



Adsorption Of Mn(II) Ions From Wastewater Using Activated Carbon Obtained From Birbira (*Militia Ferruginea*) Leaves

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Abstract - The adsorption of manganese (II) onto activated carbon derived from the leaf an indigenous Ethiopian plant, namely Birbira (*Militia ferruginea*), was investigated using flame atomic absorption spectrometer. The effects of contact time, adsorbent dose, Mn (II) initial concentration, pH and temperature were investigated. The maximum adsorption occurred after 2 hrs. There was 95.8% of Mn²⁺ adsorption at pH of 4.0. The positive value of ΔH shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy (ΔG) were negative. The decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The calculated value of ΔH is 16.05 kJmol⁻¹ and ΔS is 99.13JK⁻¹mol⁻¹. The two theoretical adsorption isotherms, namely, Langmuir and Freundlich were used to describe the experimental results. The Freundlich adsorption isotherm best fits and adsorption capacity was calculated to be 3.41 mg of Mn (II) per g of adsorbent. The adsorption followed the first order kinetics and was found to be pH dependent being maximum at pH 4.0. Reuse of the desorbed bio-adsorbent is possible. The effect of foreign ions on the removal of Mn (II) has been investigated. The removal of Mn (II) from industrial wastewater sample was also tested and showed that more than 93% removal is possible. The results showed that activated carbon prepared from Birbira (*Militia ferruginea*) leaves can be used for the removal of Mn (II) from wastewater.

Keywords : *Industrial wastewater, Manganese removal, adsorbent, Militia ferruginea, adsorption isotherm, kinetics of adsorption and flame atomic absorption spectrometer (FAAS).*

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Abstract - The adsorption of manganese (II) onto activated carbon derived from the leaf of an indigenous Ethiopian plant, namely Birbira (*Militia ferruginea*), was investigated using flame atomic absorption spectrometer. The effects of contact time, adsorbent dose, Mn (II) initial concentration, pH and temperature were investigated. The maximum adsorption occurred after 2 hrs. There was 95.8% of Mn²⁺ adsorption at pH of 4.0. The positive value of ΔH shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy (ΔG) were negative. The decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The calculated value of ΔH is 16.05 kJmol⁻¹ and ΔS is 99.13 JK⁻¹mol⁻¹. The two theoretical adsorption isotherms, namely, Langmuir and Freundlich were used to describe the experimental results. The Freundlich adsorption isotherm best fits and adsorption capacity was calculated to be 3.41 mg of Mn (II) per g of adsorbent. The adsorption followed the first order kinetics and was found to be pH dependent being maximum at pH 4.0. Reuse of the desorbed bio-adsorbent is possible. The effect of foreign ions on the removal of Mn (II) has been investigated. The removal of Mn (II) from industrial wastewater sample was also tested and showed that more than 93% removal is possible. The results showed that activated carbon prepared from Birbira (*Militia ferruginea*) leaves can be used for the removal of Mn (II) from wastewater.

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1. INTRODUCTION

Heavy metals are generally present as pollutants in a variety of industrial effluents. Industries such as metal plating, metal finishing, rubber processing, fertilizers, mining, as well as agriculture release these heavy metals into the surface and ground water [1]. At least 20 metals are classified as toxic and half of these are released into the environment in quantities that pose risks to human health [2-5]. The increasing contamination of urban and industrial wastewaters by toxic metal ions is a serious environmental problem.

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These inorganic micro-pollutants are of considerable concern because they are non-biodegradable and highly toxic [6]. The toxic actions of these trace elements are due to their bioaccumulation in the tissues of living organisms [7-10]. On the other hand, the Groundwater that contains an appreciable amount of iron or manganese or both is always devoid of dissolved oxygen and high in carbon dioxide content [11]. As far as is known, humans suffer no harmful effects from drinking water containing manganese. However, manganese interferes with laundering operation, imparts objectionable stains to plumbing fixture, and causes trouble in distribution systems by supporting growths of iron bacteria. For these reasons public water supplies should not contain more than 0.05 mg/L of manganese according to the U.S.E.P.A. secondary standard [11]. According to WHO the maximum permissible limit (MPL) of manganese in drinking water is 0.5 mg/L [11-13].

At present, a number of technologies can be used to remove heavy metals from the contaminated waste water such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation and electro remediation methods. However, most of this method might not be efficient in removing heavy metals at very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment [14-17]. For this reason, the uses of some low-cost materials for sorbent/adsorbent of metals from contaminated wastewater have been popular.

Randall et al. worked on removal of heavy metals using various barks and eventually expanded their work to peanut skins [18,19]. Others researchers also used bagasse, acacia bark, husk, paddy straw, wheat flour, and waste peanut [20, 21]. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents. Studies of removal of heavy metal ions using low-cost abundantly available adsorbents from agricultural and solid wastes such as tea waste, coffee and nut shells [22], saw dusts, bark and bin [23], palm kerner husk [24], rice hulls [25], cactus leaves and charcoal [26], were performed. In our earlier studies we have used leaves of a plant for the removal of heavy metals [27, 28]. The aim of the present investigation is to propose new biomaterial involving applications of an Ethiopian

indigenous plant material leaves, *Militia ferruginea* also known in the vernacular as birbira, in the removable of heavy metals from synthetic wastewater (spiked with manganese) and subsequently its application to industrial wastewater. For environmental degradation industries are not the only contributors but deforestation of indigenous trees for agriculture does also contribute. It is therefore of great value to solve this problems simultaneously. The search for indigenous biomaterials especially, those with high social value and economically important trees for tackling both deforestation and environmental pollution are sounding. Selection of these indigenous trees for this application will increase the farmer's attention towards planting the trees since the value of these trees will increase in terms of economy.

II. MATERIALS AND METHODS

a) Preparation of carbon from the bio-adsorbent

After it was authenticated by an expert, the leaves of Birbira (*Militia ferruginea*) were collected, dried in air and powdered. The homogenous powder was treated with concentrated sulfuric acid (sp.gr. 1.84) in a weight ratio of 2:1 (powder: acid). The resulting black product was kept in an air-free oven monitored at $195 \pm 5^\circ\text{C}$ for three hours, followed by several washings with distilled water until free of excess acid and drying at $105 \pm 5^\circ\text{C}$. The carbon obtained was ground and the portion retained between 90 and 125 μm sieves was used for the metal adsorption experiments. The yield of the carbon was about 38% of the starting powder.

b) Preparation of synthetic wastewater

Synthetic wastewater samples were prepared by using analytical grade manganese dioxide ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) (Loba Chemie) and doubly distilled water. The stock solution was prepared in a concentration of 1000 ppm. Working solutions of 5, 10, 20, 50, 60 and 100 ppm were prepared by dilution.

c) Sampling of Industrial effluent

The metal polishing industrial effluent sample was collected in polyethylene bottles. pH, electrical conductivity were measured with portable pH meter and electrical conductivity meter. Samples were filtered and preserved at 4°C . Trace metals were determined by flame atomic absorption spectrometer (FAAS) and soluble cations, anions and other parameters were determined by standard analytical methods [12].

d) Batch adsorption experiments

Each batch experiment was performed with 50 ml of a working solution and the desired adsorbent dose, shaking time pH, and temperature. The solution was transferred into a 250 ml conical flask and shaken in a mechanical Gemmy orbit shaker (model: VRN-480) at 250 rpm for a definite period. Adsorbent dose, shaking time, pH, and temperature were optimised by continuous variation method (studying one, keeping the

other parameters constant). After equilibrating, the system was allowed to settle for 20-30 minutes, filtered and analysed for manganese. The pH of the original solution and the filtrate was determined using HANNA instruments pH meter (pH 209 model).

The difference in the manganese content before and after adsorption experiment represents the amount of manganese adsorbed by the bio-adsorbent. All experiments were performed at room temperature ($23^\circ\text{C} \pm 2^\circ\text{C}$) except for the samples used for study of the temperature effect. The free ion concentration of Mn^{2+} in the test solution was measured by atomic absorption spectrometer model AA-6200, Shimadzu Japan. The concentration was measured at the wavelength of 279.5 nm with slit width of 0.2 nm for the photon hollow cathode lamp system in AAS. Each experiment was carried out in triplicate and mean values were taken for calculation.

The percent removal of metal ions can be calculated by using the formula:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} 100 \quad (1)$$

Where C_i is the initial concentration in the aqueous solution and C_f is the final concentration in the aqueous solution after adsorption procedures carried on and equilibrium is achieved.

e) Temperature Study

The effect of temperature was studied using 50 ml of 10, 20, 40 and 60 ppm of Mn^{2+} solution for 2hr at adsorbent dose of 4.0 gm. The temperature was set at 23° , 30° , 35° , 40° , 45° , 50° and 60°C .

III. RESULTS AND DISCUSSION

a) Effect of adsorption time

The effect of adsorption time using 4.0 g of the adsorbent and 50 mL of test solution containing 5, 10, 20 and 100 ppm of Mn (II) ions is shown in Figure 1. It is evident from the figure that the removal of metal ion increases at adsorption time increases. Initially the rate of uptake is fast. However, equilibrium is attained in 2 hr. Hence, in further studies the adsorption time of 2hr was used.

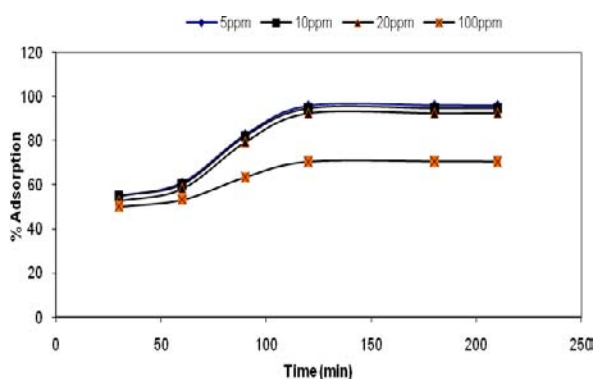


Figure 1. Effect of adsorption time

$pH = 4.0$, Adsorbent dose = 4.0 g

b) Effect of Adsorbent dose

Figure 2 shows the effect of carbon dosage on Mn (II) ion removal from aqueous solutions. Each test solution (50 mL) contained 20 ppm of manganese ions. The adsorption of manganese ions is observed to increase as the amount of adsorbent is increased from 0.25 g to 4.5 g. The maximum adsorption is obtained from the adsorbent dose of 4.0 g which is 92.6% for 20 ppm of initial concentration. A further increase of the adsorbent up to 4.5 g seems to give no more adsorption. About 4.0 g of the adsorbent were thus sufficient to adsorb the maximum ions under the experimental conditions. The increase in the removal efficiency as adsorbent dose increases is due to the availability of more adsorbing sites at higher doses. At constant initial concentration once equilibrium between adsorption desorption is reached the percent adsorption remains constant.

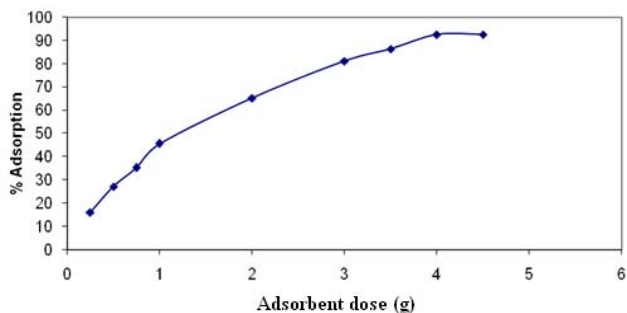


Figure 2. Effect of adsorbent dose

$pH = 4.0$, Initial concentration = 20 ppm

c) Effect of initial concentration of Manganese ions

Removal of Mn (II) ions from the aqueous solution was studied for the metal ion concentrations ranging from 5 to 100 ppm. The percentage adsorption of Mn (II) ions from 50 mL solutions of different initial ion concentrations (equilibrated with 4.0 g of adsorbent) is shown in Figure 3. As can be seen from the figure the removal of the metal ions is found to decrease with increase in initial concentration. At the experimental

conditions of 4.0 g dose of adsorbent and at pH 4 maximum adsorption is obtained for concentrations of 5 – 10 ppm.

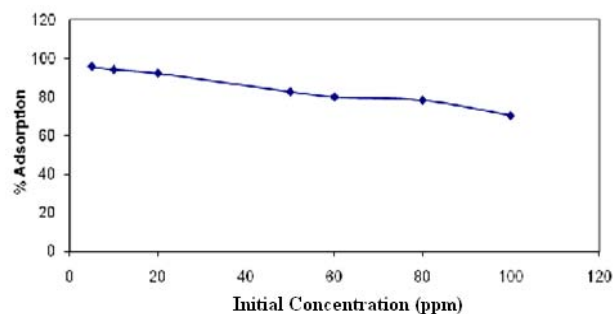


Figure 3. Effect of initial concentration

$pH = 4.0$, Adsorbent dose = 4.0 g

d) Effect of pH

The pH of a solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final one. The influences of pH are on both the adsorbent surface of the metal binding sites and the metal chemistry in water [29, 30]. In this experiment, the pH effect was studied in the range of 2.0-7.0. Removal of Mn^{2+} onto the activated carbon is pH dependent as shown in Figure 4. The maximum adsorption is obtained at pH 3.5 for both 10 and 50 ppm solutions. At $pH < 2.0$, H^+ ions compete with Mn (II) ions for the surface of the adsorbent, which would hinder Mn (II) ions from reaching the binding sites of the sorbet. At $pH > 7.0$, the Mn (II) gets precipitated due to hydroxide anions forming a manganese hydroxide precipitate. The highest efficiency was 94.2% at a pH of 4.0 for 10 ppm and 82.8% for 50 ppm. A change in the pH of the solution after adsorption was observed in this study. In all cases the pH of the solution decreases after equilibrium was achieved. The larger the adsorbent dose the greater the decrease in pH. It was presumed that adsorption of the metal ions on the surface could result in the release of more H^+ ions from the surface by ion exchange mechanism.

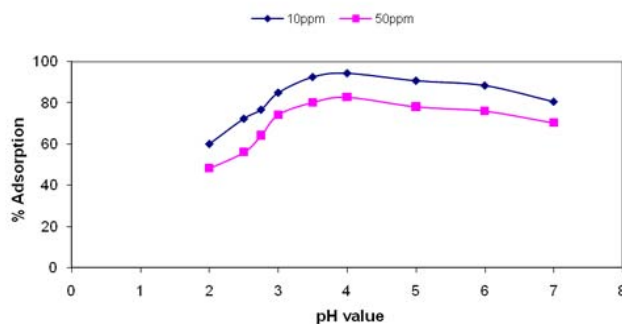


Figure 4. Effect of pH

Adsorbent dose = 4.0 g

e) Effect of Temperature

The extent of manganese ion adsorption on the activated carbon at various temperatures is given in Figure 5. As can be seen from the figure as the temperature of the system is increased, there was an increase in the percent removal of the metal. The enhancement of the adsorption capacity on increasing the temperature may be due to increase in the mobility and diffusion of ionic species. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in the enlargement of pore size due to 'activated diffusion' causing the micro-pores to widen and deepen and create more surface for adsorption.

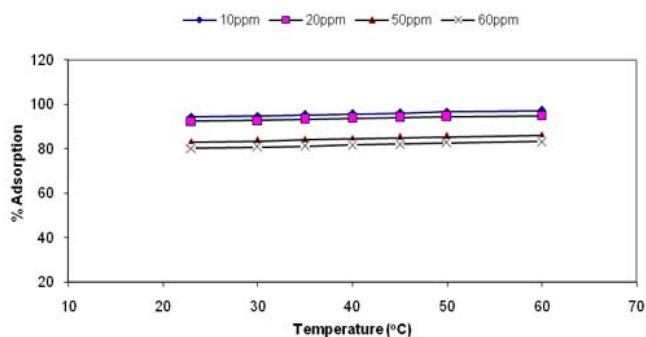


Figure 5. Effect of Temperature

Adsorbent dose = 4.0 g, pH = 4.0

Calculation of thermodynamic parameters

The value of ΔH and ΔS were calculated from the slope and intercept of the linear van't Hoff plot respectively, using the relation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

Where: ΔS = entropy change for the process
 ΔH = enthalpy change for the process
 R = gas constant
 T = absolute temperature

The distribution coefficient (K_d) of the activated charcoal surface was calculated using the equation,

$$K_d = \frac{C_i - C_e}{C_e} \frac{V}{m} \quad (3)$$

Where C_i = the initial concentration of the metal ion
 C_e = the equilibrium concentration of the metal ion
 V = the volume of the solution equilibrated in mL
 m = mass of the adsorbent in g

The change in free energy (ΔG) for the specific adsorption has also been calculated using the equation

$$\Delta G = -RT \ln K_d \quad (4)$$

Where, the symbols have their usual significance.

The thermodynamic quantities ΔH , ΔS , ΔG of manganese ion adsorption on activated carbon were calculated from the K_d values using Eqs. (3) and (4). The values of ΔH and ΔS were computed from the slope and intercept of the linear variation of $\ln K_d$ with the reciprocal of temperature (Figure 6) and was found to be 16.05 kJ mol⁻¹ and 99.13 JK⁻¹mol⁻¹ respectively (Table 1). The values of free energy of specific adsorption, ΔG at various temperatures were calculated by using Eq. (4) and are listed in Table 1. The positive value of ΔH shows that the adsorption of manganese ions on the adsorbent is an endothermic process. The values of free energy (ΔG) are negative as expected for a spontaneous process. The decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The positive value of ΔS reveals the increase in randomness at solid solution interface during the fixation of manganese ions on active site of the adsorbent.

Table 1. Adsorption Studies of Mn²⁺ Ions on Activated Carbon as a Function of Temperature

T (K)	1/T (K ⁻¹ x 10 ⁻³)	K _d (mLg ⁻¹)	ΔG (kJ mol ⁻¹)	lnk _d
296	3.38	232.01	-13.41	5.45
303	3.30	255.25	-13.95	5.54
308	3.25	277.26	-14.39	5.62
313	3.19	303.17	-14.85	5.71
318	3.14	342.85	-15.41	5.83
323	3.09	393.87	-16.03	5.97
333	3.0	478.32	-17.08	6.17

Amount adsorbent: 4.0g shaking time 2hrs, volume equilibrated 50 ml, pH of the solution 4.0, and concentration of Mn (II) 20 ppm.

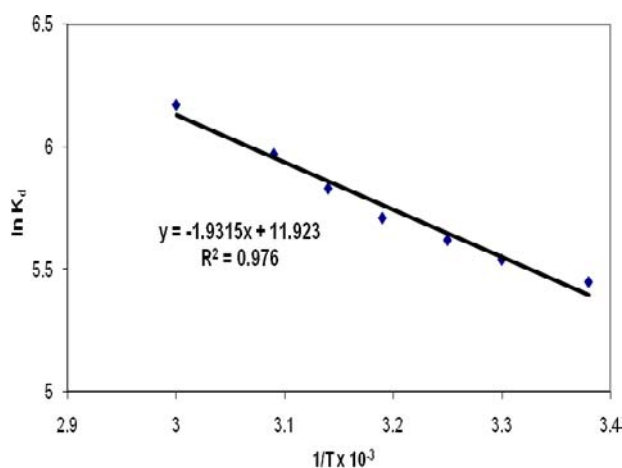


Figure 6. Plot of $\ln K_d$ vs $1/T$

Initial concentration = 20 ppm, pH = 4.0 g

f) Effects of anions and cations

The effect of anions such as F^- , Cl^- , NO_3^{-2} , SO_4^{-2} and PO_4^{-3} as well as the effect of cations such as Fe^{+2} , Ca^{+2} , Na^{+} and K^{+} on the Mn^{2+} adsorption efficiency of the bio-adsorbent was studied. There is no significant reduction in the adsorption of Mn^{2+} when the concentration of the above ions increases up to 80 ppm in the synthetic water. It is evident that with the proper treatment of the wastewater; it is possible to adsorb Mn^{2+} ions on the surface.

g) Adsorption isotherm

Equilibrium batch adsorption experiments resulted in points of the adsorption isotherm, which were approximated by the Langmuir model,

$$q = \frac{q_{max} b C_{max}}{1 + b C_{eq}} \quad (5)$$

where, q_{max} is the maximum adsorbate uptake and b is the Langmuir constant related to energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate. The evaluation of the specific uptake q was performed according to

$$q = \frac{V (C_i - C_{eq})}{m} \quad (6)$$

where, V is the volume, C_i , initial concentration of the metal ion, C_{eq} is the metal ion concentration remaining in the solution after adsorption has taken at equilibrium and m is mass of the biomaterial.

The Langmuir parameters were obtained by fitting the experimental data to linearized equation derived from Eq. (7),

$$1/q = \frac{1}{q_{max}} + \frac{1}{(C_{eq} q_{max} b)} \quad (7)$$

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir isotherm. According to Freundlich, adsorption from solution can be expressed by the equation

$$q = KC^{1/n} \quad (8)$$

where K is the measure of the capacity of the adsorbent (mass of adsorbate/mass of adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. The expression $n > 1$ indicates that the affinities decrease with increasing adsorption density. Evaluation of the coefficients K and n can be accomplished using the linearized form of equation 8,

$$\log q = \log K + \frac{1}{n} \log C \quad (9)$$

The Freundlich parameters as well as the correlation coefficient are listed in Table 2. From the values obtained for these parameters the theoretical Freundlich curves were calculated and plotted (Figure 7). It can be observed that the experimental data fit the isotherm adequately. The applicability of the Freundlich model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of the $Mn(II)$ ions. For comparison the Langmuir adsorption isotherm is also given in Figure 8.

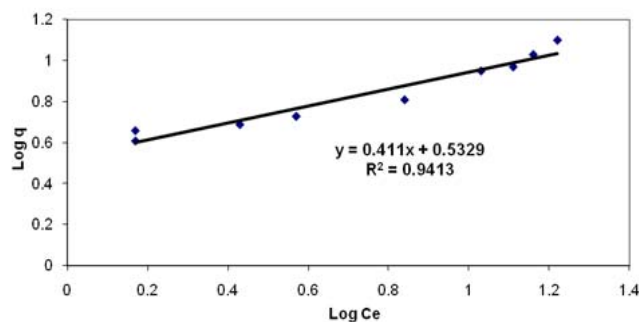


Figure 7. Freundlich adsorption isotherm of Mn (II)

Initial concentration = 20 ppm, pH = 4.0 g

Table 2. Freundlich Isotherm Parameters

Equation	K (mg/g)	n	R2
$\log q = 0.411 \log C_e + 0.5329$	3.41	2.43	0.94

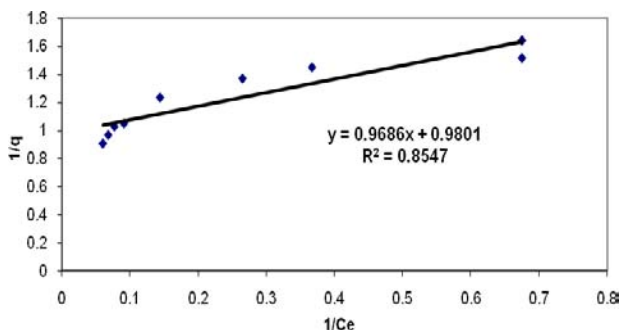


Figure 8. Langmuir adsorption isotherm of Mn (II)
Initial concentration = 20 ppm, pH = 4.0 g

h) Order of reaction of manganese ion adsorption

The rate constant (K) of the manganese ion adsorption at the adsorbent surface was calculated at 25°C with equilibration time (t) of 120 min using the following equation [31],

$$K = \frac{1}{t} \ln(C_o / C_e) \quad (10)$$

Here C_o and C_e are the initial and equilibrium concentrations of manganese ions respectively. The values of C_e and the rate constant for the adsorption process at different initial concentrations of manganese ions (C_o) were calculated. The plot of rate constant (K) versus $\ln(C_o/C_e)$ is observed to be a straight line as shown in Figure 9. The result indicates that the adsorption process of manganese ions at the surface of the adsorbent follows first order reaction kinetics.

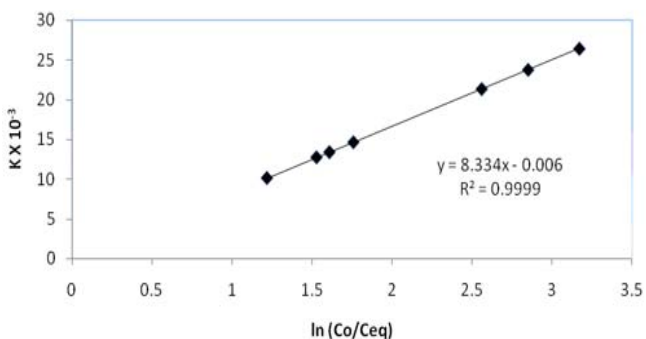


Figure 9: Kinetics of Adsorption of Mn²⁺

i) Treatment of industrial wastewater

The suitability of the bio-adsorbent material for the removal of Mn (II) was tested with a metal polishing industrial wastewater sample. The composition of the wastewater is given in Table 3. pH of the wastewater sample was maintained between 3.5-4.0. Using the adsorbent dose of 4.0 g to 50 ml of 20 ppm Mn (II) the effect of adsorption time is shown in Figure 10. It was found in this experiment that the treatment of Mn (II) ion in industrial wastewater was quite satisfactory: almost 94% removal of the metal ion from the wastewater was possible. Thus, the result was in good agreement with those obtained from batch experiments conducted for

Mn (II) removal in synthetic wastewater samples. However, a preliminary treatment of the industrial wastewater is recommended before the application of activated carbon of the bio-adsorbent.

Table 3. Determined composition of metal polishing industrial effluent

Parameters	Results
pH	3.5
Electrical conductivity (μ mhos/cm)	4367.75
Total dissolved solids (mg/L)	6846
Turbidity (NTU)	1.25
COD (mg/L)	33
Chloride (mg/L)	468
Sulphate (mg/L)	1228
Iron (mg/L)	38
Manganese (mg/L)	32.6
Cadmium (mg/L)	964
Calcium (mg/L)	86
Sodium (mg/L)	177
Potassium (mg/L)	32

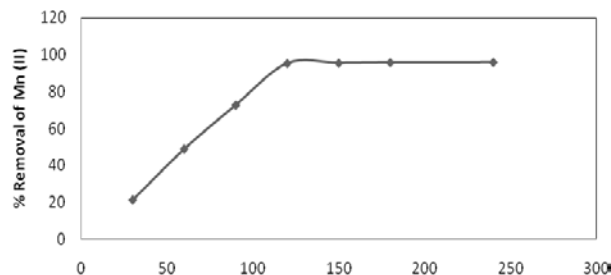


Figure 10. Effect of adsorption time
pH = 4.0, Adsorbent dose = 4.0 g

j) Desorption studies

The adsorbent (50 mg) that was used for the adsorption of the Mn²⁺ ion in solutions of 5, 10, 20, 40, 50, and 80 ppm from determination of effect of initial concentration experiment was separated from the solution by filtration. The Mn²⁺ loaded adsorbent was filtered using Whatman filter paper and washed gently with distilled water to remove the unadsorbed Mn²⁺, and the water was immediately removed. Then the adsorbent was mixed with 50 ml of distilled water, adjusted to a pH value in the range 2.0-9.0 using dilute HCl/ NaOH and agitated for 3 hours longer period than the equilibrium time. The desorbed Mn²⁺ was estimated as before. The adsorbent after desorption of the ions

the ions was checked for further adsorption capacity. The reuse of regenerated activated carbon was found to be efficient. The desorption results are shown in Figure 11.

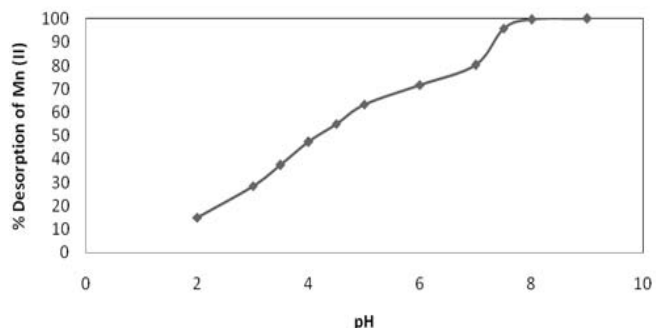


Figure 11. Desorption of Manganese ions from the spent adsorbent

IV. CONCLUSIONS

The removal of Mn (II) ion in synthetic wastewater as well as industrial effluent by activated carbon obtained from the leaves of Birbira plant has been studied. The prepared activated carbon is an efficient biomaterial for removal of manganese (II) ions from industrial wastewater. The adsorption of Mn (II) is a monolayer according to Freundlich adsorption isotherm. The percent removal of Mn (II) under the conditions employed; here is 94.2% for initial concentration of 10 ppm. Adsorption efficiency increased with increasing pH showing a maximum at pH 4.0 and then decrease at higher pH, greater than pH 9 desorption is complete. Adsorption equilibrium for the metal is reached in about 2 hrs and is endothermic in nature. The adsorption is first order in kinetics. This methodology can be applied to the removal of toxic metals from wastewater efficiently. Reuse of the regenerated bio-adsorbent is also possible.

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