

# Adsorption of Manganese(II) Ions from Aqueous Solutions onto Granular Activated Carbon (GAC) and Modified Activated Carbon (MAC)

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## ABSTRACT

The removal of Manganese(II) ions from aqueous solution by granular activated carbon (GAC) and activated carbon modified by Iron oxide (MAC) was investigated. Adsorption studies were performed by batch experiments. The effect of contact time, pH, adsorbent dose and ionic strength were explored. The equilibrium time of 30 minutes was observed and maximum adsorption was favoured at pH 4 for the two adsorbents. From the experimental data, the isotherm parameters of Freundlich, Langmuir, and Dubinin-Radushkevich were calculated. The equilibrium was best represented by the Freundlich isotherm. Langmuir adsorption capacity ( $Q_m$ ) of 14.49 mg/g and 6.94 mg/g for MAC and GAC respectively were also recorded. For both adsorbents the  $Mn^{2+}$  ions adsorption increased with the increase in ionic strength of 172.76 mg/g for MAC and 149.43 mg/g for GAC.

Keywords: Adsorption, Manganese(II), Activated Carbon, Iron oxide

## 1. Introduction

The development of industrial technology in husbandry and the growing urbanization generate in the nature several pollutants (heavy metals, colorants, and pesticides). Water pollution by heavy metals (Manganese, lead, cobalt, copper, mercury

etc.) constitutes a source of degradation of the environment and actually requires particular interest on both the local and international scale [1-4]. Indeed, heavy metals are highly toxic, usually out of certain concentration norms. They are present in a very high concentration all along the food chain and would accumulate in large quantity in certain organs of the human body [1]. Among heavy metal, Manganese is the second most abundant metal in nature. Mn(II) ions and Mn(VII) ions of this metal in nature are essential micronutrients for organisms and plants. Manganese has variety of applications in ceramics, dry battery cells, electrical coils and many alloys [2]. 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 [3]. Exceeding this concentration, it become dangerous for human survival because it causes trouble in distribution [4]; hinders the intellectual development and normal growth of infants, the Parkinson illness, pulmonary track disorder, bronchitis [1]. Thus, the removal of Manganese from water is imperative.

Several processes have been used to remove heavy metals from solutions some of which are: chemical precipitation, ion exchange, coagulation, electrochemical treatment, and adsorption [5]. However, adsorption remains the outmost process because of its simplicity, high efficiency and easy

recovery [6]. It is also one of the most effective and economic technique for removing heavy metal ions from aqueous solution [7]. Others researchers have demonstrated that different adsorbents have been used for the removal of manganese ions from aqueous solution, some of which are: activated carbon, zeolites, magnetic iron oxide [1, 3, 4]. Calcium silicate adsorbents are frequently used in water treatment and in industrial applications such as in the extraction of metals ions, organic waste and gas purification [4, 6, 8]. This is because of their high adsorption capacity, their porous structure and accessibility of their surface functional groups [8]. Although the activated carbon showed good adsorbent property, a modification could improve its adsorbent property and porous structure. Experiments show that magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after adsorption, can easily be separated from the medium by a simple magnetic attraction [9, 10]. In this study, prepared magnetic composite based activated carbon/iron oxide mixture by modification process was adopted.

Which aims at investigating the adsorption capacity of manganese(II) ions onto this?

## 2. EXPERIMENTAL METHODS

### 2.1 Adsorbent preparation

The activated carbon used here has been discussed by J. Ndi Nsami et al 2013 [6]. The composite was prepared by introducing into 250 mL conical flask (5 M) NaOH solution, 0.1 g of activated carbon and then adding to the 250 mL conical flask contain 10 g of Fe(II) and 13.93 g of Fe(III).

The mixture was then agitated on heating for 1 hour and then cold, filtered and dried in an oven at 110°C for 24 hours.

### 2.2 Preparation of aqueous solution

Synthetic wastewaters were prepared by using analytical hydrated grade manganese dichloride ( $MnCl_2 \cdot 4H_2O$ ) and distilled water. The stock solution of Mn(II) ions was prepared by dissolving 7.209 g of manganese chloride tetrahydrate in 1 liter of distilled water. Standard solutions of concentration 350, 550, 750, 950 and 1150 mg/L were obtained using simple dilution methods. Solution of hydrochloric acid (0.1 M) and sodium hydroxide (0.1M) were also prepared for pH adjustments.

### 2.3 Batch adsorption experiments

Batch adsorption was carried out at room temperature by agitating a mixture of 0.1-0.5 g of the adsorbents together with 30 mL of the solution of  $Mn^{2+}$  ions in a screw capped conical flask with initial concentration ranging from 350 to 1150 mg/L. The pH was varied between 2 and 8. The suspensions were stirred for interval of time between 5 and 60 minutes using a magnetic agitator and stirrer at a controllable speed. After agitation, the suspensions were filtered using Whatman n<sup>o</sup>.1 filter paper. The residual  $Mn^{2+}$  ions concentration were determined by complexometric titration of the solution with EDTA (1000 mg/L). The percentage removal (R) and the amount adsorbed of  $Mn^{2+}$  ions on adsorbent ( $q_e$ ) were respectively calculated using the following relations:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \dots\dots\dots (1)$$

$$q_e = \frac{C_0 - C_t}{m} V \dots\dots\dots (2)$$

Where  $q_e$  is the amount of  $Mn^{2+}$  ions adsorbed on adsorbent at equilibrium ( $mg \cdot g^{-1}$ ),  $C_o$  and  $C_e$ , the initial and equilibrium concentrations of  $Mn^{2+}$  ions ( $mg \cdot L^{-1}$ ) in solution, respectively.  $V$  is the volume of solution (L) and  $m$ , the weight of adsorbent (g).

## 2.4 ADSORPTION ISOTHERMS

### LANGMUIR Adsorption Isotherm

The Langmuir adsorption equation is one of the most common isotherm equations for modeling equilibrium data in solid-liquid systems. This equation is valid for monolayer equation onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. The general form of the Langmuir equation is [11]:

$$Q_e = \frac{Q_m K C_e}{1 + K C_e} \dots \dots \dots (3)$$

where,  $Q_e$  ( $mg/g$ ) is the adsorption capacity at the equilibrium solute concentration.  $C_e$ , the equilibrium concentration of adsorbate in solution ( $mg/L$ ).  $Q_m$  ( $mg/g$ ) is the maximum adsorption capacity corresponding to complete monolayer coverage.  $K$  is the Langmuir constant related to energy of the adsorption.

The above equation can be rearranged to obtain the following linear form:

$$\frac{1}{Q_e} = \frac{1}{Q_m K C_e} + \frac{1}{Q_m} \dots \dots \dots (4)$$

### The Dubinin-Kanga-Radushkevich Isotherm

This isotherm was developed for the adsorption of substances in trace amount from aqueous phase onto porous solids. This model is more general than that of Langmuir because it is

applicable even for the sites of non-homogeneous adsorption. This isotherm which supposes that the surface is heterogeneous is expressed as follows [12]:

$$Q_e = Q_m \exp(K' \epsilon^2) \dots \dots \dots (5)$$

Where  $Q_e$  is the quantity of solute adsorbed at equilibrium ( $mg/g$ );  $Q_m$  is the adsorption capacity of the adsorbent per unit mass  $mg/g$ ;  $\epsilon$  is the Polanyi potential express as  $RT \ln(1 + 1/C_e)$ ; where  $R$  is the ideal gas constant ( $J/K \cdot mol$ ),  $T$  is absolute temperature (K) and  $K'$  is a constant related to the energy of adsorption ( $mol^2 K/J$ ). The linear form of the D-R equation is:

$$\ln Q_e = \ln Q_m - K' \epsilon^2 \dots \dots \dots (6)$$

$K'$  is obtained from the linear plot of  $\ln Q_e$  against  $\epsilon^2$ .

### Freundlich adsorption isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption equation on multilayer and is often expressed as [13]:

$$Q_e = K_f C_e^{1/n} \dots \dots \dots (7)$$

Where  $Q_e$  is the quantity of solute adsorbed at equilibrium ( $mg/g$ ).  $C_e$  is the concentration of adsorbate at equilibrium.  $K_f$  and  $n$  are the empirical constants dependent on several factors. And  $\frac{1}{n}$  is the heterogeneity factor which indicates the strength of bond energy between sorbate and sorbent [6].

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. Mathematically, the equation is written as [14]:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \dots \dots \dots (8)$$

A plot of  $\ln Q_e$  against  $\ln C_e$  yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption.

### 3. RESULTS AND DISCUSSION

#### Functional groups analysis

In the present study, the FTIR spectra of the activated carbon (GAC) and activated carbon/iron oxide (MAC) product are shown in figure 1. The broad band around  $3398 \text{ cm}^{-1}$  and  $3150 \text{ cm}^{-1}$  can be assigned to O-H stretching vibration. The peak at  $1615$  and  $1557 \text{ cm}^{-1}$  can be attributed to C=C, the amine C-N stretch is found at  $1400 \text{ cm}^{-1}$  for MAC [10]. The absorbance peak at  $1170 \text{ cm}^{-1}$  may be associated with the stretching vibration of the phenolic structure. The adsorption bands around  $580\text{-}610$  in the IR spectra of MAC correspond to Fe-O bonds are attributed to the formation of ferrite phase [7]

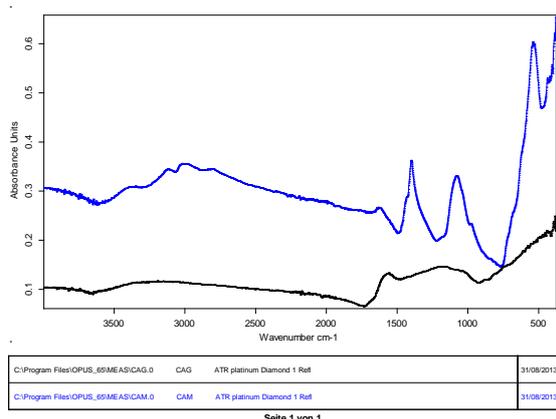


Figure 1: FTIR of GAC and MAC

#### Iodine number

Iodine number test was determined by the method described by [6, 15]. It gives an estimate of surface area and porosity. The result shows iodine values equal to  $656.7075 \text{ mg/g}$  for GAC and  $537.2334 \text{ mg/g}$  for MAC; this can be explained by the fact that the surface of MAC material is made UP of microspores.

#### pH of zero point charge ( $\text{pH}_{\text{pzc}}$ )

The point of zero charge of sorbent is the pH value at which the concentrations of acid and base species are equal [16]. After the batch equilibrium method, the  $\text{pH}_{\text{pzc}}$  values of GAC and MAC determinate were found to 5.36 and 5.91 respectively, indicating that the sorbent is slightly acidic [17]. The difference in  $\text{pH}_{\text{pzc}}$  values could be attributed to the structural change during the modification process.

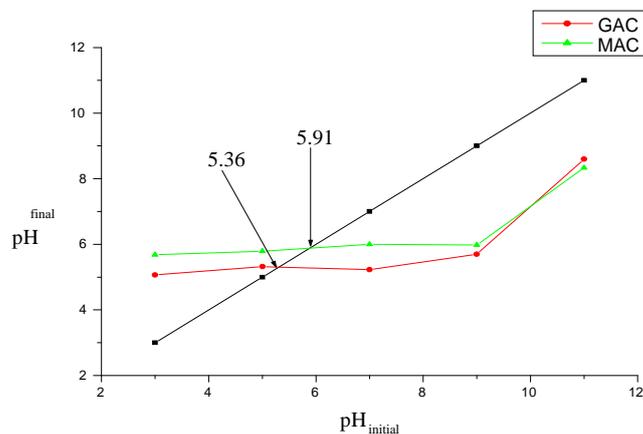
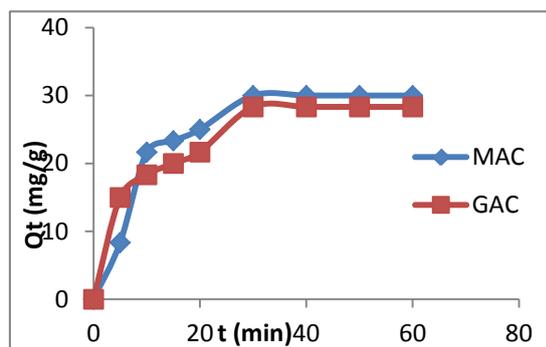


Figure 2:  $\text{pH}_{\text{pzc}}$  of GAC and MAC

#### Effect of contact time

Contact time is an important factor affecting removal of metal ions in solution. The

effect of contact time on the adsorption of Mn(II) ions in solution were shown in figure 3.



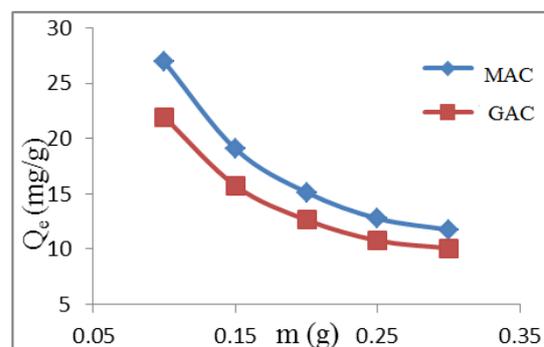
**Figure 3:** Effect of Contact time on adsorption of manganese ions on GAC and MAC

The result from the above graph show that the removal of metal ion increases as adsorption time increases. Initially, the rate of uptake is fast. However, equilibrium is attained the 30<sup>th</sup> minutes for GAC and MAC. It report that during adsorption of manganese(II) ions, the first step leads to surface adsorption and the second step leads to intraparticle transport from bulk fluid to the external surface of the porous adsorbent [6]. Thus, in the first phase, all the adsorption sites on the surface of the adsorbent materials are available [12] and the second phase might be due to the obstruction of the pores by the manganese ions.

### Effect of the amount of adsorbents

The results are given in figure 4 where it is observed that the quantity of manganese(II) ions adsorbed decreases when the mass of the adsorbents increases. This phenomenon is due to the fact that increases the mass of adsorbent leads to an agglomeration of the cells and consequently a reduction of the intercellular distances; this produced a screen effect leading to protection of the sites of connection of the adsorbate [18]. However, the maximum quantity adsorbed,  $Q_e = 21.93$  mg/g

for GAC and 26.93 mg/g for MAC, was reached with an adsorbent dose of 0.1 g.

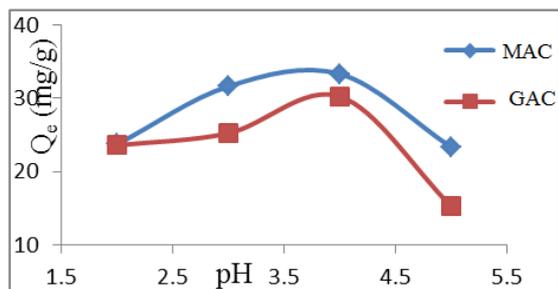


**Figure 4:** Effect of adsorbent mass on adsorption of manganese(II) ions on GAC and MAC

### Effect of pH during adsorption

The result shown in figure 5 indicates that maximum removal of Mn(II) ions takes place at pH 4 for the two adsorbents.

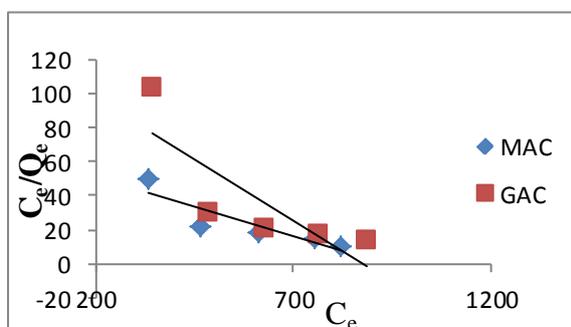
The values of  $pH_{pzc}$  of GAC and MAC are 5.36 and 5.91 respectively, where we can conclude that the surfaces of these adsorbents are negatively charged at pH above 5.36 and 5.91. At low pH, metal cations and protons compete for binding sites on adsorbent surface which results in lower sorption of metal ions [25]. The overall surface charge on adsorbent became negative [2] and at higher pH lower sorption is attributed due to reduced solubility of the metal ions and their precipitation as hydroxides anions forming manganese hydroxide precipitate [4]. Maximum quantity adsorbed are  $Q_e = 33.33$  and 30.26 mg/g for MAC and GAC respectively.



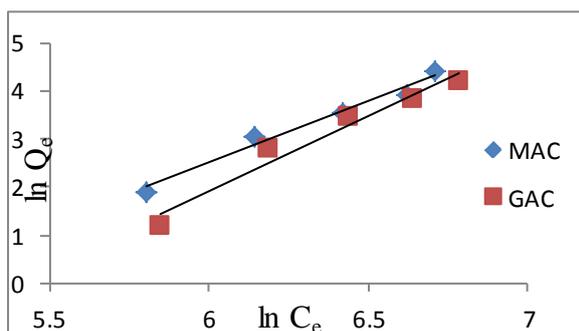
**Figure 5:** Effect of pH of solution on manganese(II) ions adsorption on GAC and MAC

**Adsorption isotherms**

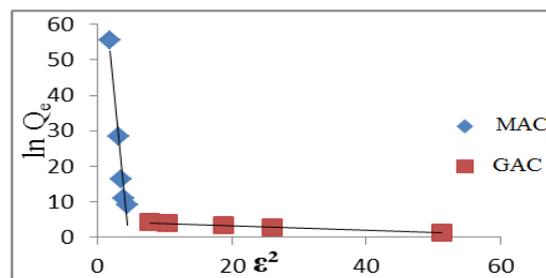
The linear transforms of the adsorption isotherms are represented by the figures below:



**Figure 6:** Linear plot of the Langmuir model



**Figure 7:** Linear Plot of the Freundlich model



**Figure 8:** Linear plot of the Dubinin-Radushkevich model

The values of Langmuir, Freundlich and D-R constants, are grouped in the following table below:

**Table 1: Parameters of isotherm models for Mn<sup>2+</sup> ions on MAC and GAC**

	MAC	GAC
<b>Langmuir</b>	$K_L$	$1.07 \times 10^{-3}$
	$Q_m$ (mg/g)	14.49
	$R^2$	0.791
	$R_L$	0.725-0.448
<b>Freundlich</b>	$K_F$	$6.4 \times 10^{-8}$
	$1/n$	2.562
	$R^2$	0.974
	$K$	-19.45
<b>D-R</b>	$Q_m$ (mg/g)	$6.435 \times 10^{38}$
	$E$ (Kj/mol)	0.16
	$R^2$	0.952
		0.994

The results obtained in this table enable us to say that the maximum quantities adsorbed are higher for the two materials using D-R isotherm. The value  $1/n$  for the two adsorbents higher than 1 is what explains the homogeneity of the surface. This also shows us that the modification of the GAC did not change the nature of the surface of the MAC. The value of  $n < 1$  shows that the adsorption process is chemical [19] and implies according to Hasnain *et al* in 2007, that the connections of adsorption are weak [20]. In addition, in comparison with the correlation coefficients (0.791 for MAC and 0.689 for GAC), we can say that the Langmuir isotherm does not describe in a satisfactory way adsorption of the manganese(II) ions. The maximum quantity obtained here is 14.49 and 6.94 mg/g respectively for MAC and GAC.

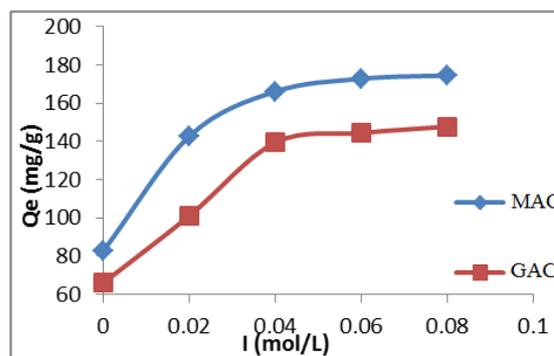
However, the calculation of the separation factor  $R_L$  allows us notes that adsorption is favorable [21] when the initial concentration increases. According to Ketcha *et al.* in 2012, the smaller the factor is, the more adsorption is favorable. Moreover, the high values of correlation coefficients of Freundlich (0.97 and 0.96) and of D-R, (0.95 and 0.99) enable us to say that they describe better the adsorption of  $Mn^{2+}$  ions by the MAC and the GAC.

**Tableau 2:** Maximum adsorption capacity  $Q_0$  (mg/g) for adsorption of Mn(II) ions by various adsorbents

Adsorbents	$Q_0$ (mg/g) $\times 10^2$	References
Activated carbon obtain from Birbira	0.0341	[2]
kaolinite	0.00446	[22]
Granular activated carbon	0.025	[1]
Pristine tamarindus nut shell	1.220	[4]
Acid treated tamarindus nut shell	1.820	[4]
Untreated volcanic ash	0.303	[1]
GAC	0.0694	This work
MAC	0.1449	This work

### Effect of ionic strength

The figures below illustrate the various shapes of curves obtained when varied the ionic strength.



**Figure 9: Effect of the ionic strength (Addition of  $CaCl_2$ )**

The figure above show that the adsorption of the manganese(II) ions by the GAC and the MAC increase with the addition of  $CaCl_2$  salt. However the surface of these materials being positively charged enables us to say that the positive electric field is one of the factors which enhances the

adsorption of the Mn(II) ions. This relation makes it possible to conclude that adsorption can occur independently of the charge on the surface of materials. Theoretically, when the electrostatic forces between the surface of the adsorbent and the ions of adsorbents are attractive, an increase in the ionic force decreases the adsorption capacity. On the other hand, when the electrostatic attraction is repulsive, the increase in the ionic force or strength

increases the adsorption capacity [23]. The experimental data of this study follow this second convention. A certain intermolecular number of forces were suggested to explain this aggregation such as: van der Waals [24] forces of attraction; Dipole-dipole forces which occur between the manganese molecules in the solution. Consequently, the high adsorption of the manganese(II) ions under these conditions can be allotted to the aggregation of the latter, induced by the action of the ions of the salt, meaning that the  $Mn^{2+}$  ions are bounded, increasing the extent of adsorption on the surface of the adsorbent. In addition, we notice that the MAC adsorbs more than the GAC with the quantities of maximum adsorption of 172.76 mg/g and 149.43 mg/g. This is explained by the fact that since the manganese(II) ions being a ferromagnetic element is strongly attracted by the iron oxides present at the surface of the magnetic MAC.

#### 4. CONCLUSION

Granular activated carbon and activated carbon modified by iron oxide have been used as adsorbent. The result reveals that the adsorption capacity is influenced by the contact time, the pH, the mass of the adsorbent and the ionic strength. Freundlich and Dubinin-Radushkevich isotherms described well the adsorption of manganese(II) ions. MAC was found to adsorb more than the GAC for the removal of manganese(II) ions from aqueous solution as confirmed by their adsorption capacities. Hence we can conclude that the modification of AC by iron oxide would be an effective means of increasing the adsorption capacity of manganese(II) ions.

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