

The Performance of Activated Carbon Based Cola Nuts Shells for the Removal of Co(II) and Ni(II) Ions from Aqueous Solution

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ABSTRACT

The removal of Ni(II) and Co(II) ions from aqueous solution by activated carbon from kola nuts shells was investigated. The influences of the contact time, adsorbent dose, pH and the initial concentration were experimentally done at 25°C by batch adsorption technique. The experimental results showed that the optimum pH of adsorption were 4.3 and 6 corresponding to 275 mg/g and 260 mg/g of the quantities of Co(II) and Ni(II) ions adsorbed respectively. The Langmuir, D-K-R and Tempkin adsorption isotherms described well the adsorption data for both adsorbates. The maximum adsorption capacities Q_{max} determined using the D-K-R isotherm model was found to be 286.862 mg/g and 302,778 mg/g respectively for Co(II) and Ni(II) ions. The pseudo-second order kinetic model fitted the adsorption of both the adsorbates owing to their correlation coefficients closer to unity. According to the DKR isotherm model, the adsorption mechanism seems to be chemisorption. Finally, results indicated that the activated carbons from kola nuts shells are performant for the removal of Ni(II) and Co(II) ions from aqueous solution.

Keywords: Activated carbons, Cola nuts shells, Nickel, Cobalt, adsorption and aqueous solution

1-INTRDUCTION

The excessive release of the heavy metals into the environment due to the rapid industrialization has created a major global concern. Consequently many heavy metals such as cadmium, copper, cobalt, nickel, lead, mercury and chromium are often detected in industrial wastewaters. Mostly

from the metal plating, mining activities, smelting, battery manufacture, pesticides, pigment manufacture, printing, paint manufacture, tanneries petroleum refining and photographic industries [1]. These heavy metals have harmful effect on human physiology and other biological system when they exceed the tolerance levels. The major problem is that they are not biodegradable and tend to accumulate in living organisms thus causing various diseases and disorders [2].

It's well demonstrated that Cobalt and Nickel are widely dispersed in the environment. Humans are frequently exposed to their effect by breathing air, drinking water and eating food [3, 4]. However, some techniques are available for the removal of these heavy metals ions from aqueous solution. Amongst these techniques are ion exchange, solvent precipitation, flocculation, reverse osmosis, membrane separation processes and adsorption [5, 6]. Nevertheless, these techniques have some disadvantages like their high operational cost and appropriate disposal of the residual metal sludge [7]. Adsorption technique compare to the afore mentioned appears to be an attractive process due to its high efficiency and easy implementation process which do not required the utilization of other chemical reagents.

In the present work, activated carbon prepared with a local and available biomass (Kola nut shells) found in the North-west region of Cameroon have been used for the removal of Co(II) and Ni(II) ions. The effect of some factors as contact time, pH, dose of adsorbent and initial concentration of metal ions were investigated. The kinetics study of Co(II) and Ni(II) ions was analyzed using various kinetic models. Whereas the equilibrium study was done using Langmuir, Freundlich, Dubinin Kaganer Radushkevich (D-K-R) and Tempkin models

2-Materials and methods

2-1 Adsorbent

The Kola nuts shells from the North-west region of Cameroon were initially washed with tap water, then with deionized water, sun dried, ground and sieved through a sieve (RETSCH) to get particles sizes of ≤ 1.5 mm. The sample obtained was kept into an oven at 110°C for 24 hours. Before each impregnation process, the sample was removed from the oven and cooled in a desiccator for 30 min. The impregnation ratio of 1:1 (mass reagent KOH/mass of sample) was done in a beaker and the mixture was dried for 24 hours in an oven at 110°C .

2-2 Carbonization

The carbonization and activation were done by a single step process by carrying out thermal decomposition of the Kola nuts shells impregnated with KOH as activating agent in the absent of oxygen in a carbonite furnace at 500°C for a resident time of 1hour. When the activation was achieved, the furnace was allowed to cool to room temperature. The pyrolysed carbon was first washed with 1% HCl (v/v) followed by distilled water several times until a neutral pH. Later, the activated carbon obtained was dried for 24 hours in an oven at 110°C , collected and kept in closed bottle for further use.

2-3 Preparation of Co(II) and Ni(II) ions solutions

All the reagents used in this work were of analytical grade. A stock solution of both Ni(II) and Co(II) ions of concentration 3000 mg/L was prepared by dissolving 12.525g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 14.966g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in two different volumetric flask of 1L. The two conical flasks were stirred on a magnetic agitator for 30 min to obtain a homogeneous mixture. Other experimental solutions were prepared by dilution of each stock solution to the required concentrations.

2-4 Adsorption experiments

The batch adsorption tests were carried-out at room temperature. For each run, the known initial concentration (1200-2000 mg/L) of Co(II) and Ni(II) ions were kept into contact with a known weight of activated carbon. After agitation, the solutions were filtered and the filtrate were subsequently analyzed

for metal ion concentration by using a UV/Visible spectrophotometer, model FA05005. A similar measurements were carried-out for the various adsorbents doses, pH and initial concentration of Co(II) and Ni(II) ions. The percentage removal (%R) of Co(II) and Ni(II) ions and the amount adsorbed (Q_e) per unit mass of adsorbent were calculated by using the following expressions:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

$$\%R = \frac{(C_0 - C_e) \cdot 100}{C_0} \quad (2)$$

where, C_0 and C_e are the initial and equilibrium concentration respectively, V represents the volume of the solution and m is the mass of the adsorbent.

2-5 Adsorbent characterization

For the characterization of the adsorbents, FTIR spectroscopy was used to identify the functional groups and the chemical bonds on the activated carbon. The BET method and the iodine number calculations were equally used to calculate the specific surface area and the morphology of the activated carbon.

2-6 Adsorption isotherms

- The Langmuir isotherm

The Langmuir isotherm describes the adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is often expressed as:

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

Where Q_e (mg/g) is the quantity adsorbed at equilibrium, C_e is the equilibrium concentration of adsorbate in solution (mg/L), Q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage, K_L is the Langmuir constant related to the energy of adsorption (L/mg) [8]. The linear form of its equation is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}} K} + \frac{C_e}{Q_{\text{max}}} \quad (4)$$

- The Freundlich isotherm

The Freundlich isotherm model is applied to the adsorption on a heterogeneous surface with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent [9]. The expression for the Freundlich model is given by:

$$Q_e = K_f C_e^{1/n} \tag{5}$$

The linear form is given by the following equation:

$$\ln Q_e = \ln K_f + \ln C_e \tag{6}$$

Where Q_e is the quantity adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and C_e is the concentration at the equilibrium (mg/L). The values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\ln Q_e$ against $\ln C_e$.

- The D-K-R isotherm

The Dubinin–Kaganer-Radushkevich isotherm is generally used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The DKR adsorption isotherm and its mean free energy are often expressed as [10]:

$$\ln Q_e = \ln Q_{max} - K_{DKR} \varepsilon^2 \tag{7}$$

$$\varepsilon = RT \ln (1 + 1/C_e) \tag{8}$$

Where, Q_e is the quantity adsorbed at the equilibrium (mg/g), Q_{max} is the theoretical isotherm saturation capacity (mg/g), K_{DKR} is the Dubinin–Kaganer-Radushkevich isotherm constant (mol/kJ). The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate

(for removing a molecule from its location in the sorption space to the infinity)

- The Tempkin isotherm

This isotherm contains a factor that takes into account the adsorbent–adsorbate interactions. The Tempkin model assumes that the heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmic. As implied in the equation, its derivative is characterized by a uniform distribution of binding energies which was carried out by plotting the quantity adsorbed Q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equation [10]:

$$Q_e = RT/b_T \ln(K_T \cdot C_e) \tag{9}$$

The linear form of this equation is:

$$Q_e = B \ln K_T + B \ln C_e \tag{10}$$

$B = RT/b_T$ Constant related to heat of sorption (J/mol), R is the universal gas constant and T is absolute temperature (K).

2-7 Adsorption kinetics

The study of the adsorption kinetics describes the resistances to solute transfer from the solution up to the boundary layer of the solid-liquid interface to the pore water and then to the solid.

- Pseudo-first order model

The pseudo-first order equation was suggested by Lagergren for the adsorption of solid-liquid system. It is generally expressed as follows [11]:

$$\frac{dQ_t}{dt} = K_1 (Q_e - Q_t) \tag{11}$$

Where Q_e and Q_t are the adsorption capacities at the equilibrium and time, t , respectively (mg/g), K_1 is the rate constant of pseudo-first order equation (min^{-1}). After the integration and applying boundary conditions, $t=0$ to $t=t$ and $Q_t=0$ to $Q_t=Q_t$ the integrated form of this equation becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{12}$$

This equation is verified if the plot of $\ln(Q_e - Q_t)$ as function of time gives a straight line. K_1 is deduced from slope and Q_t from the vertical intercept.

- Pseudo-second order model

The pseudo-second order adsorption kinetic rate equation is expressed as [11]:

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \quad (13)$$

Where, K_2 is the rate constant of the pseudo-second order adsorption. From the boundary condition, $t=0$ to $t=t$ and $Q_t=0$ to $Q_t=Q_t$; the integrated rate law can be written as [11]:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2 t \quad (14)$$

This equation can be rearranged to the linear form as follows:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (15)$$

- The Elovich model

The Elovich equation is generally expressed by:

$$\frac{dQ_t}{dt} = \alpha e^{-\beta Q_t} \quad (16)$$

Where α is the initial sorption rate (mg/min/g) and β is the desorption rate constant (g/mg) during any experiment. To simplified Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$ and by applying the boundary condition $t=0$ to $t=t$ and $Q_t=0$ to $Q_t=Q_t$, the linear form can be written as follows [8]:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (17)$$

Thus, a plot of Q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and intercept of $1/\beta \ln(\alpha\beta)$ if the sorption process fits the Elovich equation.

- The intraparticle diffusion model

When the intraparticle mass transfer resistance is a rate limiting step, then the sorption process describes as being controlled by the particle diffusion. The intraparticle diffusion model is expressed as equation [8]:

$$R = K_{id} t^a \quad (18)$$

Where R is the adsorbed percentage (%), K_{id} the intraparticle diffusion rate constant (mg/min) and a the adsorption mechanism. A linear form of the equation (18) is given as:

$$\ln(R) = \ln K_{id} + a \ln(t) \quad (19)$$

The plot of $\ln(R)$ versus $\ln(t)$ give a linear, relationships which help to deduce the constant, a and K_{id} from the slope and intercept of the plot respectively.

3- Results and Discussion

3-1 Surface chemistry

The functional group is an important characteristic of the activated carbon since it determines the surface properties of carbons and has significant implications on their behaviors [12]. The FTIR spectra registered for the activated carbon is plotted in fig.1. A broad band located around 3321cm^{-1} is attributed to hydroxyl groups or adsorbed water [9]. The band around 1574cm^{-1} is usually caused by C=C (skeletal) vibrations [13, 14]. The band at 1416cm^{-1} is compatible with presence of N-H vibration. Another peak at the wave length number around 1371cm^{-1} is attributed to the C=O bond in carboxyl group double bond [12]. The earlier parts of the spectra located in the wave length number of $1000-1500\text{cm}^{-1}$ are also quite similar in both the adsorbent material. This part represents various configuration of C, O, N, H bonds in the activate carbon structure. For example the two badly visible peaks at 1163cm^{-1} and 1089cm^{-1} may be assigned to C-O-C vibration in ether type structure and ester C-O vibration respectively [15]. Finally, low intensity bands at $873, 802$ and 753cm^{-1} may be related to substitution in aromatic rings (tri, di and mono substitution respectively) [12,15].

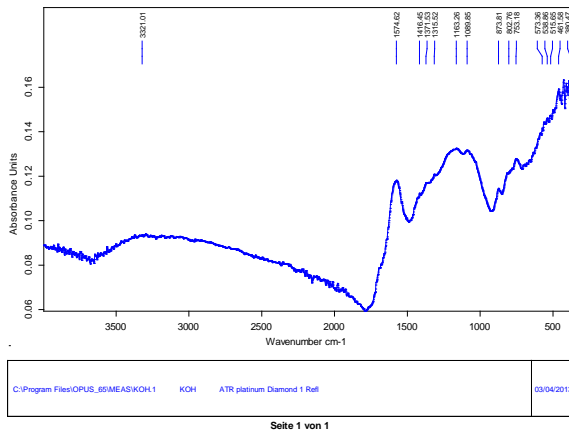


Fig-1: The FT-IR spectra of Kola nut shell activated carbon before adsorption

3-2 Porous structure and iodine number analysis

Table1 shows the total volume of pores, the surface area of activated carbon and the iodine number. The N₂ -BET specific surface area of cola nut shells activated carbon is very low (2,048m²/g); the average pores diameter is 94Å which implies the presence of mesopores. This activated carbon has almost the presence of micropores according to its iodine number of 513,945mg/g. In the scientific literature, the same range of values of iodine number has been obtained but the microporosity was predominant on the activated carbon [16].

Table1: Characteristics (specific surface area, pores volume, iodine number, porosity) of cola nut shells activated carbon

BET Surface area (m ² /g)	2, 0448
adsorption cumulative Surface area of pores (m ² /g)	0,992
désorption cumulative Surface area of pores (m ² /g)	2,6723
total Volume of pores (cm ³ /g)	0,004816
Average diameter of pores (Å)	94
Iodine number (mg/g)	513,945

4- Adsorption

4-1 Effect of the contact time

The contact time is inevitably a fundamental parameter in the mass transfer phenomena like the adsorption. Therefore it is important to study its effect on the adsorption capacity of Co(II) and Ni(II) ions by cola nut shells activated carbon. Fig.2 presents the effect of the contact time on the

adsorbed quantities of Co(II) and Ni(II) ions. The initial concentration of the two metal ions is 1600 mg/L, the adsorbent dose of the activated carbon is 0.05g, the pH of solutions are 5.7 and 6.5 for Co(II) and Ni(II) solutions respectively.

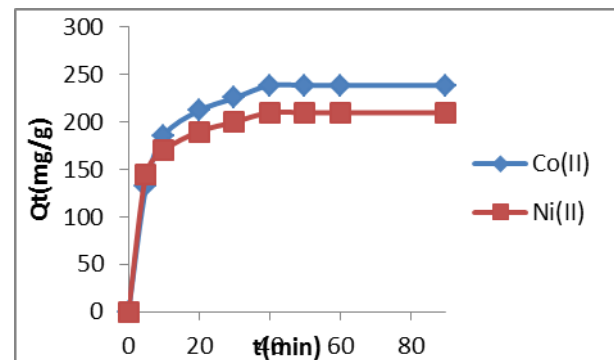


Fig2: Effect of contact time on the removal of Co(II) and Ni(II)

Fig.2 shows that the adsorption of Co(II) and Ni(II) ions increase rapidly with time from 0 to 20 min and then becomes almost constant. Equilibrium is reached after 45 min for the adsorption of the two metal ions. The first part of the graph which seems to be a rapid phase occurred because of the availability of the large number of adsorbent sites and rapid diffusion of metal ions from solution to the surface of the activated carbon. Additionally, the enhancement of these two metal ions with increase in agitation time may be due to the decrease of the boundary layer resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ions. The second part of the graph which seems to be a slow phase may be due to the decrease of the number of active sites which causes retardation in adsorption process [12, 17, 18].

4-2 Effect of the adsorbent dose

In order to study the effect of the adsorbent dose on adsorption of Co(II) and Ni(II) ions, a series of adsorption experiments were carried-out with different masses of the adsorbent varying from 0.025 to 2 g at the initial concentration 1600 ppm.

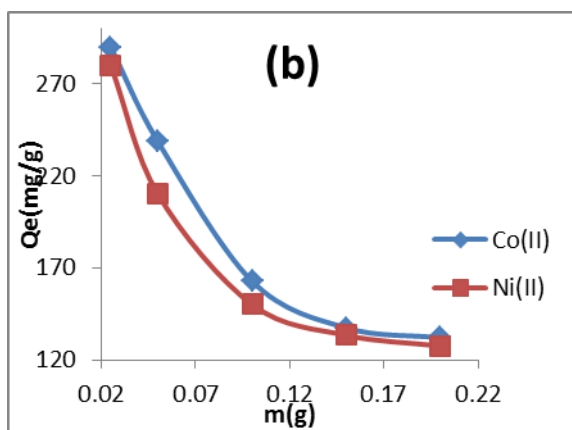
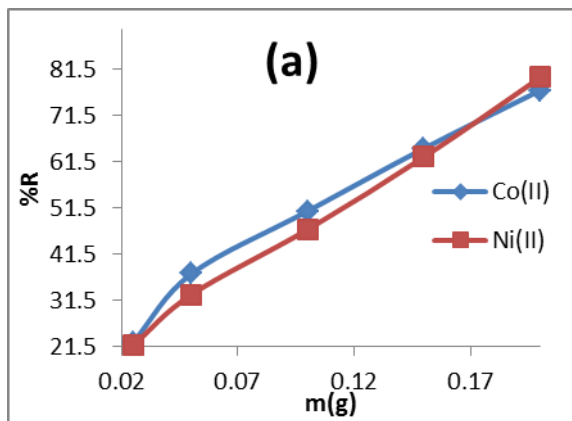


Fig.3: Effect of adsorbent dose (a) percentage of metal ions removal as a function of mass (b) quantity of metal ions adsorbed in function of mass

Fig.3, (a) shows that the percentage removal of the two metal ions increases with the adsorbent dosage. This trend is expected because as the adsorbent dose increases, the number of adsorbent particles increases and thus more Co(II) and Ni(II) ions will be attached to the surface of the adsorbent [19,20,21].

However, fig.3 (b) shows that when the adsorbent dose increase the quantity adsorbed of Co(II) and Ni(II) ions decreases. This may be due to the fact that as the amount of the adsorbent increases, the total surface area available for the adsorption of metal ions reduces as a result of the overlapping or aggregation of adsorption sites [22]. The maximum quantities adsorbed are 290 mg/g for Co(II) and 280 mg/g for Ni(II) for an adsorbent dose of 0.025 g. Further experiments had been done with 0,05 g of adsorbent because this mass of the activated carbon is consistent and also has a high adsorption capacity.

4-3 Effect of the pH

The pH of the aqueous solution is an important parameter for controlling the adsorption process. It affects the degree of ionization of the heavy metals ions in solution and also controls the binding of metal ions with the surface functional groups [15, 23]. The batch adsorption study at different pH values were carried out in the range of 2-7 for Ni(II) and of 2-6 for Co(II) ions using initial concentration of 1600 mg/L for both Ni(II) and Co(II) ions and the activated carbon dose of 0,05 g.

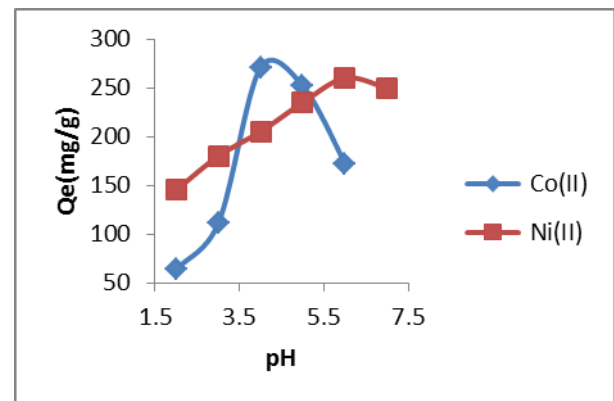


Fig.4: Effect of initial pH of the solution

Fig.4 presents the effect of pH on the two metal ions adsorption. These results revealed that the maximum adsorption occurred at pH 4.3 and 6 for Co(II) and Ni(II) respectively. At lower pH, the Co(II) and Ni(II) ions removal was inhibited. This can be attributed to the adsorption competition between the hydrogen ions, Co(II) and Ni(II) ions on the adsorption sites. In fact, at low value of the pH, the medium contains a high concentration of hydrogen ions [23, 24]. While a decrease of the pH favored the deprotonation on the surface of the adsorbent thus enhancing the metals adsorption [25]. In addition, there are also possible sites on the unmodified activated carbon surface for specific adsorption of H⁺ ions that can be exchange with the metal cations in the solution [25]. At pH values higher than 6 for Co(II) ions and 7 for Ni(II) ions, the insoluble cobalt and nickel hydroxide starts respectively, precipitating from the solution making the true adsorption studies impossible [23, 26]. The working pH values for Co(II) and Ni(II) ions onto activated carbon was chosen to be 4.3 and 6 for Co(II) and Ni(II) ions respectively and the other adsorption experiments were performed at these pH values.

4-4 Effect of the initial concentration

The effect of the initial concentration on the adsorption capacity of activated carbon from cola nut shells for Co(II) and Ni(II) is showed in the fig.5.

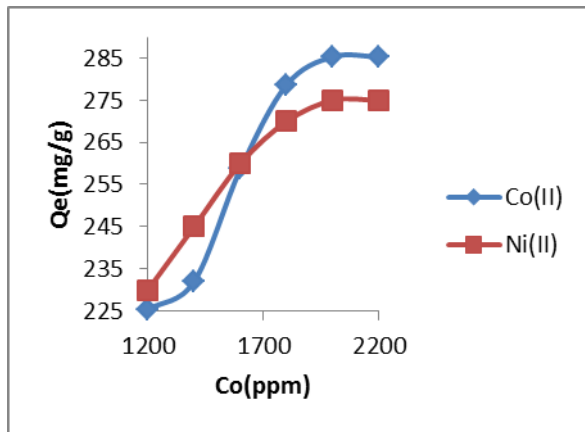
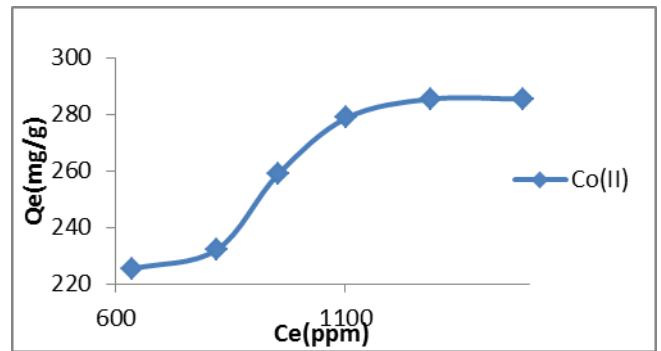


Fig.5: Effect of Initial Concentration on Co(II) and Ni(II) ions

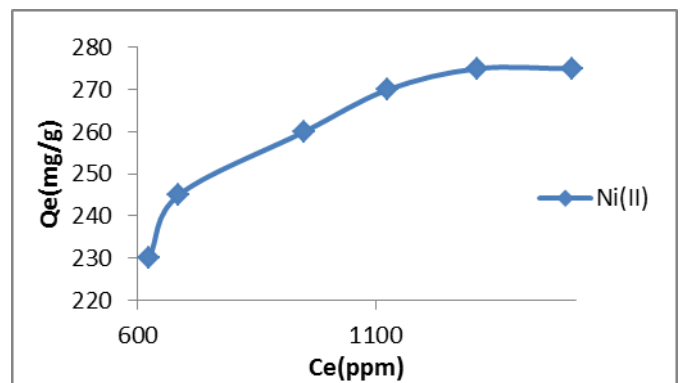
The results showed that the quantities of metal ions adsorbed per unit of mass of activated carbon increase with increase in the initial concentration and becomes constant at 2000 ppm. This increase of the quantities of both the Co(II) and Ni(II) ions adsorbed is due to the decrease of the resistance uptake of the metal ions with an increase in the metal ions concentration [26]. However, at higher concentration (2000 to 2200 mg/L), the metal ions need to diffuse to the adsorbent surface by intraparticle diffusion and greatly hydrolyzed ions which diffuse at slower rate because all the adsorption sites are occupied [27, 28].

4-5 Effect of equilibrium concentration

The figs. 6a and 6b present isotherms which are obtained by plotting the quantity adsorbed versus the equilibrium concentration:



(a)



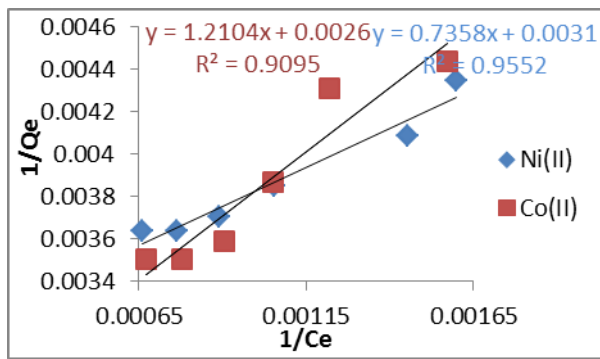
(b)

Fig.6: Effect of equilibrium concentration of Ni(II) and Co(II) ions

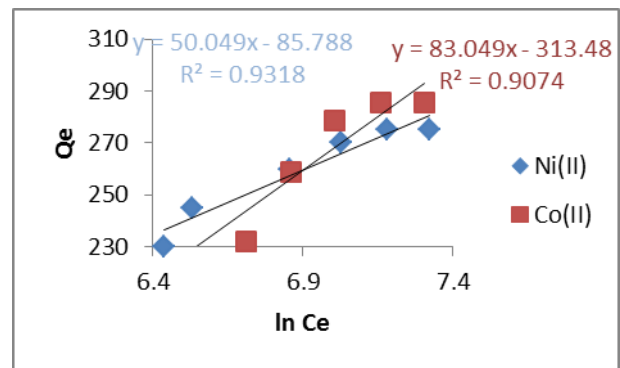
These figures showed that the isotherms that were obtained are of the type IV which involves porous adsorbent possessing pores mainly in the mesopore range; also the interaction adsorbate-adsorbent is stronger than interaction adsorbate-adsorbate. This confirmed the BET results obtained.

4-6 Adsorption isotherms studies

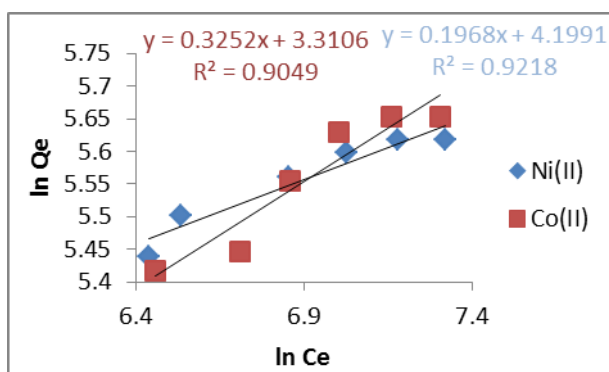
The isotherm experiment data were confronted to the Langmuir, Freundlich, D-K-R, and Tempkin equations and the adsorption parameters were determined (Table 2). The experimental data and the models equations used for both Co(II) and Ni(II) adsorption equilibrium isotherms are shown in fig.7.



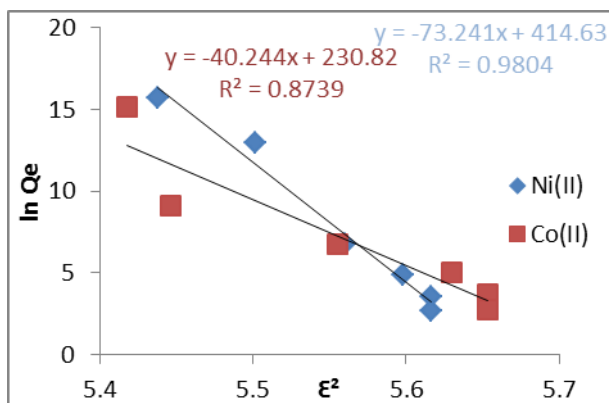
(a)



(d)



(b)



(c)

Fig.7: Adsorption isotherm of Co(II) and Ni(II) ions onto activated carbon. a) Langmuir (b) Freundlich (c) D-K-R (d) Tempkin

The adsorption constant of a given isotherm allows, not only to evaluate the adsorbent properties of a sample, but also to determine if the adsorption is favorable or not. The constant of Langmuir K_L evaluates the intensity of adsorption. If the value of K_L is high, we have strong affinity between the metal ions and the surface of activated carbon. The values obtained from the Langmuir isotherm model are 4.082 g/L and 1.653 g/L for Ni(II) and Co(II) ions respectively and suppose that we have a middle interaction between the Co(II) and Ni(II) ions onto activated carbon. The correlation coefficients for this model are lower than 0.96 thus the Langmuir model is not suitable to explain the adsorption of both Co(II) and Ni(II) ions onto activated carbon.

The values of Freundlich constants, n determines if the adsorption of metal ions onto activated carbon is favorable or not. If the constant n is between 1 and 10, then the adsorption is favorable with great intensity of adsorption; and if the term $1/n$ is between 0 and 1 then we have on the activated carbon heterogeneous surface. For these experiments, the values of n were 5.1 for Ni(II) ions and 3.07 for Co(II) ions which consequently are between 1 and 10. On this basis it appears that the adsorption of both the two metal ions is favorable with great intensity. The exponent $1/n$ lies between 0 and 1 and shows that the surface of the cola nut shells activated carbon is heterogeneous and confirms the results of the characterization. But it can also be seen that the Freundlich model has values of the correlation coefficients lower than 0.96 which restricts the utility of this model to describe well the metal ions adsorption onto this sample.

The Tempkin adsorption model explains the nature of adsorbent-adsorbates interaction and also the energetic information of the adsorption process. If the Tempkin constant B is positive, then the adsorbent-adsorbates interaction is gravitational. For the cola nut shells activated carbon, these constant are all positive. Thus the metal ions-carbon interactions are gravitational. The functional groups (fig.1) present at the surface of this material are the carbonyl (-CO), the amine (-N-H), the carboxyl (-COOH) and the hydroxyl (-OH) which have free electrons and the metal ions have a deficit of electrons and these characteristics explain well why the behavior of interactions are gravitational. We also noticed that, the attraction is much stronger for the Co(II)-carbon than for the Ni(II)-carbon with values of constant B equal to 50.04 and 83.04 J/mol for Ni(II) and Co(II) ions respectively.

The D-K-R model gives information of the binding energies. The average free energy E, of a molecule of adsorbent expresses the energy released when a molecule of the adsorbate passes from the solution into the adsorbent. The energy was calculated using the equation below:

$$E = 1 / (2K_{DKR})^{1/2} \tag{20}$$

The values of the energy of adsorption were 4.880 and 6.202 KJ/mol respectively for Co(II) and Ni(II) ions and are characteristics of Van Der Waals forces. The D-K-R model seems to be more general, so it is very suitable to explain the adsorption of metal ions on various adsorbents. This model explain well the adsorption of Ni(II) ions because the value of $R^2 > 0.96$ [29].

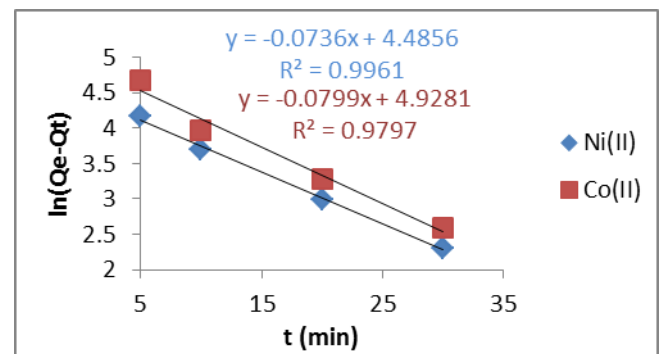
The theoretical values of the adsorption capacities determined by the D-K-R model approach those determined experimentally, so we can deduced that this activated carbon has a high efficacy at low concentration [29].

Table 2: Parameter values of the adsorption isotherm of Co(II) and Ni(II) ions onto activated carbon from cola nut shells

ISSN 2348 – 7968			
LANGMUIR	Q_{max} (mg/g)	333.333	500
	K_L (L/mg)	$4.082 \cdot 10^{-3}$	$1.653 \cdot 10^{-3}$
	R^2	0.955	0.909
FREUDLICH	K_F	66.620	27.385
	1/n	0.196	0.325
	R^2	0.921	0.904
D-K-R	K'	0.013	0.021
	Q_{max} (mg/g)	286.862	302.778
	E (KJ/mol)	6.202	4.880
	R^2	0.980	0.873
TEMPKIN	B	50.04	83.04
	A	0.180	0.023
	R^2	0.931	0.907

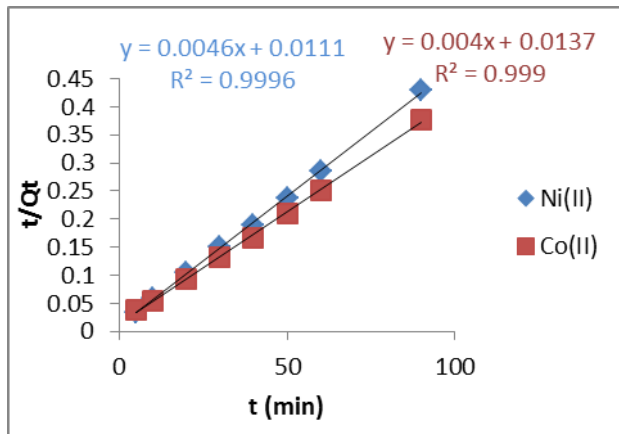
4-7 Adsorption kinetics

In this work, the kinetic of adsorption of Co(II) and Ni(II) ions onto activated carbon was studied. Four types of kinetic models namely the pseudo first order, pseudo second order, Elovich and intra particle diffusion models were used to confront the experimental data:

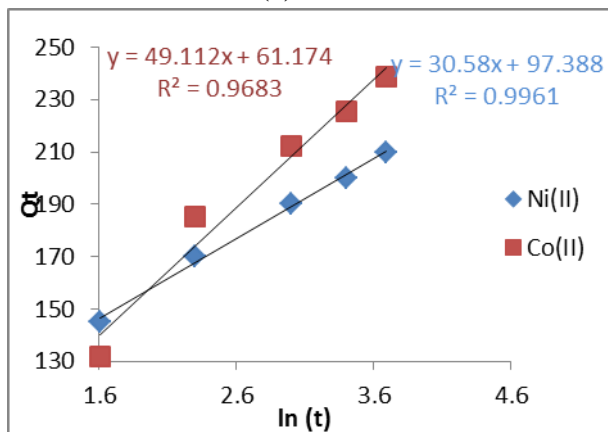


(a)

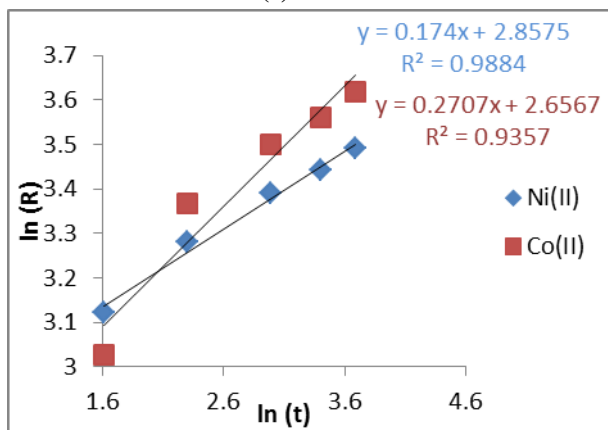
ADSORBATES	Ni(II)	Co(II)
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(b)



(c)



(d)

Fig.8: Adsorption kinetics of Co(II) and Ni(II) ions onto activated carbon. a) Pseudo first order b) pseudo-second order c) Elovich model. d) Intra particle model

The straight lines plot showed a good agreement of the experiment data with the pseudo second order, Elovich and pseudo first order model. Table 3 listed the results of the rate constants studies for different kinetic models. The Comparison of the R^2 values of these three models show a significant agreement with the adsorption mechanism with

successfulness of the pseudo second order model. The pseudo first order model involves physisorption; which explains why the energies of adsorption showed low energies values of the Van Der Walls type. Nevertheless, the pseudo second order and Elovich models involve the variation of energy of chemisorption with heterogeneous actives sites in the activated carbon [22,30]. The Elovich model has been applied satisfactorily to some chemisorption processes and has been found to cover a wide range of slowed adsorption rate [30].

The intra particle diffusion constants k_{id} give an enhancement in the rate of adsorption whereas the values of a , illustrate a better adsorption mechanism. This related to improve bonding between both Co (II) and Ni (II) ions and the adsorbent particles.

The high values of R^2 coefficients of all these models make it difficult to distinguish which kinetic model is better fitted. It is responsible to conclude that both physical and chemical adsorption equally participate in the overall process of Co(II) and Ni (II) metal ions adsorption on the cola nut shells activated carbon. This result shows that the intra-particle diffusion process is one of the rate limiting steps, besides many processes which control the overall rate of adsorption. All of which will be operating simultaneously [24,31]. The pseudo first order model showed that physisorption is the phenomenon which limits the rate and involves the Van Der Walls forces in the reaction between adsorbate molecule and adsorbent. Similarly, the Elovich model shows that the rate limiting step is chemisorption involving the valence forces caused the exchange of electrons between the adsorbent and the adsorbate.

Table.3: The parameter values of the kinetics of the adsorption of Co(II) and Ni(II) ions onto activated carbon from cola nut shells

ADSORBATES		Ni(II)	Co(II)
PSEUDO-FIRST ORDER	$K_1 (\text{min}^{-1})$	0.073	0.079
	Co(II)	88.667	138.103
	R^2	0.996	0.979
PSEUDO-SECOND ORDER	$K_2 (\text{g} \cdot \text{min}^{-1} \cdot \text{m}^{-1})$	1.455×10^{-3}	1.231×10^{-3}
	$Q_E (\text{mg/g})$	250	250
	R^2	0.999	0.999
ELOVICH	B	0.033	0.020
	A	753.544	169.936
	R^2	0.996	0.968
INTRAPARTICLE DIFFUSION	Kid	17.409	14.239
	A	0.174	0.270
	R^2	0.988	0.935

4-8 Adsorption Mechanism:

In order to understand the adsorption mechanism, a large quantity of work has been done to investigate the influence of adsorption process on the kinetic model, isotherm model and Fourier Transform infrared (FTIR) technology. The main mechanisms include hydrogen-bonding, physisorption, chemisorption, ion exchange and precipitation [32].

The highest value of the correlation coefficient R^2 of the pseudo second order model show that chemical adsorption is the main mechanism of metal ions ($R^2 > 0,99$). The values of intra particle diffusion constant show that it is not the limiting process and thus do not control the step. After the film diffusion, the adsorbate is attracted by the functional groups such as oxygen, nitrogen of the surface of the activated carbon and result to the attractive interaction for both adsorbent and adsorbates. Metal ions being the positives ions which have deficiencies of electron will react as Lewis acid on the surface more than the electrons. Consequently they form dative bonds between adsorbent and adsorbate

These results are confirmed by FTIR spectra after the adsorption bellow:

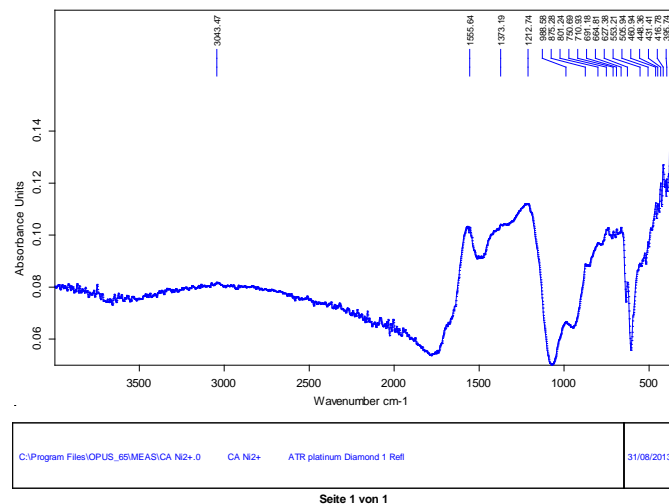
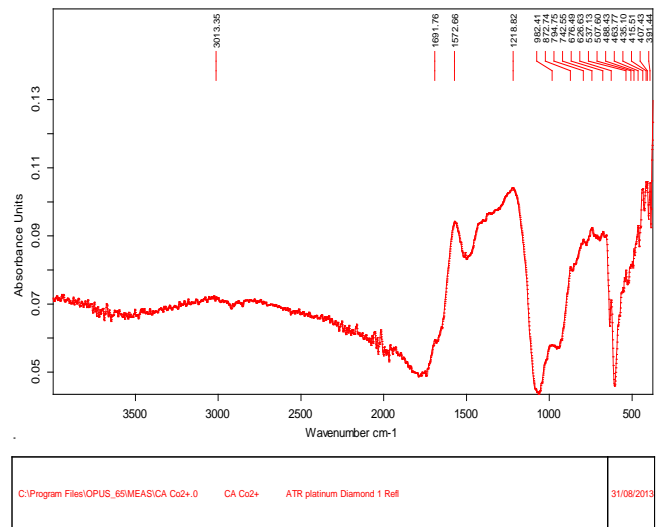


Fig.9: The FT-IR spectra of cola nut shells activated carbon after adsorption a) Co(II) ions onto activated carbon (in red) b) Ni(II) ions onto activated carbon (in blue).

The disappearance of –OH, vibrating at 3321 cm^{-1} and other pics at $1371, 1315, 1163,$ and 1089 cm^{-1} on the spectra before adsorption and the appearance of pics at $626, 676 \text{ cm}^{-1}$ on the spectra 9-a) and $664, 691 \text{ cm}^{-1}$ (spectra 9-b) for the vibration of CO – Co O – Ni were observed respectively.

Also the appearance of vibration pics at $435, 488 \text{ cm}^{-1}$ and 415 cm^{-1} (spectra 9-a) and $448, 431$ and 416 cm^{-1} (spectra 9-b) indicate the formation of the N – Co and N – Ni vibrations respectively [32, 33].

This is the relationship with values of kinetics and isotherms models which showed the existence of strong interaction between the adsorbates and the activated carbon. The formation of multi-layer can be explain by the fact that, after the formation of the first layer on the activated carbon surface, the residual strength founded still allow the adsorbent to attract other molecules of adsorbate which are in the bulk of the solution.

5- Conclusion

The adsorption of Co(II) and Ni(II) by cola nut shells activated carbon from aqueous solution was found to be greatly dependent on solution pH and the initial concentrations. The pseudo-second order, pseudo first order and Elovich kinetic models revealed that these three models may explained the adsorption mechanisms and that chemisorption is the process which controls more the overall rate of the adsorption. The results of this investigation proved that the cola nut shells activated carbon is a reliable and dependable adsorbent with good potential for removal of metal ions from aqueous media.

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