optimum pH for manganese adsorption was 5.0 at the biocarbon dose rate of 2.5g/100mL for the maximum removal of 92.8%. The SEM micrograph shows particle grains and leaves like surfaces and FTIR analysis results shows different functional group in the biocarbon matrix such as O–H, C=O, and C=C stretching which might be responsible for the metal uptake in biosorption process.

Keywords: Acalypha indica, Manganese, Biosorption, Biocarbon, Wastewater.

Introduction

The toxic heavy metals and its substances are released from several industrial activities into aquatic environment is a major concern for human and environmental health[1,2]. Heavy metals are non-biodegradable and toxic in nature even in lower concentration and causing harmful effects to living organisms in aquatic environment[3,4]. Manganese is the second most abundant metal in earth crust. The main sources of manganese is from the industrial operations such as ceramics, dry battery cells and electrical coils, manganese alloying manufacturing and paints. It is also an essential metal for the functions of human system and enzymes activation[5].

However, it is considered as an environmental pollutant basically due to its organoleptic properties in high concentrations, it causes neurological disorders[6]. Therefore, remediation of such toxic heavy metal from industrial discharges is very important. In this context, concerted efforts have been made by several researchers and developed many methods such as filtration, chemical precipitation, chemical coagulation, flocculation, ion exchange, reverse osmosis, membrane technologies and solvent extraction[7–10]. Most of these conventional processes are ineffective and expensive, especially when the heavy metal ions are present in high concentrations. Many of the methods produces secondary effluent and large amount sludge and thereby creating disposal problem.

In addition, adsorption is the best process due to its high efficiency, simplicity of design, convenience and ease of operation and availability of different adsorbents and cost effectivenessis generally preferred for the removal of heavy metalions in wastewater treatment[11]. Commercial activated carbon is a preferred adsorbent to the removal of pollutants from wastewaters; however, its extensive use is limited dueto its higher cost[12]. As a result, a new search for cheaper and innovative adsorbent materials is started worldwide. Several researchers have reported the use of agricultural by-products and other waste materials for adsorption process for the removal of toxic heavy metals[13-20].

The main objective of this study is the use of the biocarbon generated from Acalypha indica plant leaves as a low-cost adsorbent for the removal of Mn(II) ions from synthetic wastewater. The biocarbon material was used without any surface and chemical modification. The effects of various biosorption parameters such as pH of the metal solution, initial metal ion concentration, biocarbon dose, contact time and temperature were investigated.

Materials and methods

Preparation of metal solution: The concentration of 1000 mg/L of Mn(II) ions was prepared by dissolving 3.0764g of

$MnSO_4·H_2O$ analytical grade substance in de-ionized water. Further, working solutions were prepared by dilution with de-ionized water to obtain the concentration of 25 – 100mg/L.

Preparation of biocarbon: Acalypha indica is an important medicinal plant widely distributed in agricultural fields. The plant leaves were collected and air dried for 48 h. The dried leaves were grounded in ball mills and the screened homogeneous powder was used for the preparation of biocarbon. It is prepared by treating the leaves powder with the concentrated sulphuric acid (Sp. gr.1.84) in a weight ratio of 1:1.8 (biomaterial: acid). The resulting black product is kept in an air-free oven, maintained at 160 ± 5°C for 6h followed by washing with double distilled water until free of excess acid, then dried at 105 ± 5°C. The particle size of biocarbon screened between 100 and 120µm was used. This material is used as adsorbent in the treatment of industrial wastewater[21].

Biosorption process: In the biosorption process, optimization of biocarbon does and respective contact time is very much essential. Hence, in the biosorption experiment, the contact time is kept constant at 180 min and pH of the original test solution was 5.0. The influence of biocarbon dose was carried out by varying from 0.5 – 4.0g with the initial concentration of Mn (II) as 100mg/L in eight Erlenmeyer flask of 250mL capacity. All the experimental flask were fitted in Remi orbital shaker system and equilibrated at 250rpm for predetermined contact time.

Thereafter, by fixing the biocarbon does of 2.5g/100mL. The effect of pH was carried out at in the range of 2–8. The pH of the metal solution was adjusted using 0.1M NaOH and 0.1M HCl. The effect of contact time was conducted by varying the contact time from 30 to 210 min and the effect of temperature was investigated from 30 to 80°C using a temperature controlled agitation system. The impact of initial metal ion concentration on the removal of Mn (II) ions was also performed using the concentration from 25 to 75 mg/Lat a pH value of 5.0. After the completion of each experiment, the content of the flasks was filtered and Mn (II) ions concentrations in filtrates were determined using the Perkin Elmer AAS. The amount of metal ions adsorbed in milligram per gram was determined using the mass balance equation:

$$q_e = \left(\frac{C_o - C_e}{w} \right) \times V \quad (1)$$

Where: q_e = amount of metal ions adsorbed (mg/g), V = volume of synthetic wastewater (mL), w = mass of biocarbon (g), C_o = initial metal ions concentration (mg/L) and C_e = concentration of metal ions at equilibrium (mg/L). The percent of metal ions removal was evaluated from the equation:

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (2)$$

The analytical data were analysed and standard deviations of the statistical tests were carried out using programme of analysis of variance (ANOVA) by using SPSS program.

Results and discussion

Characterization of Biocarbon: Characterization of biocarbon generated from the medicinal plant Acalypha indica is very important to evaluate the biosorption potential of pollutants in wastewater. The physico – chemical characteristics of the biocarbon is presented in the Table-1. The result reveals that, the biocarbon has good fixed carbon content (94.3%) and less ash content (1.25%). The surface area of the biocarbon particle is relatively high, which is very important for the adsorption process.

Table-1: Characterization of the Acalypha indica biocarbon (AIBC).

Sl.No	Parameters	Values
1.	pH	6.78
2.	Bulk density (g/mL)	0.85
3.	Apparent density (Kg/m^3)	1.55
4.	Moisture (%)	4.98
5.	Ash (%)	1.25
6.	Volatile matter content (%)	18.5
7.	Yield of activated carbon (%)	92.5
8.	Fixed carbon content (%)	94.3
9.	Phenol Number (mg/g)	76.2
10.	Iodine number (mg/g)	60.0
11.	Methylene blue index (mL/g)	38.4
12.	Surface area (m^2/g)	335.0

Surface Analysis by SEM: Analysis of surface morphology is an important part in characterization of biocarbon. It reveals about the presence of micropores and flake likestructure in the carbon matrix. It is believed that the porosity of the biocarbon is a function of the precursor used for the synthesis and adsorption process of the metal ions. The surface morphology of pure and metal adsorbed biocarbon is presented in the Figures-1(a) and 1(b). In the pure biocarbon there are many micro and macropores and cavities are present. It is also observed that, the surface matrix shows a lot of grooves, cracks and crevices. These are main active sites and responsible for the adsorption of metal ions. The macropores are highly developed deep inside the surface leaving greater adsorption. In Figure-2, many of the macropores are covered, which indicates the sorption of metal ions onto the biocarbon matrix[22].

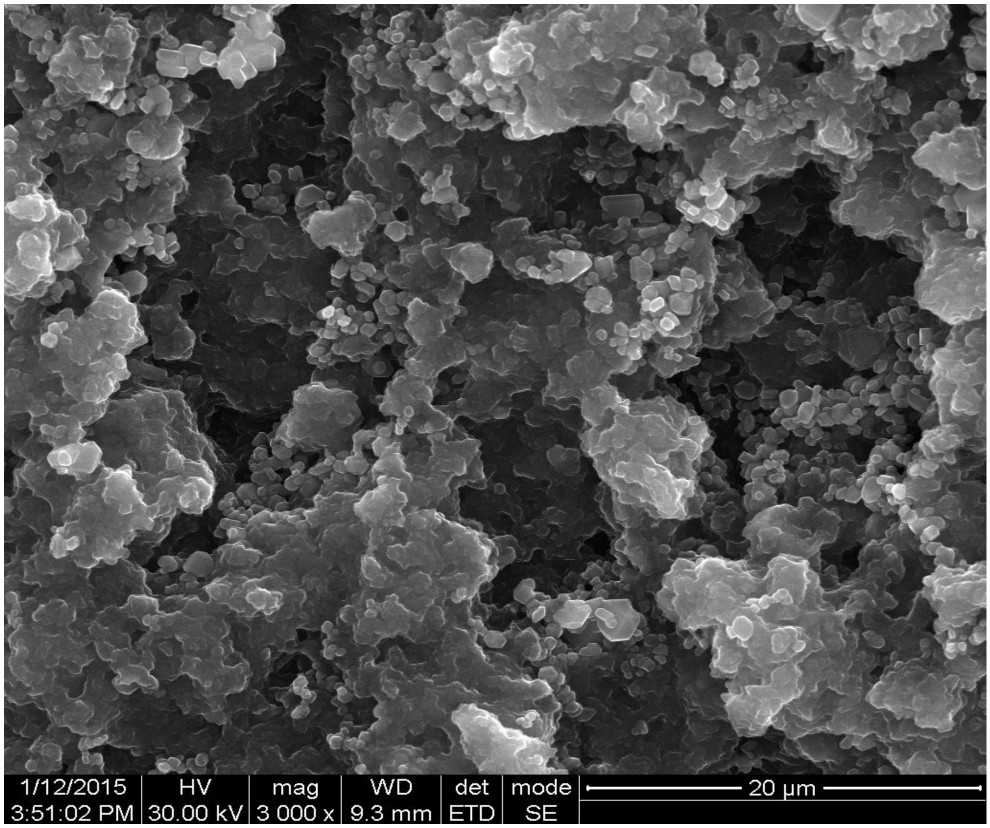

Figure-1(a): SEM photograph of pure biocarbon.

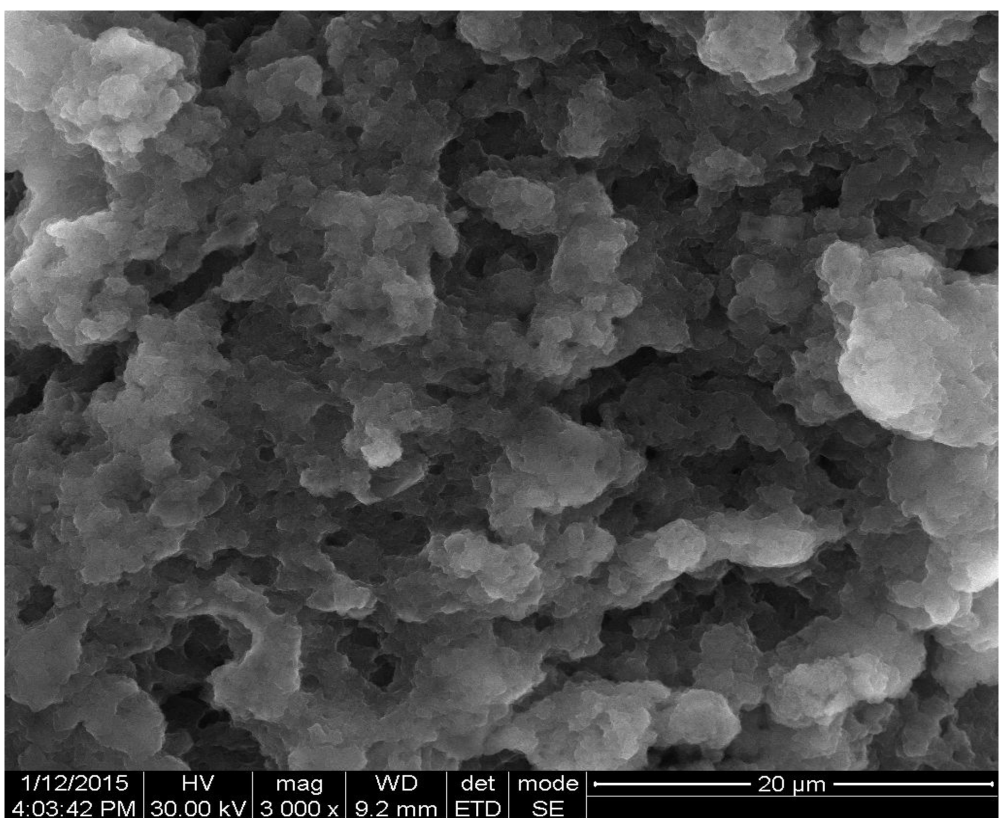

Figure-1(b): SEM photograph of biocarbon after adsorption of Mn (II) ions.

XRD Analysis: The XRD spectra of pure and metal adsorbed biocarbon are shown in Figure 2(a) and 2(b). XRD gave useful information about crystalline and amorphous phases of the adsorbent. The presence of sharp and weak peaks suggests the presence of crystalline and anamorphous phases in the adsorbent [23] and the amorphous nature of biocarbon indicates that, Mn (II) ions in solution can easily enter its surface for efficient adsorption[24].

FTIR Analysis: The FTIR spectra of pure biocarbon and after metal ions adsorption are shown in Figures-3(a) and 3(b) respectively. The peaks observed in the spectrum of the biocarbon indicated that, it is composed of specific functional groups responsible for binding of the metal ions. The bands at 3730.33cm^{-1} and 3766.98cm^{-1} correspond to the inner OH stretching vibration, while that at 3637.75cm^{-1} represents the outer surface OH stretching vibrations present in the biocarbon. The band observed around 2922.16cm^{-}1 is attributed to C–C stretching vibration. The band at 1701.22cm^{-1} to 1724.36cm^{-1} is ascribed to carbonyl C–O groups[25]. The bands observed in the region between 1681.93cm^{-1} and 1421.54cm^{-1} were attributed to C=C symmetrical stretching and C=O of carboxylic groups present in the biocarbon matrix[26].

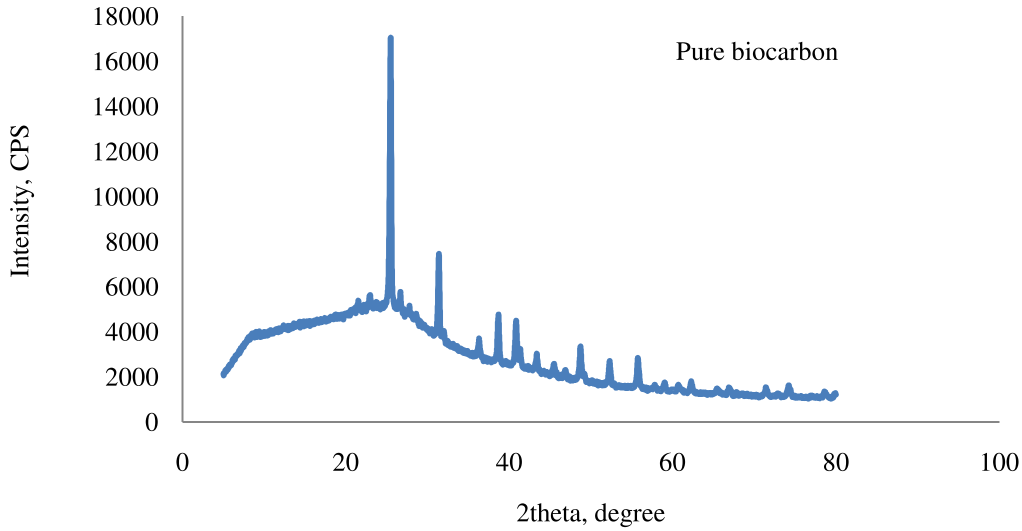

Figure-2(a): XRD pattern of pure biocarbon.

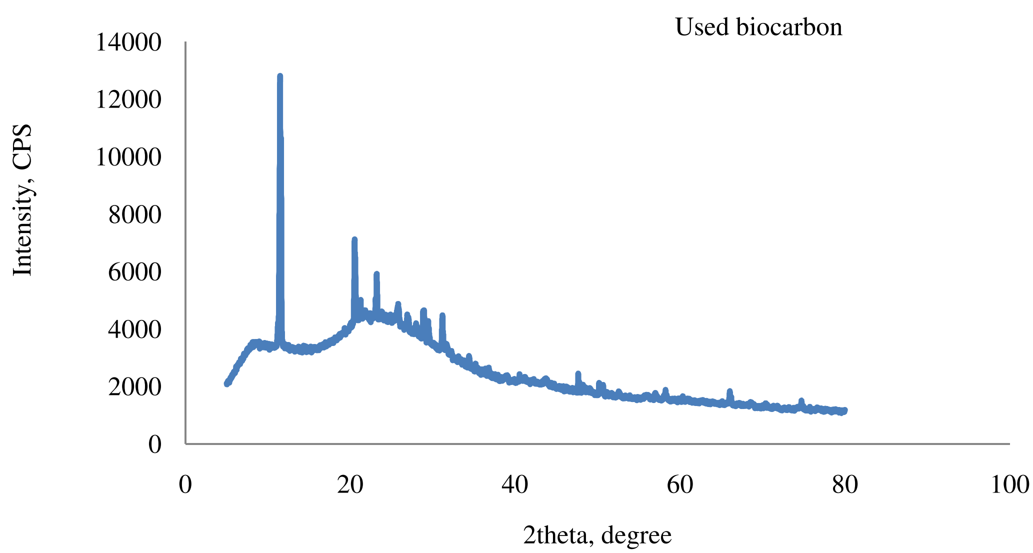

Figure-2(b): XRD patter of biocarbon after adsorption of Mn (II) ions.

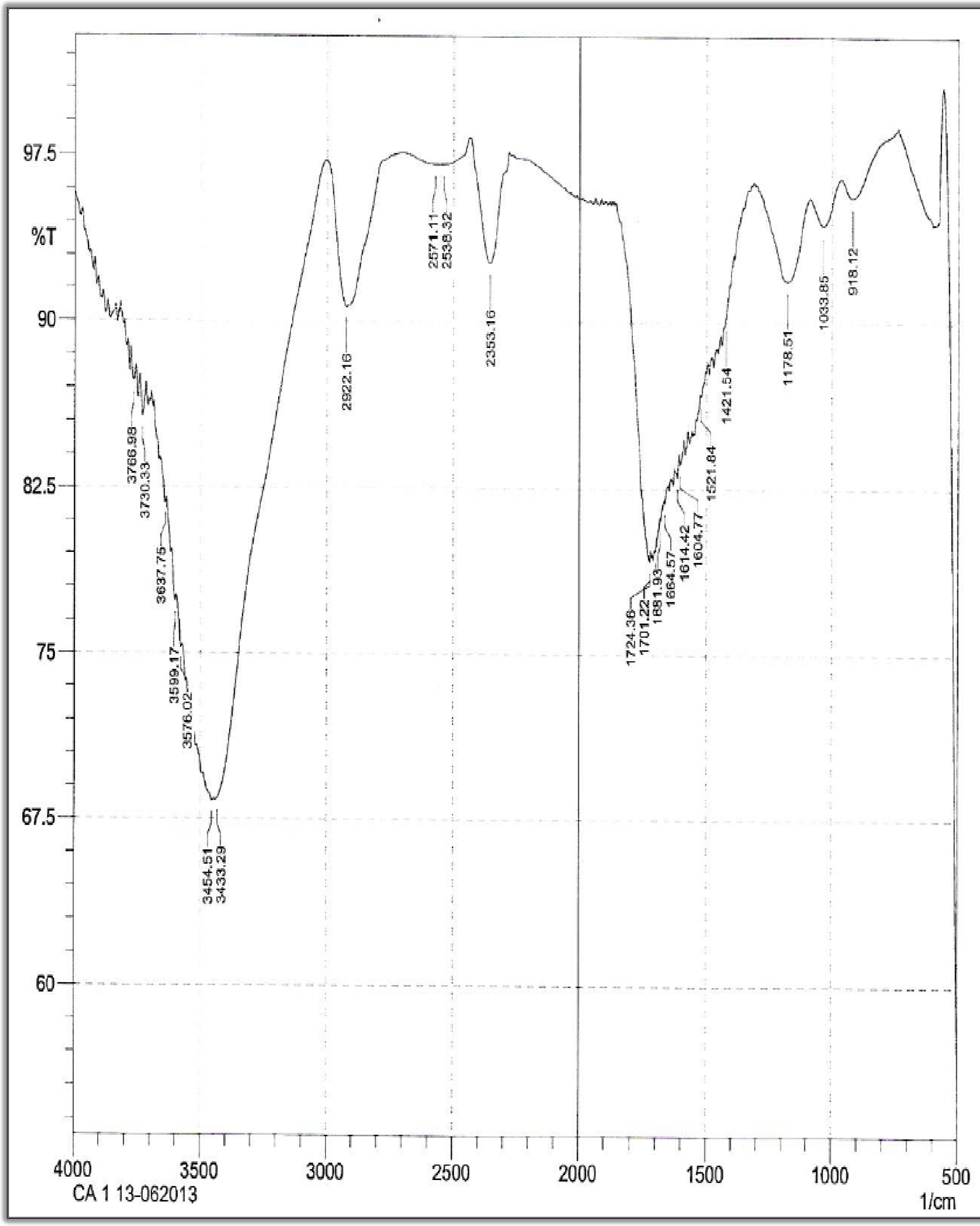

Figure-3(a): FTIR spectrum of pure biocarbon.

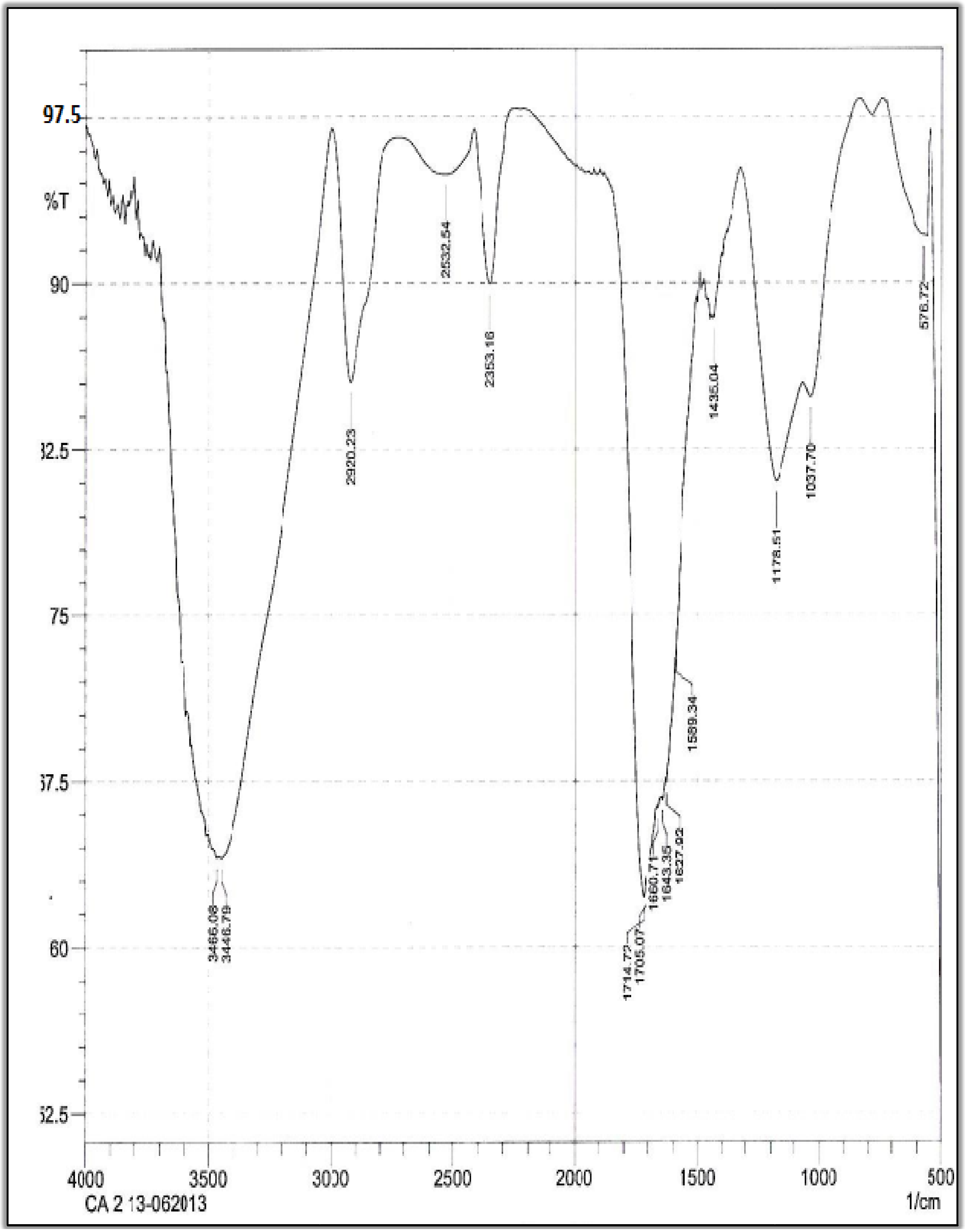

Figure-3(b): FTIR spectrum of biocarbon after adsorption of Mn (II) ions.

Effects of Biosorption Parameters: In the process of biosorption process, the studies on the influence of biosorption parameters such as effects pH, contact time, adsorbent dose, initial metal ions concentration and temperature are very important. All these parameters have a significant role in the process of any adsorption of metal ions in chosen adsorbents. The pH of a solution is an important parameter in adsorption process, as metal ion removal usually increases with increased pH. The pH of a solution affects the surface properties of the adsorbent[27].

The effectof pH on the removalof Mn(II) ions from synthetic wastewater on the biocarbon surface is shown in Figure-4. Adsorption of the metal ions increased with increasing pH, with significant adsorption in the range of pH 4–6. An optimum pH of 5.0 was selected and usedin all biosorption experiments. Normally at lower pH, higher concentrations of H^+ions are present in solution, which generates a competition between the protons andmetal ions for the active sites of the adsorbent. The increased removal of Mn(II) ions with increasing pH are might be due to less competition between protons and metal ions for active sites, which results in lesselectrostatic repulsion between the surface and metalions before ion exchange[28].

The effect of contact time on adsorption of Mn (II) ions was performed at different contact times for an initial concentration of 100mg/L containing 2.5g/100L at pH 5. As shown in the removal efficiency of metal ion on the biocarbon rapidly increase during the first 150 min of contact time (Figure-5). In the initial stages, the removal efficiency of the metal ion on the sorbent increased rapidly due to the rich availability of active binding sites[29]. The results showed that 92.8% of the sorption capacity of biocarbon for Mn (II) ions is achievable during the 150min of contact time. Beyond this point, the removal further increased but with a slower rate.

The information on the amount of adsorbent dosage is a valuable parameter for determining the adsorption capacity of an adsorbent for a given initial metal ions concentration. The effect of the amount of biocarbon dose on the sorption of Mn (II) ions and maximum sorption was observed at 2.5g/100mL of synthetic wastewater (Figure-6). The observation shows that the percent removal of metal ions increases when the dose of adsorbent increases; this may be due to the presence of high surface area and micropore structure in the biosorbent[30]. It is further noted that a higher adsorbent dose may provide more active adsorption sites so that adsorption sites remain unsaturated during adsorption[31].

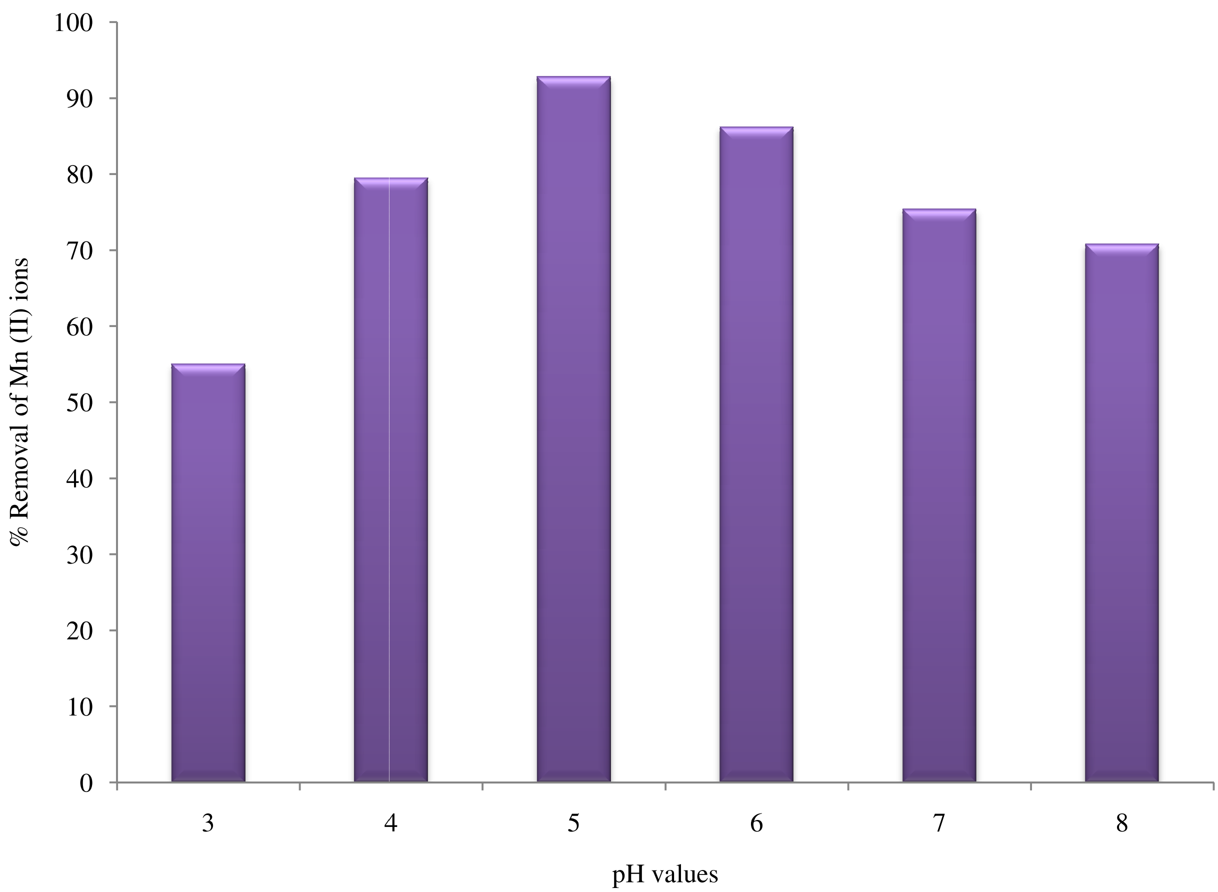

Figure-4: Effect of pH on the removal of Mn (II) ions.

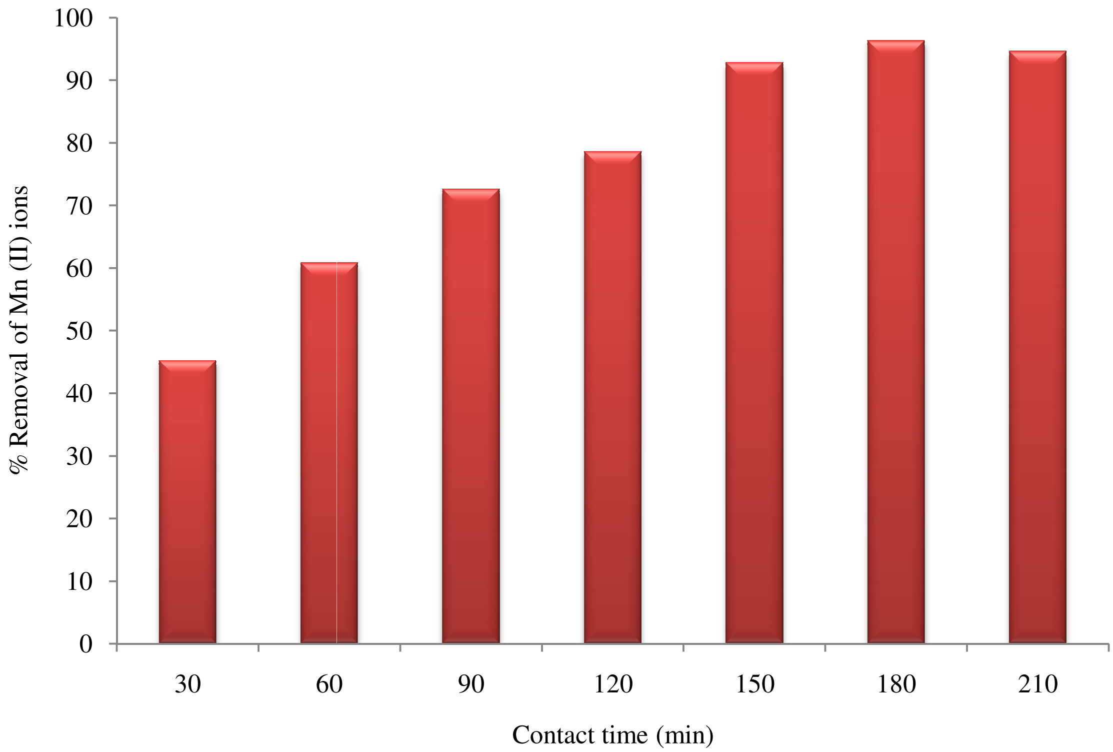

Figure-5: Effect of contact time on Mn (II) ions removal.

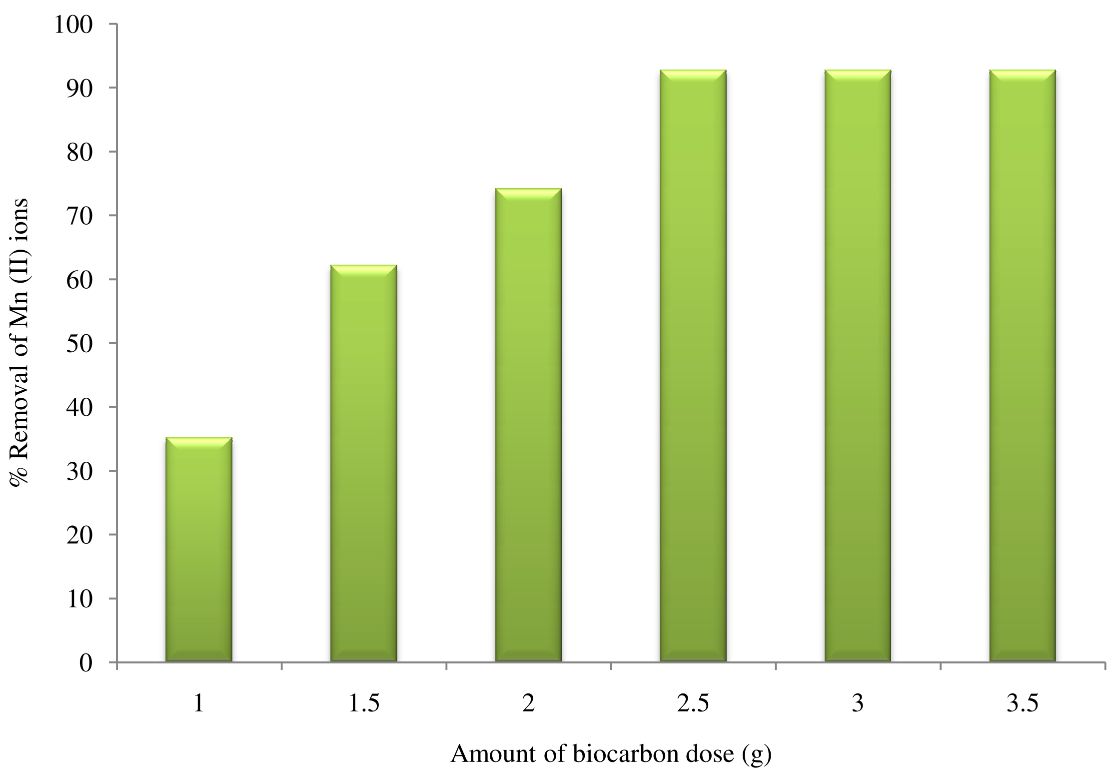

Figure-6: Effect of biocarbon dose on the removal of Mn (II) ions.

The sorption of Mn (II) ions onto biocarbon was carried out at different initial concentrations ranging from 25 to 100mg/L, at pH 5. Figure-7 indicates that by increasing the concentration there is an increase in the percentage removal. In lower concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions is competing for available binding sites in the biocarbon increased[32].

The influence of temperature on the metal ions adsorption on the biocarbon surface was determined at six different temperatures, i.e. 30 to 80^{o}C, the results are shown in Figure-8. The adsorption of metal ions was found to decreasein the higher temperature, which indicatedthe exothermic nature of the adsorption process. Hence, the removal of Mn (II) ions by the biocarbon was more favorable at the temperature of 50 – 60^{o}C. This may be due to the increase in the tendency of adsorbed molecules to escape from the adsorbed phaseto the bulk phase by increasing the temperature. Similar results have been reported in the literature by some researchers working on liquid adsorption[33].

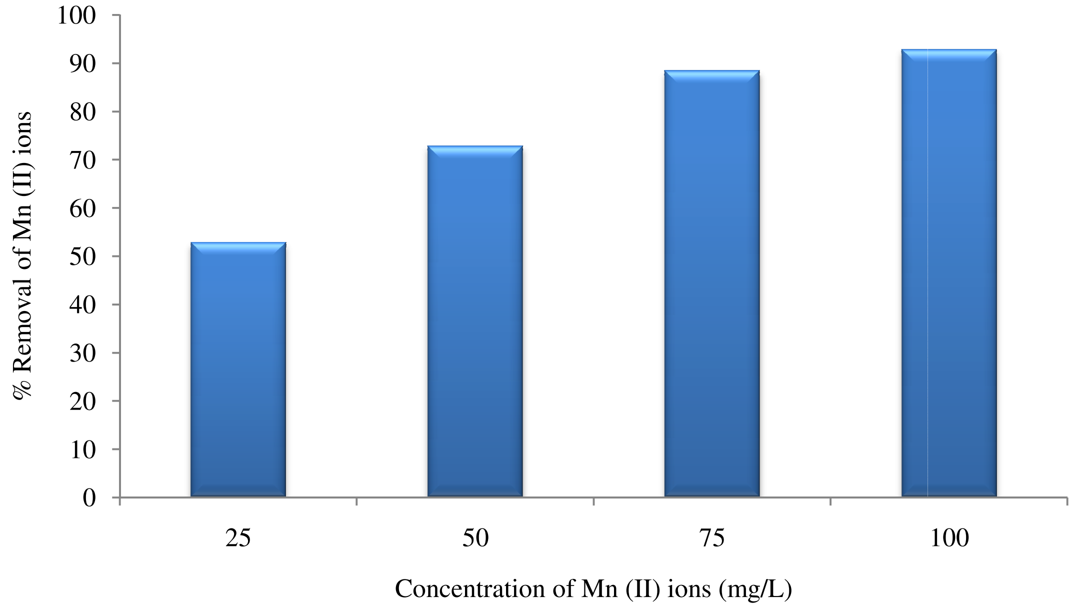

Figure-7: Effect of initial metal ions concentrations.

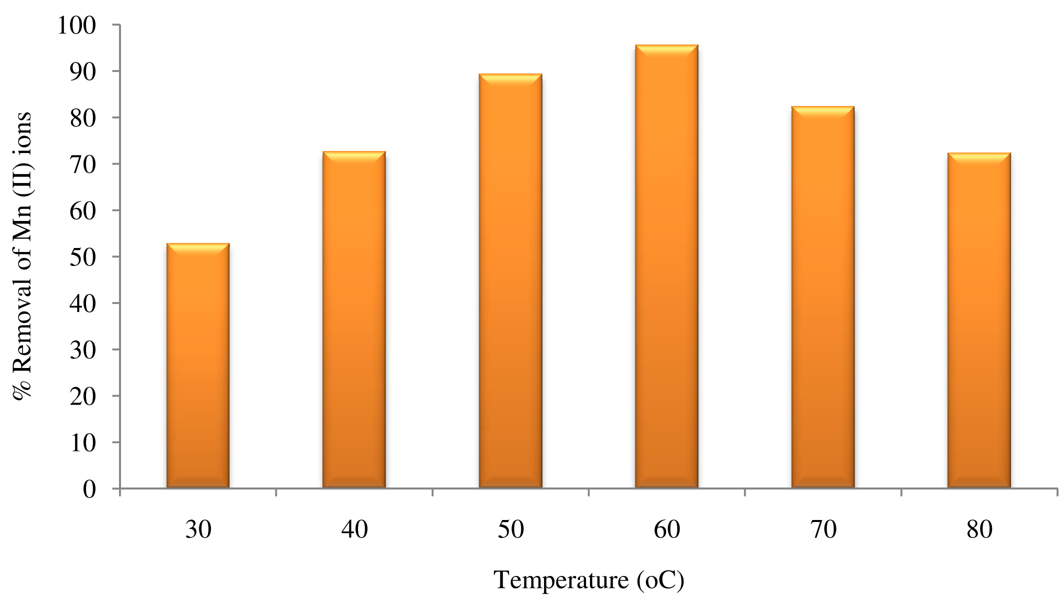

Figure-8: Effect of temperature on the removal of Mn (II) ions.

Conclusion

The effect of solution pH, biocarbon dose, contact time, initial metal ions concentration and temperature on the adsorption capacity of the adsorbate was investigated. The results suggest that the adsorption process was relatively fast and equilibrium was established at the time of 150 min. The optimum pH for manganese adsorption was 5.0 at the biocarbon dose rate of 2.5g/100mL for the maximum removal of 92.8%. The SEM micrograph shows particle grains and leaves like surfaces.It was clearly established from SEM micrographs that highly developed macropores and micropores are available for adsorption. FTIR analysis results indicate that, presence of different functional group in the biocarbon matrix such as O–H, C=O, and C=C might be responsible for the metal uptake in biosorption process.The results obtained by using low-cost biocarbon prepared from the leaves of Acalypha indicaplantin the present study is encouraging in terms of both economic and environmental health aspects and could improve the adsorption process for the removal of toxic heavy metals like Mn (II) and other hazardous materials from industrial and sewage wastewater systems.

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