Journal of Environmental Science and Technology

ISSN 1994-7887

science alert

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OPEN ACCESS **Journal of Environmental Science and Technology**

ISSN 1994-7887
DOI: 10.3923/jest.2016.226.237

Research Article
Removal of Mn (II) from Aqueous Solutions by Activated Carbons Prepared from *Coula edulis* Nut Shell

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Abstract

The batch removal of Mn (II) from aqueous solution using activated carbon prepared from *Coula edulis* nut shell was performed. Different experimental conditions such as: pH (2-6), Mn (II) ions solution concentrations (39.05, 86.66, 121.01, 155.23 and 191.27 mg L^{-1}), contact time (10, 20, 40, 60 and 80 min) and temperature (25, 35 and 45°C) were investigated. The adsorption of Mn (II) is highly pH-dependent and the optimum pH for the removal was found to be 4 for all types of carbon. The adsorption capacity of Mn (II) removal increased with increasing in initial concentration of Mn (II) ions in solution. Freundlich and Langmuir isotherm models fitted well the experimental data. Kinetics of adsorption showed that this reaction followed the pseudo-second order. The adsorption process is spontaneous under the experimental conditions. Activated carbons prepared from *Coula edulis* nut shells may be used efficiently at the removing of Mn (II) from aqueous solution.

Key words: *Coula edulis*, manganese (II), kinetic study, environmental pollution, adsorption

Received: November 02, 2015 Accepted: January 16, 2016 Published: February 15, 2016

Citation: M. Zue Mve, T. Makani and F. Eba, 2016. Removal of Mn (II) from aqueous solutions by activated carbons prepared from *Coula edulis* nut shell. J. Environ. Sci. Technol., 9: 226-237.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Manganese is one of Gabon metal ores deposit. However, its opencast mining poses the problem of environmental pollution in the extraction area (Ontod *et al*., 2013). Some works, permitted to study Mn (II) toxicity in soil, its accumulation in edible part harvested in plant cultivated around Moanda region (Ontod *et al*., 2013; Eba *et al*., 2007) and bioaccumulation in the tissues of living organisms (Kebede and Wondimu, 2004). Manganese is a trace element useful for the functioning of the human body (2-5 mg day^{-1}), but as a heavy metal it is potentially toxic, especially after exposure to high doses. The long time exposure to manganese affects several systems in the human body, most appreciable being the central nervous system (Esfandiar *et al*., 2014), also respiratory, reproductive, cardiac systems (Mergler and Baldwin, 1997) and in ultimate neurosis or neurological illness clinic called manganism (Ostiguy *et al*., 2006). Because of that problems occur due to presence of manganese in water, as well as of their toxicity, non-biodegradability and persistent nature, their removal becomes an absolute necessary and manganese deserves to be removed from wastewaters and public water supplies. According to WHO the maximum permissible limit of manganese in drinking water is 0.5 mg L^{-1} (Celik and Demirbas, 2005).

Adsorption is the method developed in this study because it is an economically favourable and technically simple method (Das *et al*., 2013; Karthikeyan *et al*., 2005). The use of biomaterials has enlarged the field of low-cost sorbents/adsorbents (Deng *et al*., 2010; Gueu *et al*., 2007). A limited report of these biomaterials includes. Peanut hull-based (Zhong *et al*., 2012), tea waste (Gurten *et al*., 2012), Bamboo (Liu *et al*., 2010), palm nut shells (Atheba, 2009) and coconut shells (Devi *et al*., 2012).

Coula edulis is a tree species encountered in forest regions in western and central Africa. Very little is known about this species (Moupela *et al*., 2011) which has many local uses and its fruits are eaten and marketed by various communities. A *Coula edulis* fruit is constituted of pulp, cockle and an almond. While almonds of *Coula edulis* is consumed as food (Moupela, 2013), its cockles are rejected as garbage. This garbage is a biomass used in this study as a raw material for the preparation of *Coula edulis* nut shells activated carbons. The transformation of this lignocellulosic garbage is interesting for two reasons: (i) Reduction of the quantity of plant garbage that constitutes by their abundance a specific pollution. (ii) Transformation of garbage in useful materials for the purification of wastewaters.

The main objective of this study was to investigate the adsorption capacity of activated carbon prepared from *Coula edulis* nut shells impregnated in acidic solution (HAC), Zn^{2+} salt solution (ZAC) and not impregnated (ACo) to remove Mn (II) ions from aqueous solutions. The experimental parameters were pH (2-6), initial Mn (II) solution concentrations (39.05, 86.66, 121.01, 155.23 and 191.27 mg L^{-1}), contact time (10, 20, 40, 60 and 80 min) and temperature (25, 35 and 45°C).

MATERIALS AND METHODS

Preparation and characterization of bio sorbent: *Coula edulis* nut shells were provided from region of Libreville (GABON). They were collected and washed with distilled water to remove the surface adhered particles, then dried in oven at 110°C for 24 h. They were then milled and sieved to obtain particles sized in diameter range of 0.83-1 mm. After drying for several hours, the fine powder of *Coula edulis* nut shells (CES) was heated at 600°C during 5 h and cooled to ordinary temperature. The powder of activated carbon was then washed with demineralized water, filtered and dried in an oven at 110°C for 24 h. A fraction of activated carbon is plunged into a solution of HCl (HAC) or in a Zn^{2+} salt (ZAC) solution during 48 h at 120°C, washed with demineralized water under the obtainment of a pH in the order of 6.5. This constituted a chemical activation, while a simple pyrolyzed of *Coula edulis* nut shell was considered as physically activated carbon (ACo). The final powder is preserved in a tight glass for use as adsorbents. Activated carbons were characterised.

Preparation of Mn (II) ion solutions: Adsorption of Mn (II) solution was carried out using batch method by adding 0.15 g of AC powder to 50 mL of Mn (II) solutions of known concentrations. The solutions were stirred using a magnetic stirrer at predetermined times intervals and are kept in a bath at different temperature (25, 35 and 45°C) by a thermostat with external circulation. After that, the mixture was filtrated and Mn (II) ions in filtrates were analysed using ICP-AES. Calibration curve were obtained with standard Mn (II) solutions by recording the absorbance values of various concentration of Mn (II) at maximum.

The adsorption capacity q_e (mg g^{-1}) were calculated using following Eq. 1:

$$q_e = \frac{(C_O - C_e)}{m} \times V \qquad (1)$$

where, Co (mg L^{-1}) and Ce (mg L^{-1}) are the initial and equilibrium concentrations of Mn (II) ions solution, respectively, V (L) is the volume of solution and m (g) is the mass of activated carbon used.

RESULTS AND DISCUSSION

Characterization of activated carbon: Activated carbons are a widely used adsorbent due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface, respectively. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico chemical properties of the chosen adsorbents are listed in Table 1.

The quantitative assessment of the acido-basic functions of surface was achieved by the method of Boehm (1966), which gave the results consigned in the Table 2. This procedure has already been used by several researchers (Eba *et al*., 2011; Gueu *et al*., 2007).

Dealing with the acidic functions, both weak and strong acidic groupings, neutralized by CH_3CONa were more numerous in carbons chemically treated (ZAC or HAC) than in unprocessed ones (AC). Acidic groupings possessing lactonic and phenolic functions, which are neutralized by NaOH were found in the order AC>HAC>ZAC. Carboxylic functions neutralized by $NaHCO_3$ were found in the order AC<ZAC<HAC. The total acidity on activated carbon surface increased according the sequence AC<ZAC<HAC and total basic function obeyed to the order AC<HAC<ZAC. Basic functions are lower than acid functions. Similar results were reported by Bamba *et al.* (2009).

Other characteristics of these materials such as mineral composition of *Coula edulis* nut shell ash, micro and meso porosities and surface area according to iodine measurements, respectively, pH of zero charge and FTIR are presented, respectively in Table 2-4.

Effect of pH: The pH effect was studied in the range of 2.0-5.0 at 25°C and keeping temperature at 25°C, initial concentration of Mn (II) ions solution of 191.27 mg L^{-1}, an agitation speed of 200 rpm and interaction time of 80 min. The results obtained are shown in Fig. 1.

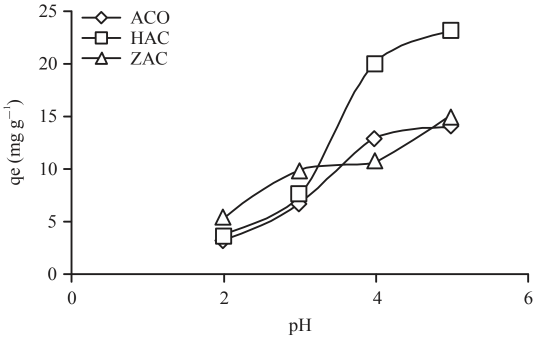

Fig. 1: Variations of the amount of Mn (II) ions adsorbed per unit mass as a function of pH using activated carbons: ACo, HAC and ZAC which are respectively activated carbons obtained after pyrolysis at 600°C and after pyrolysis at 600°C followed by an impregnation into acidic solution and after pyrolysis at 600°C followed by an impregnation into Zn^{2+} salt solution, respectively (initial concentration at 191.27 mg L^{-1}, agitation speed 200 rpm, contact time 60 min and adsorbent 3 g L^{-1} at 25°C)

Table 1: Boehm titration

Activated carbons	NaOH Lacton+phenol (meq g^{-1})	$NaHCO_3$ Carboxylic (meq g^{-1})	CH_3CONa Strong+weak acidities (meq g^{-1})	Total acidity (meq g^{-1})	Previous reports on coconut shell or palm nut shell Total acidity (meq g^{-1})	HCl Total basicity (meq g^{-1})	Previous reports on coconut shell or palm nut shell Total Basicity (meq g^{-1})
ACo	0.26	0.06	0.38	0.70	Gueu *et al.* (2007)	0.02	Atheba (2009)
HAC	0.24	0.10	0.48	0.82		0.04	Bamba *et al.* (2009)
ZAC	0.18	0.08	0.48	0.74		0.08	This work

pH pzc is the pH of point of zero charge and ACo, HAC and ZAC are activated carbon obtained without the impregnation, activated carbon obtained through the impregnation into acidic solution and activated carbon obtained through the impregnation into Zn^{2+} salt solution, respectively

Table 2: Mineral composition of *Coula edulis* nut shell ash

Parameters	Content (mg kg^{-1})	Previous report on coconut shell
Potassium (K)	660.46±66.04	1511.77 mg kg^{-1} Thebo *et al.* (2014)
Calcium (Ca)	904.87±30.74	556.3 mg kg^{-1} Thebo *et al.* (2014)
Magnesium (Mg)	1402.52±140.2	2593.06 mg kg^{-1} Thebo *et al.* (2014)
Iron (Fe)	768.68±40.24	997.97 mg kg^{-1} Thebo *et al.* (2014)
Manganese (Mn)	14.34±1.43	8.67 mg kg^{-1} Thebo *et al.* (2014)
Sodium (Na)	633.17±63.3	107.9 mg kg^{-1} Amjad *et al.* (2004)
Aluminum (Al)	403.73±36.73	This work
Lead (Pb)	23.49±3.37	0.3 mg kg^{-1} Amjad *et al.* (2004)

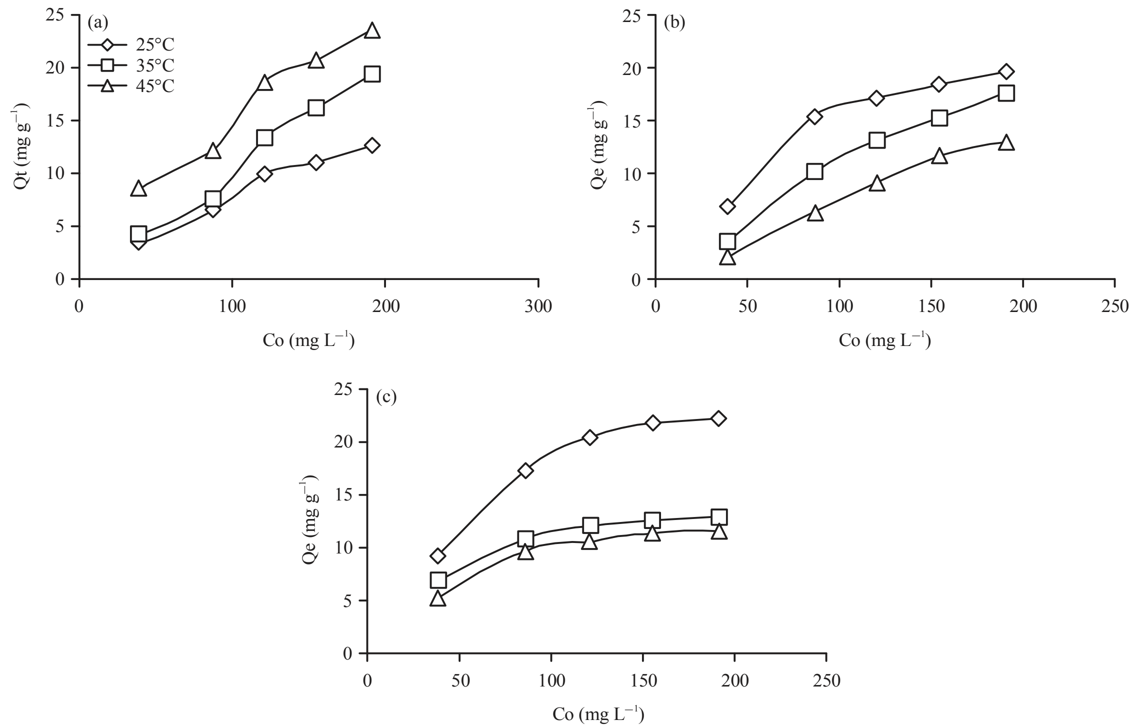

Fig. 2(a-c): Variations of amount of Mn (II) ions adsorbed per unit mass as a function of initial concentration of Mn (II) ions solution using activated carbons obtained after pyrolysis at 600°C (a) ACo, (b) Impregenation into acidic solution and (c) Into Zn^{2+} salt solution (experimental conditions: contact time 60 min, pH(5), adsorbent 3 g L^{-1} and agitation speed 200 rpm at 25, 35 and 45°C)

Table 3: Point of zero charge, iodine number and surface area of *Coula edulis* activated carbon

Activated carbon	pH pzc	Iodine number (mg g^{-1})	Surface area (m^2 g^{-1})
ACo	3.0	359.21	107.41
HAC	3.0	474.71	259.24
ZAC	3.5	558.49	224.86

ACo, HAC and ZAC are activated carbon obtained without the impregnation, activated carbon obtained through the impregnation into acidic solution and activated carbon obtained through the impregnation into Zn^{2+} salt solution, respectively

Table 4: FT-IR characteristics of *Coula edulis* activated carbon

ACo	HAC	ZAC	FT-IR band (cm^{-1})
-C-C-	-C-C-	-C-C-	1033.3-1049
-C-O	-C-O	-C-O	1184.79-1240.03
-C = O and –C = C-	-C = O and -C = C-	-C = O and –C = C-	1594.15-1606.17
-C-O-C-			1099.46

ACo, HAC and ZAC are activated carbon obtained without the impregnation, activated carbon obtained through the impregnation into acidic solution and activated carbon obtained through the impregnation into Zn^{2+} salt solution, respectively

The amount of Mn (II) ions adsorbed increases with the increase in pH from 2-5. Similar results have been reported by Ahmed *et al.* (2015). For pH lower than 3, the uptake of Mn (II) ions adsorbed on the activated carbons ACo, HAC and ZAC increased slowly and for pH higher than 3 the uptake of Mn (II) ions adsorbed on ZAC, increased greatly while on ACo and HAC the uptake continuous to increase moderately. This behaviour occurred because of: (i) at pH <3.0; 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, (ii) In the side with pH >3, the concentration of H^+ is negligible, the interaction adsorbent-adsorbate concerns preponderantly adsorption sites on the surface of activated carbon and Mn (II) ions and the amount of Mn (II) ions adsorbed is high. Similar results have been reported by Mengistie *et al.* (2012).

Effect of initial concentration of Mn (II) solution: The study of the effect of initial concentration of Mn (II) solution was performed at adding 0.15 g of activated carbon into 25 mL of Mn (II) solution at varying concentrations (39.05, 86.66, 121.01, 155.23 and 191.27 mg L^{-1}) and keeping agitation speed (200 rpm), pH (5) and interaction time (80 min) constant. The results are shown in Fig. 2a (concerning ACo), b (concerning HAC) and c (concerning ZAC), respectively.

It is observed that the variations of the amounts of Mn (II) ions adsorbed increased gradually with the increase in initial concentrations of Mn (II) ions aqueous solutions. This result is

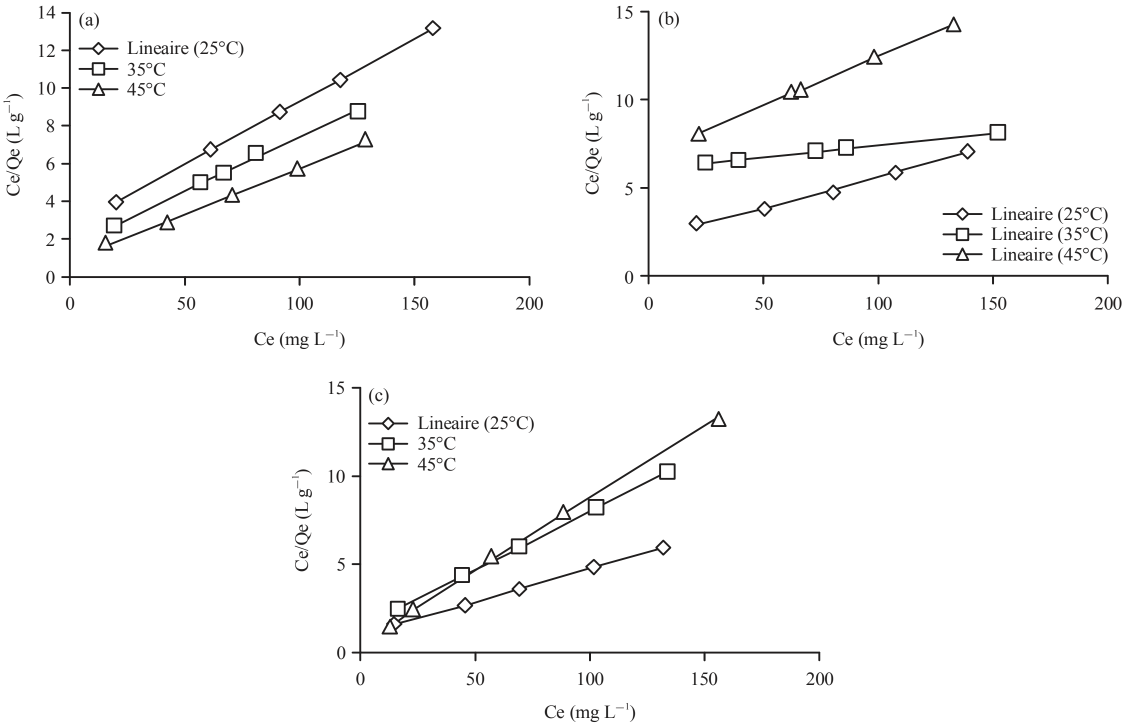

Fig. 3(a-c): Plots of variations of the ratio of the equilibrium concentration on amount Mn (II) adsorbed per unit mass as a function of the equilibrium concentration related to the Mn (II) ions adsorption using activated carbons obtained after pyrolysis at 600°C (a) ACo, (b) Impregnation into acidic solution and (c) Into Zn^{+2} salt solution (experimental conditions: pH (5), adsorbent 3 g L^{-1}, contact time 60 min and agitation speed 200 rpm at 25, 35 and 45°C)

similar to that reported by Ghasemi *et al.* (2013) for the study on the adsorption of Ni (II) onto activated carbon prepared from askari grape dust.

These results correspond to the fact that at relative low Mn (II) ions concentrations, the number of available adsorption sites on the adsorbent surface is relatively higher than of the number of Mn (II) ions given by the adsorbate solution and consequently the amount of Mn (II) ions adsorbed is weak in this case. In the opposite, when the concentration of Mn (II) solutions is progressively high, the adsorption becomes more and more efficient, because of the increase of Mn (II) ions number liberated by Mn (II) solutions which compete to adsorption sites (Gupta *et al.*, 2003).

Adsorption isotherms: The good description, at a fixed temperature, of the adsorptive process for the removal of solute from solution onto adsorbent, depends of successful applicability of adsorption isotherm model to experimental data. An adsorption isotherm model is expressed by an equation which contains some constant parameters describing the surface properties and affinity of the adsorbent. Two kinds among several isotherm equations were tested to fit the experimental data.

The Langmuir equation can be described by the linearized form (Nwabanne and Igbokwe, 2012):

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \qquad (2)$$

where, K_L is the Langmuir constant (L mg^{-1}) and q_m is the maximum amount of adsorbate retained on the medium used (mg g^{-1}). Equilibrium parameter or separation factor (R_L), which characterizes the adsorption, is defined by the following equation:

$$R_L = \frac{1}{(1 + K_L C_O)} \qquad (3)$$

where, C_0 is the initial concentration of the adsorbate (mg L^{-1}). The R_L value indicates the mode of sorption of the isotherm process, if the process is unfavourable (R_L>1) or linear (R_L = 1) or favourable (0<R_L<1) or irreversible (R_L = 0). The plotting C_e/q_e versus (Ce) results straight line of slope $1/q_m$ and intercept $1/K_L q_m$. Results are shown in Fig. 3a (ACo), b (HAC) and c (ZAC).

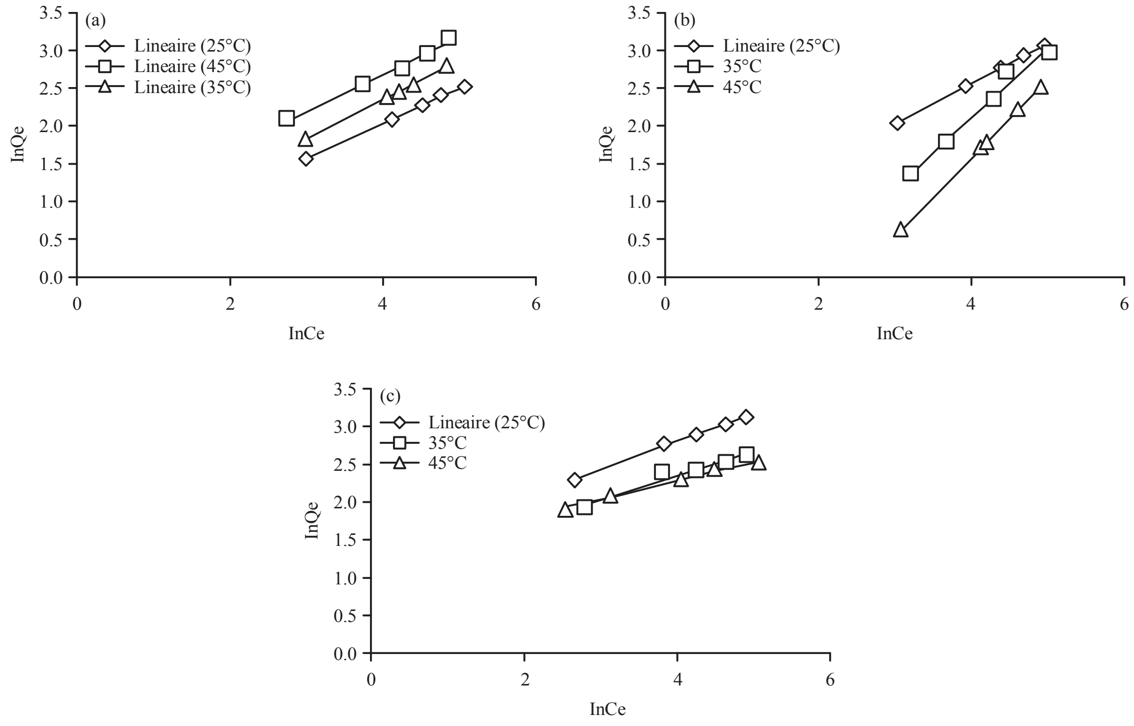

Fig. 4(a-c): Plots of variations of the logarithm of amount Mn (II) adsorbed per unit mass as a function of the logarithm of equilibrium concentration of Mn (II) ions using activated carbons obtained after pyrolysis at 600°C (a) ACo, (b) Impregnation into acidic solution and (c) Into Zn^{+2} salt solution (experimental conditions: pH (5), adsorbent 3 g L^{-1}, contact time 60 min and agitation speed 200 rpm at 25, 35 and 45°C)

The linearized Freundlich equation is represented by the following expression (Nwabanne and Igbokwe, 2012):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

where, K_f is the Freundlich constant (mg g^{-1}) and n is the intensity adsorption factor. Plotting $\ln q_e$ versus $\ln C_e$ results straight line of slope 1/n and intercept $\ln K_f$. Results are shown in Fig. 4a (ACo), b (HAC) and c (ZAC).

The Langmuir and Freundlich constants for the adsorption isotherm models and statistical are summarized in Table 5.

The values of Langmuir constant: K_L for ACo and HAC increased with the increase in temperature from 25-35°C and to 45°C, contrary to the case of ZAC. At a given temperature K_L for HAC is lower than those of ACo and ZAC. The Langmuir monolayer adsorption capacities, q_m increased by the increasing in temperature for ACo (15.151, 17.006 and 20 mg g^{-1}) and decreased for HAC (27.778, 22.22 and 18.518 mg g^{-1}) and ZAC (27.027, 15.1515 and 12.3456 mg g^{-1}) with increase in temperature. Values of Langmuir maximum adsorption capacities in similar ranges have been reported by Eba *et al.* (2011) from study of adsorption of Pb (II) onto activated carbons. The R_L values of this work have been obtained in conformity with the requirement, $0<R_L<1$ of favourable adsorption (Rachel *et al.*, 2015). The experimental data fitted well parameters obtained from Langmuir isotherm equation and that confirmed the monolayer adsorption of Mn (II) onto the ACo, HAC and ZAC surface.

The Freundlich constant: K_f, increased with the increase in temperature for ACo and decreased under the same conditions for HAC and ZAC. The levels of these constants were found in the order: ZAC>ACo>HAC.

Values of Freundlich constant: The n, related on the intensity of the adsorption, decreased with the increase in temperature for AC and ZAC contrary to the case of HAC. The adsorption intensity was found more elevated for ZAC than for Ac and then for HAC. As n values higher than 1 express a chemical control of the adsorption process, the adsorption of Mn (II) ions onto surfaces of *Coula edulis* activated carbons is largely a chemical phenomenon.

Table 5: Langmuir and Freundlich isotherm fitted parameters for the adsorption of Mn (II) onto *Coula edulis* activated carbon (pH (5), adsorbent 3 g L^{-1}, agitation speed 200 rpm contact time 60 min)

	Langmuir											
	ACo				HAC				ZAC			
T (°C)	K_L (L mg^{-1})	Qm (mg g^{-1})	R^2	R_L	K_L (L mg^{-1})	Qm (mg g^{-1})	R^2	R_L	K_L (L mg^{-1})	Qm (mg g^{-1})	R^2	R_L
25	0.0251	15.151	0.99	0.172 - 0.505	0.0076	27.778	0.982	0.407 - 0.771	0.062	27.027	0.999	0.077 - 0.292
35	0.0387	17.006	0.975	0.119 - 0.398	0.0122	22.22	0.993	0.299 - 0.677	0.05053	15.1515	0.999	0.094 - 0.336
45	0.062	20	0.955	0.077 - 0.292	0.0184	18.518	0.97	0.221 - 0.582	0.0387	12.3456	0.999	0.119 - 0.398

	Freundlich											
	ACo				HAC				ZAC			
T (°C)	K_f (mg g^{-1})	n	1/n	R^2	K_f (mg g^{-1})	n	1/n	R^2	K_f (mg g^{-1})	n	1/n	R^2
25	1.168	2.132	0.469	0.926	1.491	0.952	1.05	0.927	3.7247	4	0.25	0.99
35	1.289	2.087	0.479	0.99	0.22	1.118	0.89	0.998	3.691	3.039	0.32	0.996
45	2.054	2.04	0.49	0.99	0.073	1.851	0.54	0.99	3.6583	2.673	0.374	0.995

T is the temperature in Kelvin, q_m is the Langmuir monolayer maximum capacity, K_L is the Langmuir equilibrium constant, R_L is the Langmuir dimensionless factor, R^2 is the correlation coefficient, K_f is the Freundlich equilibrium constant, n is the intensity adsorption factor and ACo, HAC and ZAC are activated carbon obtained without the impregnation, activated carbon obtained through the impregnation into acidic solution and activated carbon obtained through the impregnation into Zn^{2+} salt solution, respectively

The applicability of Langmuir and Freundlich isotherm models to experimental data gave models parameters with correlation coefficients higher to 0.95. This indicates that Langmuir and Freundlich isotherm models describe in a satisfactory manner, the adsorption of the manganese (II) ions onto AC, HAC and ZAC (Nwabanne and Igbokwe, 2012).

Kinetic studies: Effect of contact time: The effect of contact time on the removal of Mn (II) ions was carried out at varying the interaction duration of a mixture of 0.15 g of activated carbon and 50 mL of Mn (II) ions solution under constant agitation speed (200 rpm), pH (5). The results are shown in Fig. 5a (ACo), 5b (HAC) and 5c (ZAC).

It is observed that, the growth of Mn (II) ions uptake, initially was rapid and then gradually diminished to attain an equilibrium time beyond which there was no significant increase in the removal. The equilibrium was nearly reached before 60 min for these tree different activated carbons. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface (Farghali *et al*., 2013) and that the duration of the interaction permitted to each Mn(II) ion enough time to reach adsorbent binding site.

Adsorption kinetic modelling: The experimental variations of the adsorption capacities as a function of time were analysed using Lagergren first order (Das *et al*., 2013) and pseudo-second order (Raoul *et al*., 2014) kinetic models.

The Lagergren first order Eq. 5 is represented as:

$$\ln(q_e - q_t) = \ln q_e - \frac{K_1 t}{2.303} \quad (5)$$

where, q_e and q_t are the amounts of Mn (II) adsorbed (mg g^{-1}) at equilibrium and at time t, respectively and k_1 is the Lagergren rate constant of first order kinetic adsorption (min^{-1}). Values of q_e and k_1 at different concentrations were calculated from the slope and intercept of the plots of ln (q_e-q_t) versus t (Fig. 6a (ACo), b (HAC) and c (ZAC)). The respective values are given in the Table 6.

The pseudo second order rate equation is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_R^2} + \frac{t}{q_e} \quad (6)$$

where, k_2 is the rate constant of second order kinetic adsorption (g/mg/min). Values of k_2 and qe were calculated from the plots of t/qt versus t (Fig. 7a-c).

Table 3 summarizes the results obtained for the two types of kinetic models. The experimental equilibrium uptakes $(q_e)_{exp}$ were compared with those calculated theoretically $(q_e)_{th}$ from pseudo-first-order or pseudo-second-order kinetic models

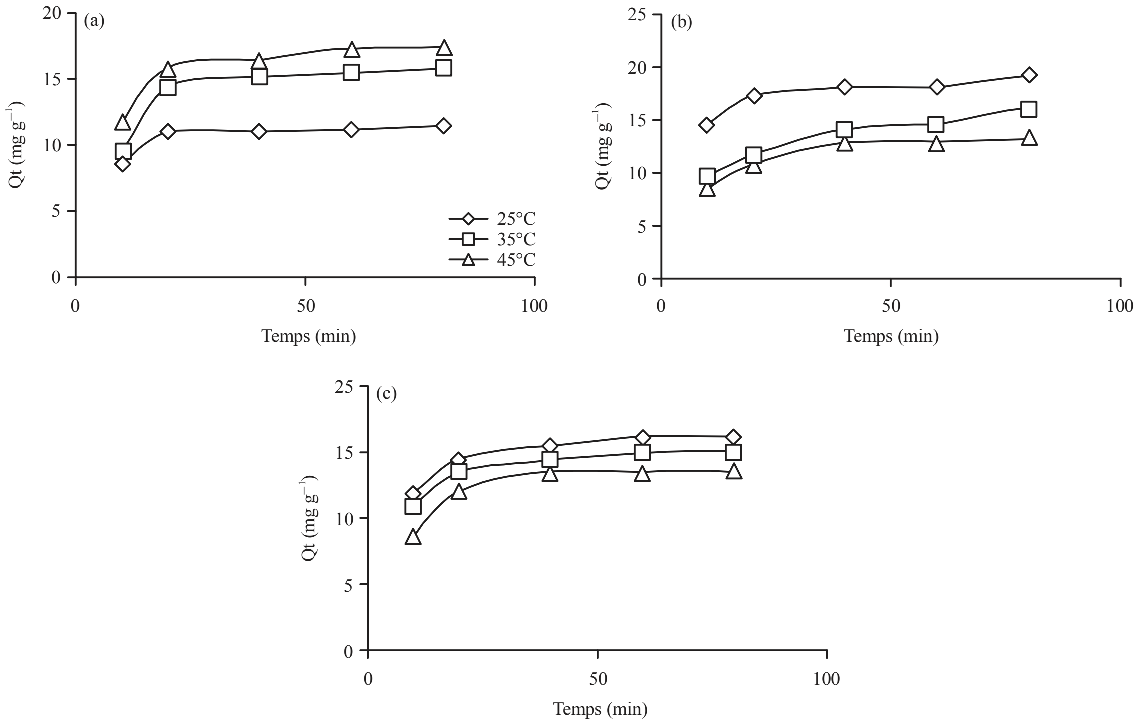

Fig. 5(a-c): Variations of amount of Mn (II) ions adsorbed per unit mass as a function of contact time using activated carbons obtained after pyrolysis at 600°C (a) ACo, (b) Impregnation into acidic solution and (c) Into Zn^{+2} salt solution (experimental conditions: initial concentration 191.27 mg L^{-1}, pH (5), adsorbent 3 g L^{-1} and agitation speed 200 rpm at 25, 35 and 45°C)

Table 6: Lagergren first and pseudo second order kinetics parameters for the adsorption of Mn (II) ions at 25, 35 and 45°C (experimental conditions: pH (5), adsorbent 3 g L^{-1}, agitation speed 200 rpm)

Lagergren first order

T (°C)	Activated carbon	$q_{e\,(exp)}$ (mg g^{-1})	$q_{e\,(th)}$ (mg g^{-1})	K_1 (1/min)	R^2	Deviation (%)
	CA_0	13.46	7.0568	0.048	0.985	47.57
25	CAH	19.20	3.0222	0.019	0.905	84.25
	CAZ	16.24	7.3522	0.075	0.909	54.72
	CA_0	16.76	8.9441	0.035	0.989	46.63
35	CAH	16.08	6.2463	0.025	0.948	61.15
	CAZ	15.05	6.6326	0.077	0.898	55.92
	CA_0	20.40	8.6971	0.018	0.987	57.36
45	CAH	13.28	4.6181	0.046	0.916	65.22
	CAZ	13.66	6.7328	0.081	0.904	50.71

Pseudo second order

T (°C)	Activated carbon	$q_{e\,(exp)}$ (mg g^{-1})	$q_{e\,(th)}$ (mg g^{-1})	K_2 (g/mg/min)	R^2	Deviation (%)
25	CA_0	13.46	13.889	0.0096	0.973	-3.187
	CAH	19.20	19.6078	0.0191	0.998	-2.123
	CAZ	16.24	16.9491	0.02135	0.999	-4.366
35	CA_0	16.76	18.181	0.0072	0.995	-8.478
	CAH	16.08	17.2413	0.0058	0.992	-7.222
	CAZ	15.05	15.625	0.0248	0.999	-3.82
45	CA_0	20.40	21.276	0.0053	0.968	-4.294
	CAH	13.28	14.0845	0.0166	0.998	-6.057
	CAZ	13.66	14.0845	0.0311	0.999	-3.107

T is the temperature in Kelvin, q_e (exp) is the experimental monolayer maximum capacity, q_e (th) is the theoretical monolayer maximum capacity, K_1 is the Lagergren first order constant, R^2 is the correlation coefficient, K_2 is the pseudo second order constant and ACo, HAC and ZAC are activated carbon obtained without the impregnation, activated carbon obtained through the impregnation into acidic solution and activated carbon obtained through the impregnation into Zn^{2+} salt solution, respectively

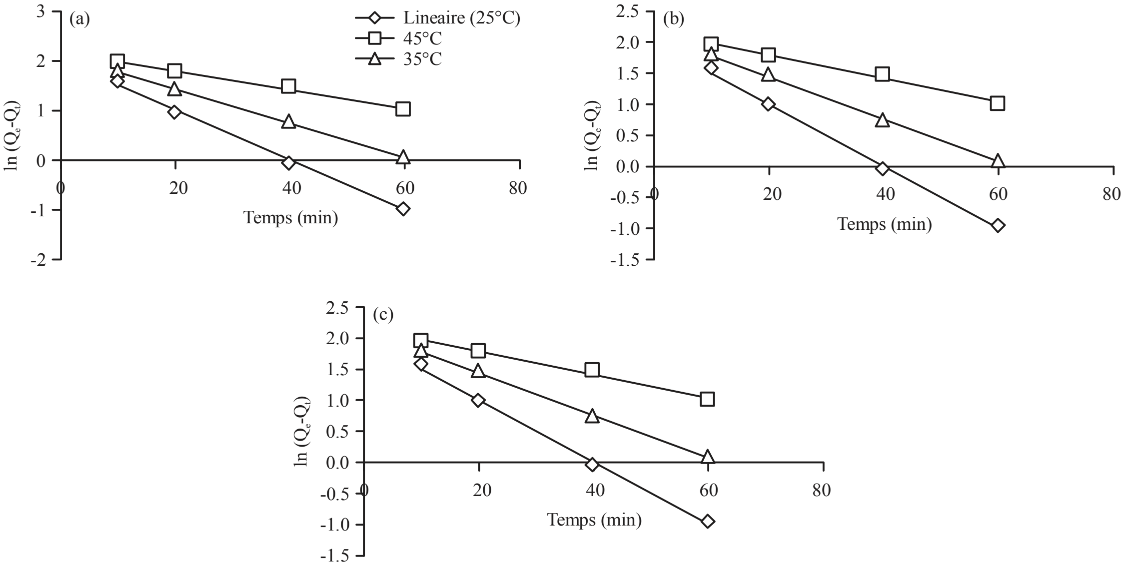

Fig. 6(a-c): Plots of variations of the logarithm of difference between the equilibrium Mn (II) ions uptake and Mn (II) ions uptake per unit mass for any times as a function of time (Lagergren first-order kinetic model) for the adsorption of Mn (II) ions using activated carbons obtained after pyrolysis at 600°C (a) ACo, (b) Impregnation into acidic solution and (c) Into Zn^{+2} salt solution (experimental conditions: pH (5), agitation speed 200 rpm and adsorbent 3 g L^{-1} at 25, 35 and 45°C)

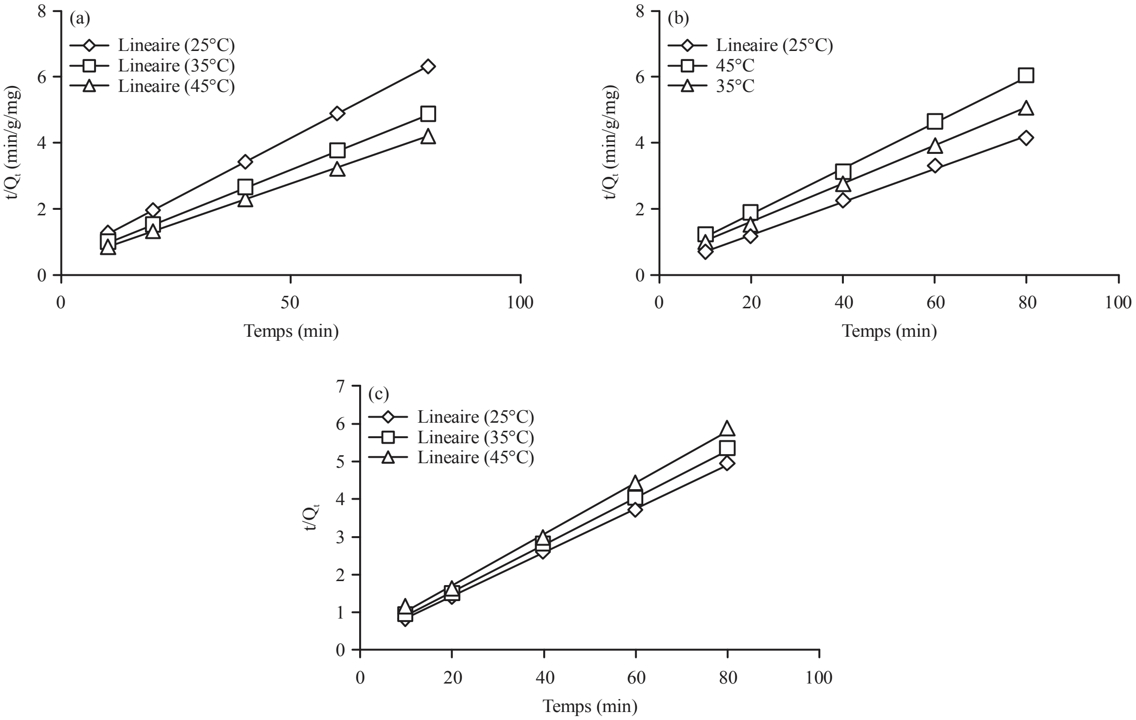

Fig. 7(a-c): Plots of variations of the ratio of time on adsorption capacity related any time as a function of time (pseudo- second-order kinetic model) for the adsorption of Mn (II) ions for the adsorption of Mn (II) ions using activated carbons obtained after pyrolysis at 600°C (a) ACo, (b) Impregnation into acidic solution and (c) Into Zn^{+2} salt solution (experimental conditions: pH (5), agitation speed 200 rpm and adsorbent 3 g L^{-1} at 25, 35 and 45°C)

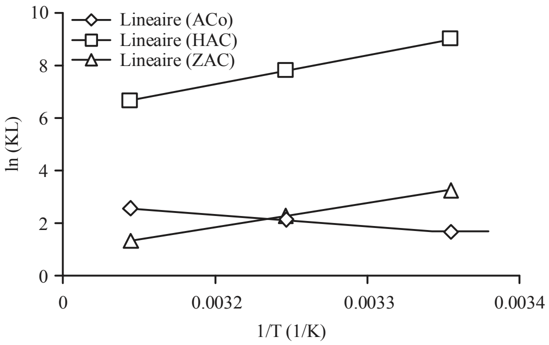

Fig. 8: Plots related to the variations of Langmuir equilibrium energetic constant (K_L, L/g) as a function of the temperature reverse (1/T, K^{-1}) for Mn (II) ions adsorption using activated carbons (experimental conditions: pH (5), contact time 60 min, agitation speed 200 rpm, initial concentration 191.27 mg L^{-1} and adsorbent 3 g L^{-1}). ACo, HAC and ZAC are respectively activated carbons obtained after pyrolysis at 600°C and after pyrolysis at 600°C followed by an impregnation into acidic solution and after pyrolysis at 600°C followed by an impregnation into Zn^{2+} salt solution, respectively

Table 7: Thermodynamic parameters: The enthalpy change (H°), entropy change (S°) and the free energy change (ΔG°)

Activated carbon	ΔH (KJ mol^{-1})	ΔS (J mol^{-1})	ΔG (KJ mol^{-1})	T (K)	R^2
			-2.74	298	
ACo	23.7	88.87	-3.629	308	0.99
			-4.51	318	
			-14.80	298	
HAC	-60.7	-153.80	-13.35	308	0.98
			-11.82	318	
			-8.04	298	
ZAC	-76.3	-229.05	-5.75	308	0.99
			-3.46	318	

T is the temperature in Kelvin, R^2 is the correlation coefficient and ACo, HAC and ZAC are activated carbon obtained without the impregnation, activated carbon obtained through the impregnation into acidic solution and activated carbon obtained through the impregnation into Zn^{2+} salt solution, respectively

through the rate of deviation and correlation coefficients values have been chosen as parameters at determining the reaction order.

The rate constant related to the Lagergren model (K_1) increased with the increase in temperature for HAC and ZAC contrary to the case of AC. The rate constant values were found in the order ZAC>HAC>AC. Despite correlation coefficients higher than 0.95, the applicability of Lagergren model gave theoretical $(q_e)_{th}$ values, with deviations rate to experimental measurements remained between 47.57 and 57.37% for AC, between 84.27 and 65.22% for HAC and between 54.72 and 50.71% when temperature varied from 25-45°C.

The rate constant for the pseudo-second-order kinetic model (K_2) decreased by increasing in temperature for AC and for HAC (Kobiraj *et al*., 2012) contrary to the case of ZAC (Abechi *et al*., 2011). The K_2 values were classified in the order ZAC>HAC>AC. The pseudo-second-order kinetic parameters have been determined with correlation coefficients higher than 0.95. So, the theoretical $(q_e)_{th}$ values have been obtained with deviation rate to experimental data lower than 10%.

The results analysis indicated clearly that the adsorption of Mn (II) ions on the surfaces of the *Coula edulis* activated carbons: AC, HAC and ZAC, followed the pseudo-second-order kinetic model rather to Lagergren kinetic model.

Thermodynamic studies: In order to determine the thermodynamic feasibility and the thermal effects of the sorption, the Gibbs free energy (ΔG°) the entropy (ΔS°) and the enthalpy (ΔH°) where calculated. The G° is the fundamental criterion to determine if a process occurs spontaneously. For a given temperature, a phenomenon is considered to be spontaneous if the G° has a negative value. Moreover, if H° is positive, the process is endothermic and if it is negative, the process is exothermic. For the determination of H° and S°, the relationship between sorption equilibrium K_L was used:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

Values of H°, S° were calculated from the plots of ln (K_L) versus 1/T (Fig. 8) and those of free energy change from the expression 8:

$$\Delta S^\circ = H\Delta^\circ\text{-}T\Delta S \tag{8}$$

The respective values of thermodynamic parameters for adsorption of Mn (II) onto ACo, HAC and ZAC are given in the Table 7.

The positive value of ΔH for ACo (23.7 KJ mol^{-1}) indicated that the studied adsorption process is endothermic. This result is in agreement with those of Andal and Sakthi (2010). Whereas the negative values for ZAC (-76.3 KJ mol^{-1}) and HAC (-60.7 KJ mol^{-1}) showed that the adsorption of the Mn (II) ions on these activated carbons was exothermic (Aarfane *et al*., 2014).

The positive ΔS value for AC suggested the increased disorder and disorganized distribution of Mn (II) ions on activated carbons surfaces. However, in the case where ΔS is negative as in the case of ZAC (-229.05 J/mol.K) and of HAC (-153.8 J/mol.K), it might be considered a decrease in the freedom of Mn (II) ions distribution on adsorbents. Comparable result was reported by Huang *et al.* (2007).

The negative values of ΔG° indicated that the adsorption of Mn (II) ions on the activated carbons surfaces favourable and spontaneous process.

CONCLUSION

The adsorption of the Mn (II) ions on the three samples of activated carbon prepared from *Coula edulis* nut shells has been studied in order to test their capacities to remove Mn (II) ions from aqueous solutions.

These activated carbons: ACo, HAC and ZAC, have shown a total surfacic acidity higher than the total surfacic basicity. It was also, obtained that:

- The adsorption capacity of the surfaces of activated carbons for Mn (II) ions increased with the increase in pH and initial concentration of Mn (II) ions solutions. It increased also with the increase in temperature for ZAC and HAC contrary in the case of ACo
- The testing of Freundlich and Langmuir isotherm models to experimental data showed that these models fitted both the experimental results
- The applicability of Lagergren kinetic and the pseudo second order kinetic models showed that the adsorption of Mn (II) ions on activated carbons obeyed to the kinetics of the second order
- The thermodynamic results of ACo indicated that, the adsorption of Mn (II) ions on activated carbons was realised in a spontaneous manner under experimental conditions used. The adsorption was found endothermic during the interaction between Mn (II) ions and the activated carbons ZAC and HAC contrary to the case of with ACo, then, it was found exothermic

The results obtained indicated that the activated carbons prepared from *Coula edulis* nut shells used as adsorbents during this study showed high adsorption capacities, which are important in adsorption technology and able to be exploited in the removing of heavy metal ions, as Mn (II) ions, contained in aqueous effluents.

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