

Nickel (II) Adsorption from Aqueous Solutions by Physico-Chemically Modified Sewage Sludge

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ABSTRACT: *This study assesses the potential of activated carbon prepared from sewage sludge for nickel ions adsorption from aqueous solutions. Activated carbon physicochemical properties were determined. Batch adsorption experiments were performed as a function of pH solution, adsorbent dose, initial metal ions concentration, contact time and temperature. The experimental data were analyzed by the Langmuir, Freundlich, and Temkin isotherm models. The Freundlich model showed a better representation of equilibrium data ($R^2 > 0.99$) and the Langmuir monolayer adsorption capacity of activated carbon was found to be 11.52 mg/g. The kinetics of nickel ions was discussed using different kinetic models and the adsorption experiments indicated that the pseudo-second-order model well fitted the kinetic data ($R^2 = 0.999$). Thermodynamic parameters have also been evaluated. It was found that the adsorption process was feasible, spontaneous and endothermic. Desorption experiment and recovery of Ni(II) ions from activated carbon was found to be 100 % using hydrochloric acid. The results suggest that the activated carbon prepared from sewage sludge could be used beneficially for nickel adsorption from aqueous solutions for environmental cleaning purpose.*

KEYWORDS: *Nickel(II) adsorption; Sewage sludge; Equilibrium; Kinetics; Thermodynamics.*

INTRODUCTION

Water pollution is considered a serious menace to the environment and especially to human health [1]. Nickel a toxic heavy metal and it can be present in wastewater from electroplating, refining and welding industries [2, 3]. According to the U.S. Environmental Protection Agency (EPA), the permissible level of nickel in drinking water is 0.015 mg/L and the same prescribed by World Health Organization (WHO) is 0.02 mg/L [4]. The chronic toxicity of nickel to humans and the environment has been well documented and high

the concentration of nickel causes cancer of the lungs, nose, and bone [5]. Several processes have been employed for the removal of nickel ions from water and wastewater and these include chemical precipitation [6], ion flotation [7], ion-exchange [8], membrane filtration [9], electrochemical treatment [10], adsorption [11] and other methods [12, 13]. Among these methods, adsorption is preferred for the removal of heavy metals from wastewater due to its simplicity, lower cost, and high efficiency.

Activated carbon is a potential adsorbent for

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removing pollutants from contaminated water due to its high surface area, microporous structure, high adsorption capacity, chemical nature of its surface and relatively easy regeneration. Activated carbon is commonly produced from a variety of materials with high carbon content. These materials are generally organic precursors such as coir pith [2], almond husk [5], rice stems [11], scrap tire [14], cashew nut shell [15], rice husk [16], waste of tea factory [17], hazelnut shell [18], apricot stone [19] and sewage sludge [20-27]. Activated carbon prepared from sewage sludge is very interesting because it reduces sludge volume by giving a reusable byproduct.

Sewage sludge is produced as a result of wastewater treatment and its production is expected to gradually increase through environmental necessity and legal requirements for wastewater treatment [23]. Sewage sludge is carbonaceous in nature and rich in inorganic materials. Hence, it has the potential to be converted into activated carbon if pyrolyzed under controlled conditions or with some chemical treatment [24]. Generally, two different activation methods are used to prepare activated carbon; physical activation where raw materials are carbonized at a high temperature in an inert atmosphere followed by oxidation treatment with steam, air or carbon dioxide [25]. Whereas, chemical activation involves impregnation of the raw material with chemical agents such as $ZnCl_2$ [22], H_2SO_4 [26], H_3PO_4 [23], $NaOH$ [25] and KOH [25, 26].

It can be found some reports dealing with potassium hydroxide as an activation agent; however, in these works the ground hydroxide lents KOH were mixed with dried sewage sludge at different ratios [25, 26]. In spite of the great surface area obtained for these carbons, this method is critical. First, mixing ground KOH and sewage sludge in these proportions could produce an amount of heat which could be difficult to manage. Second, sewage sludge is produced in great quantities and using the same amounts or greater of potassium hydroxide is not economically viable. In addition, the impregnation method has advantages over the physical mixing method due to a large contact surface and better distribution of chemical agent into the carbonaceous particle mass. Only one paper used liquid 3 M KOH [27] as an activated agent for chemical activation to prepare activated carbon from sewage sludge. But the activation step was done under an atmosphere of steam and the prepared activated

carbon was used for adsorption of a dye, Acid Brilliant Scarlet GR. Based on these observations, the KOH solution was used in the present work instead of solid KOH .

In this study, we investigated the impregnation process of dry sewage sludge with KOH solution to produce activated carbon. As far as we know, there is no report on the preparation of activated carbon from sewage sludge using KOH activation for adsorption of nickel ions from aqueous solutions. The effects of different operating parameters have been investigated. Activated carbon was characterized by different analyses to clarify the adsorption process. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics and mechanism of $Ni(II)$ ions adsorption on the prepared adsorbent. Thermodynamic studies were also carried out to estimate the standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°).

EXPERIMENTAL SECTION

Chemical reagents

All the chemical reagents used in this study were of analytical reagent grade and obtained from Sigma-Aldrich®. A stock solution of 1000 mg/L of nickel (II) was prepared by dissolving hexahydrate Nickel (II) sulfate ($NiSO_4 \cdot 6H_2O$) in distilled water. The stock solution was diluted with distilled water to obtain desired concentrations ranging from 10 to 50 mg/L.

Preparation of adsorbent

Sewage sludge was collected from a Waste Water Treatment Plant (WWTP) located in the north of Guelma city (Algeria). The sewage sludge was dried at 105 °C for 24 h to achieve constant weight, then comminuted and sieved into a uniform size. The resulting average particle size of initial sewage sludge is 209.65 μm and the particle size interval of our sewage sludge samples is 20-350 μm . These values are similar to those obtained in the literature [28-30]. The chemical activation of sewage sludge was carried out as follows: dried sewage sludge was impregnated with KOH solution (3 M) with an impregnation ratio of 1:2 (dry sewage sludge: volume KOH), then stirred thoroughly and left to stand for 24 h. A ratio of 1:2 (sewage sludge: KOH solution) was chosen for activation considering economic and environmental concerns. After the supernatant liquid was removed,

the sample was dried at 105 °C for 24 h. The resulting chemical loaded sample was then carbonized at 750 °C in a muffle furnace (Controlab, TS 9021) for 2 h with the rate of 30 °C/min. The obtained material was cooled at room temperature. Then, it was treated to eliminate the remains of the chemical activator. The carbonized material was washed with 0.1 M HCl solution, followed by filtration. The carbon so obtained was rinsed with distilled water to remove all the free acid. After the first rinse, the pH value is under 2. Then we repeat the rinsing steps until a stable pH value above 6.5 was obtained. Subsequently, the samples were dried at 105 °C for 24 h. The produced activated carbon was kept in a desiccator until characterization and adsorption studies.

Characterization of activated carbon

The pH and electrical conductivity values of activated carbon were determined by agitating 1 g of activated carbon with 100 mL of distilled water at room temperature, followed by measuring pH and electrical conductivity of filtrate with a combined pH-EC meter (HANNA, HI 2550). The yield (%) of activated carbon was calculated based on the following equation:

$$\text{Yield} = \frac{\text{activated carbon weight}}{\text{raw material weight}} \times 100 \quad (1)$$

Particle size distribution of powder activated carbon was determined by using a Malvern Mastersizer 2000 particle size analyzer capable of analyzing particles between 0.02 to 2000 µm.

The iodine number was determined according to the procedure followed by *Haimour and Emeish* [31]. It is defined as the milligrams of iodine adsorbed by 1 g of carbon when the iodine concentration of the residual filtrate is 0.02 N. Dry sample of the activated carbon is weighed and added to 10 mL of 5 % HCl acid and mixed until the sample is wetted. After that, the mixture is boiled for 30 s then cooled. 100 mL of standardized iodine solution of normality N_I is added to the mixture and the content was shaken for 30 s and filtered. A volume of 50 mL of the filtrate is titrated with standardized 0.1 N sodium thiosulfate solution using Starch indicator. The iodine number (mg/g) of the activated carbon is then calculated by the following equation [31]:

$$\text{Iodine number} = \frac{X}{m} A \quad (2)$$

Where A is the correction factor obtained after the calculation of the residual filtrate normality, m (g) is the weight of activated carbon, X (mg) is the weight of adsorbed iodine and is given by [31]:

$$X = (N_1 100 - N_2 V 110/50) 126.93 \quad (3)$$

Where N_I (N) is the normality of iodine solution, N_2 (N) is the normality of thiosulfate solution, V (L) is the volume of thiosulfate solution used for titration.

Iodine surface area was calculated with the following formula [32]:

$$S_I = IN \frac{N_A}{M_I} \sigma_I \quad (4)$$

Where S_I (m²/g) is the iodine surface area, IN (mg/g) is the adsorption capacity obtained for iodine, N_A is Avogadro's number, M_I (126.92 g/mol) is the molecular weight of iodine and σ_I (0.2096 nm²) is the area occupied by an adsorbed iodine molecule.

The Methylene Blue (MB) number was determined according to the procedure followed by *Baccar et al.* [33]. A dry sample of the prepared activated carbon (0.3 g) is agitated with 100 mL of 1000 mg/L methylene blue solution. After agitation during 24 h at room temperature, the suspension was filtered and the final MB concentration was determined using a Jasco UV-Vis.V530 spectrophotometer by measuring the light absorbance at a wavelength of 666 nm [34]. A previously established linear Beer-Lambert relationship was used for the concentration determination. The methylene blue number (mg/g) of the activated carbon is then calculated using the following equation [33]:

$$\text{Methylene blue number} = \frac{C_0 - C_f}{m} V \quad (5)$$

Where C_0 is the initial concentration of methylene blue (1000 mg/L), C_f (mg/L) is the final concentration after desorption and m is the weight of activated carbon (0.3 g).

Methylene blue surface area (S_{MB}) is a specific surface area of solids using methylene blue adsorption. It can be calculated using the following equation [35]:

$$S_{MB} = b \frac{N_A}{M_{MB}} \sigma_{MB} \quad (6)$$

Where S_{MB} (m²/g) is the methylene blue surface area, b (mg/g) is the adsorption capacity obtained for

methylene blue, N_A is Avogadro's number, M_{MB} (319.87 g/mol) is the molecular weight of methylene blue and σ_{MB} (130 Å²) is the area occupied by an adsorbed methylene blue molecule.

The specific surface area and pore structural parameters of activated carbon were determined from the nitrogen adsorption-desorption isotherm at 77 K using Micromeritics ASAP 2010 system. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) equation. The total pore volume (V_T) was estimated to be the liquid volume of N₂ at a relative pressure (P/P_0) of 0.95. The Dubinin-Radushkevich equation was applied to obtain micropore volume (V_{mic}). The mesopore volume (V_{mes}) was the deduction of V_{mic} from V_T .

The average pore diameter (D_p) was estimated from the BET surface area (S_{BET}) and total pore volume using the following equation [21]:

$$D_p = \frac{4 V_T}{S_{BET}} \quad (7)$$

The X-Ray Diffraction (XRD) pattern of the activated carbon was obtained with Rigaku DMAX 2500 diffractometer using CuK α radiation at 40 kV with the scanning range (2θ) of 3-80°. The Fourier Transform InfraRed (FT-IR) spectra of the samples were recorded from 4000 to 450 cm⁻¹ using Perkin Elmer 1600 FT-IR spectrophotometer.

Batch adsorption experiments

The effects of experimental parameters: solution pH (2-8), adsorbent dose (2-10 g/L), initial metal ions concentration (10-50 mg/L), contact time (10-120 min) and temperature (25-55 °C) on the adsorptive removal of Ni(II) ions were studied in a batch mode using 50 mL of each Ni(II) solutions. Preliminary experiments showed that after 90 min there is no significant change in nickel adsorption. Hence, the suspensions were stirred for 90 min during the effect of pH, adsorbent dose, initial concentration and temperature studies. After the adsorption process, the adsorbent was separated by filtration. Nickel solutions were analyzed using a flame atomic absorption spectrometer (Perkin Elmer AAnalyst 400) at a wavelength of 232.0 nm. Adsorption experiments for the effect of pH were conducted as follows: 0.2 g of activated carbon was added to 50 mL solution containing 50 mg/L

of nickel ions. The pH of the various solutions was adjusted from 2 to 8 by adding HCl (0.1 M) or NaOH (0.1 M) solutions. The removal rate R (%) and the equilibrium amount of Ni(II) ions adsorbed per unit mass of adsorbent q_e (mg/g) were, respectively, calculated from the following equations:

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (8)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (9)$$

Where C_0 (mg/L) is the initial Ni(II) ions concentration; C_e (mg/L) is the equilibrium Ni(II) ions concentration; V (L) is the volume of the solution; and m (g) is the mass of the adsorbent.

Adsorption equilibrium studies

For adsorption equilibrium, Ni(II) ions solutions with concentrations varying from 10 to 50 mg/L were mixed with 0.2 g adsorbent dose into 100 mL beaker under magnetic stirring at 300 rpm for 90 min at room temperature.

Adsorption kinetic studies

For kinetic studies, 50 mL of 50 mg/L of Ni(II) ions concentration was mixed with 0.2 g of adsorbent using a magnetic stirrer at room temperature. The samples were collected at different time intervals, and the metal concentration was determined. To investigate the controlling mechanism of adsorption processes, the pseudo-first-order, pseudo-second order, Elovich model and intraparticle diffusion kinetic models were applied to model the kinetics studies of the nickel adsorption. The amount of Ni(II) ions adsorbed at time t , q_t (mg/g), was calculated by the following expression:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (10)$$

Where C_t (mg/L) is the concentration of Ni(II) ions solution at time t .

Thermodynamics studies

Thermodynamics studies for Ni(II) removal from aqueous solutions were conducted at different temperatures in the range of 25 to 55 °C at pH 5.6 for 50 mL solution

containing 50 mg/L of Ni(II) ions. The adsorbent dose was fixed at 0.2 g; whereas the contact time was fixed at 90 min.

Desorption experiment

To investigate the possibility of Ni(II) ions desorption, the activated carbon was first saturated with Ni(II) by mixing 0.5 g of activated carbon with 50 mL of 50 mg/L solution for 90 min. After the adsorption equilibrium, the saturated activated carbon was separated from the solution by filtration and was treated with 50 mL of 0.1 M HCl at room temperature with stirring for 90 min. After filtration, the activated carbon was washed several times with distilled water in order to remove excess acid and then dried at 105 °C for 2 h.

RESULTS AND DISCUSSION

Activated carbon characterization

Physico-chemical properties and textural characteristics of the elaborated activated carbon are presented in Table 1. pH and conductivity values of activated carbon obtained in this work are favorable and agree with other adsorbents [36-38]. The yield of the resulting activated carbon (82.8 %) is significantly higher than those observed for other activated carbons [20, 25, 26]. From the distribution particle size, it was determined that the average particle size of activated carbon was 187 μm and 50 % of the particles had a particle size smaller than 45 μm . Before thermal treatment, the average particle size of initial sewage sludge is 209.65 μm and only 2 % of the particles are smaller than 50 μm . We conclude that the loss of size is probably due to the heating processes [40, 41].

The nitrogen adsorption-desorption isotherm on the activated carbon is illustrated in Fig. 1. As shown by this latter, the isotherm plot of the activated carbon was found to be of type II (based on IUPAC classification) isotherms for the typical hysteresis loop in the mesopore range. The results show that the textural characteristics (BET surface area, total pores volumes) and an iodine number of activated carbon are fairly low if compared to other activated carbons prepared from the same precursor material [22, 24-26]. This could be attributed to the fact that the carbonization of activated sewage sludge has been done in the absence of an inert atmosphere (nitrogen or argon). On the contrary, the methylene blue number

Table 1: Physico-chemical properties and textural characteristics of prepared activated carbon.

Parameter	Value
pH	6.96
Conductivity ($\mu\text{S}/\text{cm}$)	236
Yield (%)	82.8
Iodine number (mg/g)	216.44
Methylene blue number (mg/g)	263.05
S_{BET} (m^2/g)	132.7
V_{T} (cm^3/g)	0.23
V_{mic} (cm^3/g)	0.06
V_{mes} (cm^3/g)	0.17
D_{p} (nm)	6.93
S_{I} (m^2/g)	215.28
S_{MB} (m^2/g)	643.9

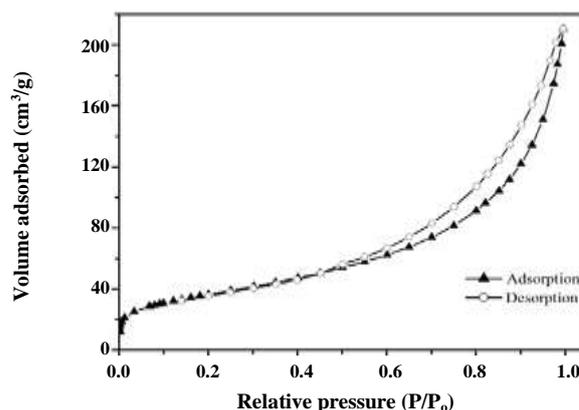


Fig. 1: Nitrogen adsorption-desorption isotherm at 77 K on the prepared activated carbon.

value is higher than that of other activated carbons which have a great value of BET surface area [22]. It has been demonstrated that the adsorption capacities of activated carbon are not only dependent on the specific surface area, but also on the surface properties, such as the functional groups and the surface charge of activated carbon [25]. The mesopores volume and average pore diameter value of the prepared activated carbon ($2 \text{ nm} < D_{\text{p}} < 50 \text{ nm}$) indicate that the activated carbon was highly mesoporous.

X-ray diffraction analysis of activated carbon prepared from sewage sludge is presented in Fig. 2.

The main crystalline species were identified depending on previous studies and by using JCPDS files. It shows a slight crystalline nature of the activated carbon. XRD analysis indicates the presence of important amounts of quartz (SiO_2) and calcite (CaCO_3). This is in agreement with previous studies [25, 41].

The FTIR spectra of activated carbon (before adsorption, after adsorption, and after desorption) are shown in Fig. 3. The samples exhibited similar IR spectra, but there is an only a slight difference with activated carbon after adsorption of nickel. The functional groups were determined by the interpretation and comparing of the IR spectra with the standard spectrum group frequencies. The accurate assigning of the specific wave number to a given functional group was not easy to do because the adsorption bands of various functional groups overlap and shift depending on their molecular structure. Also, they are affected by different peripheral functional groups.

The bands from 3614 to 3191 cm^{-1} could be assigned to phenolic, carboxylic acid and isolated non-bonded hydroxyl (OH) groups [42]. An intense and medium peak at 1658 - 1660 and 1628 cm^{-1} might be ascribed to the C=O stretching vibration of carbonyl groups [10, 14]. A broad absorption band around 1300 - 833 cm^{-1} with a maximum at 1035 cm^{-1} (before adsorption), 1048 cm^{-1} (after desorption) and 1081 cm^{-1} (after adsorption) is assigned to C-N, Si-O, C-O stretching and O-H bending mode of alcoholic, phenolic and carboxylic groups [16, 21]. The bands observed at about 780 and 690 cm^{-1} could be assigned to C-H and C-Cl stretching vibrations [31, 43]. The bands located at about 556 cm^{-1} were attributed to the O-H stretching vibration [31]. The shoulder at around 1425 which appears in the spectra related to activated carbon before and after desorption could be ascribed to C-O of carboxylic functional groups [15]. This peak does not appear in activated carbon spectrum after adsorption and suggests that it could be responsible of binding the Ni(II) ions to the adsorbent [15].

Batch adsorption experiment

Effect of pH

The adsorption of Ni(II) ions onto activated carbon with initial pH values ranging from 2 to 8 were performed (Fig. 4). We did not extend the study to higher pH values because of Ni(II) precipitation to giving formation of $\text{Ni}(\text{OH})^+$ and/or $\text{Ni}(\text{OH})_2$ with $\text{pH} > 8.5$ [20, 44].

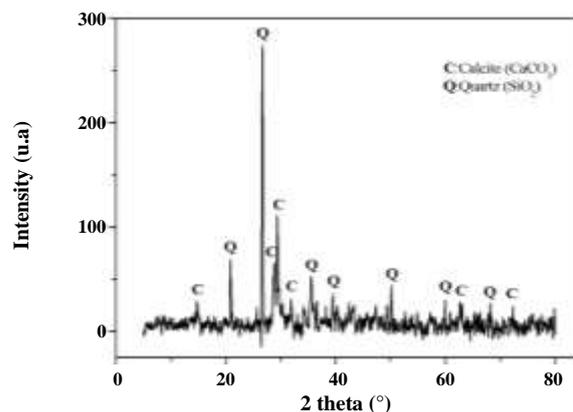


Fig. 2: X-ray diffraction pattern of the prepared activated carbon.

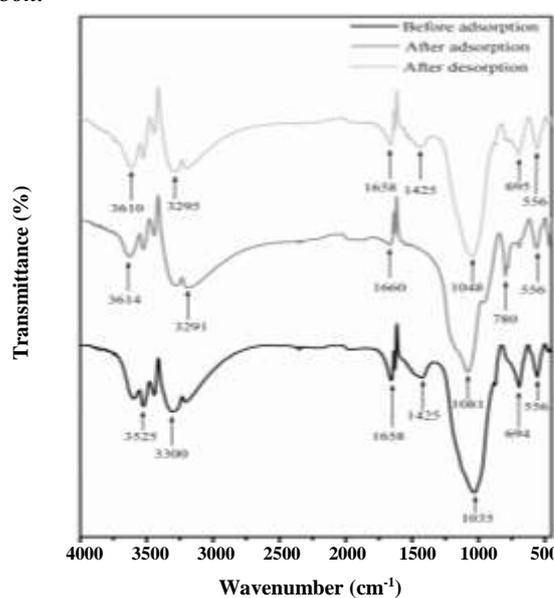


Fig. 3: FT-IR spectra of activated carbon before adsorption, after adsorption and after desorption of Ni(II) ions.

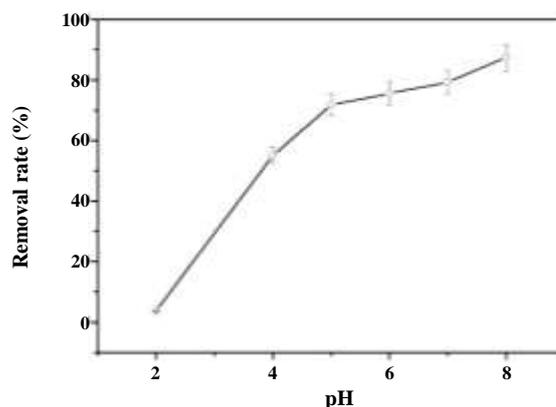


Fig. 4: Effect of solution pH on adsorption of Ni(II) onto activated carbon (adsorbent dose: 4 g/L , C_0 : 50 mg/L , temperature: $25 \pm 1\text{ }^\circ\text{C}$, contact time: 90 min).

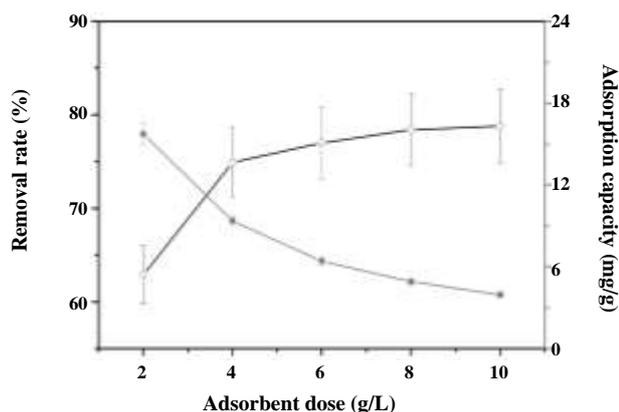


Fig. 5: Effect of adsorbent dose on the adsorption of Ni(II) by activated carbon (C_0 : 50 mg/L, temperature: 25 ± 1 °C, pH: 5.6, contact time: 90 min).

Results indicate that the rate removal of Ni(II) ions increases sharply with increase in pH solution from 2.0 to 5.0. After that, we observe a slight increase between 5.0 and 8.0. The maximum removal rate was obtained at pH 8.0, it was found to be 82.42 %. The evolution of removal the rate of Ni(II) ions is linked to the H^+ concentration and the adsorption competition between both ions. At lower pH, the low removal rate is mainly due to the high concentration of H^+ in the solution, which preferentially adsorbs on the active adsorption sites of activated carbon. When pH increases the Ni^{2+} could be adsorbed on H^+ free adsorption sites [2].

Effect of adsorbent dose

The adsorbent dose is one of the parameters that strongly affect the adsorption process. The effect of this latter in the range of 2 to 10 g/L was used for the adsorption experiments and the results are given in Fig. 5. The results show that the increase of adsorbent dose increases the removal rate but decreased the adsorption capacity. The removal rate increases from 62.9 to 78.8 % on the other side the adsorption capacity decrease from 15.72 to 3.94 mg/g. This variation in removal rate and adsorption capacity of Ni(II) ions could be attributed to surface functional groups and the number of active adsorption sites. The removal rate observed at an adsorbent dose of 4 g/L is considered as equilibrium value and was taken as the optimal adsorbent dose for the subsequent experiments. Similar results have been reported by Zhai *et al.* [20].

Effect of initial Ni(II) concentration

Fig. 6 illustrates the effect of initial Ni(II) ions concentration on the adsorption capacity of Ni(II) ions. We note that this latter increases along with an increase in initial Ni(II) ions concentration. The equilibrium adsorption capacity from 2.36 to 9.36 mg/g could be attributed to the ratio of the available adsorption active sites to the initial number of Ni(II) moles. Higher values are obtained on almond husk activated with sulfuric acid [5]. However, our results are better than those obtained on cashew nutshell [15], coirpith [2] and sewage sludge [22].

Effect of contact time

The effect of contact time on the Ni(II) ions adsorption was determined and the corresponding variation of adsorption capacity is shown in Fig. 7. The obtained results show that the adsorption capacity increases rapidly during the first 60 min and thereafter increases slowly up to 90 min, then the adsorption capacity remains almost constant. The figure shows that equilibrium adsorption capacity of the activated carbon was achieved at 90 min with 9.36 mg/g, equivalent to a removal rate of 75 %. The initial adsorption capacity could be due to the abundance of active binding sites on the adsorbent, and with gradual occupancy of these sites, the adsorption becomes less efficient in the later stage. According to these findings, an equilibrium time of 90 min was selected for adsorption kinetics studies.

Effect of temperature

Fig. 8 shows that the equilibrium adsorption capacity of Ni(II) ions on activated carbon increases with the increase in temperature. The equilibrium adsorption capacity increases from 9.36 to 12.39 mg/g in the temperature range of 25-55 °C. The increase in equilibrium adsorption capacity of Ni(II) ions could be due to the intraparticle diffusion rate of Ni(II) ions into the pores of activated carbon which is accelerated at higher temperatures. The results indicate that the adsorption reaction of Ni(II) onto activated carbon is an endothermic process. The effect of temperature on the equilibrium adsorption capacity of Ni(II) ions is in agreement with previously reported results by using scrap tires as a precursor material [14].

Adsorption equilibrium studies

The Langmuir, Freundlich and Temkin adsorption isotherms, often used to describe the adsorption of solutes from a liquid phase, were applied to our experimental results.

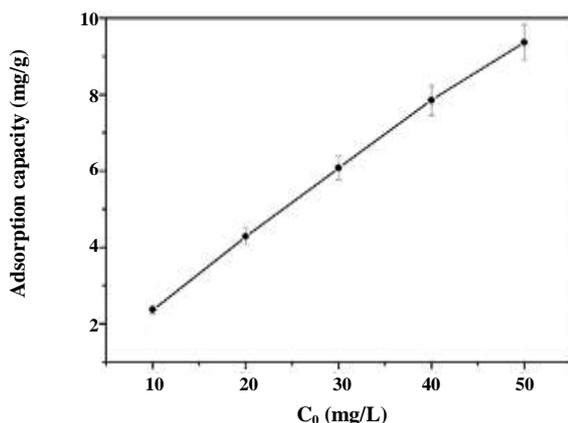


Fig. 6: Effect of initial Ni(II) concentration on the adsorption capacity of activated carbon (adsorbent dose: 4 g/L, pH: 5.6, temperature: 25 ± 1 °C, contact time: 90 min).

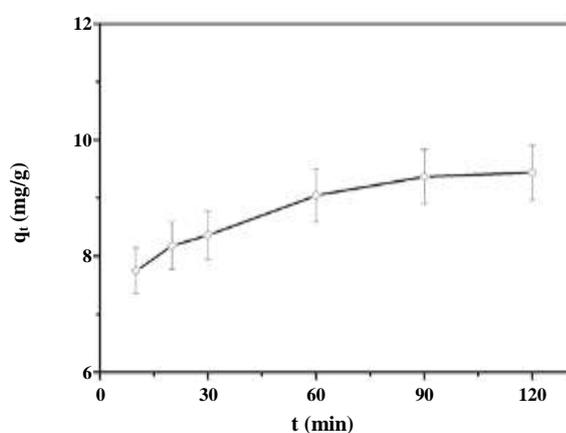


Fig. 7: Effect of contact time on the adsorption capacity of Ni(II) by activated carbon (adsorbent dose: 4 g/L, C_0 : 50 mg/L, pH: 5.6, temperature: 25 ± 1 °C).

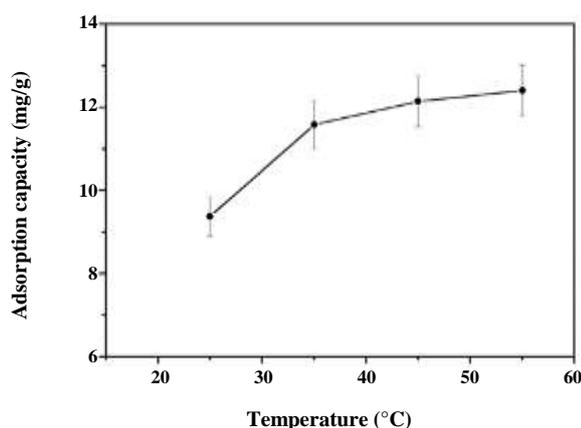


Fig. 8: Effect of temperature on the adsorption capacity of Ni(II) by activated carbon (adsorbent dose: 4 g/L, C_0 : 50 mg/L, pH: 5.6, contact time: 90 min).

The Langmuir isotherm is one of the models that describe monolayer coverage. It assumes a homogenous adsorption surface with binding sites having equal energies. The linear form of the Langmuir isotherm equation can be expressed as follows [44]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (11)$$

Where K_L (L/mg) is the Langmuir constant, Q_{\max} (mg/g) represents the maximum adsorption capacity under the experimental conditions. Q_{\max} and K_L are determined from the slope and intercept of plotting C_e/q_e versus C_e , respectively.

Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. The linearized Freundlich isotherm equation is represented by the following equation [45]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (12)$$

Where K_F (mg/g) (L/g)^{1/n} is the Freundlich constant related to the bonding energy. n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. K_F and n are, respectively, determined from the intercept and slope of plotting $\ln q_e$ versus $\ln C_e$.

The Temkin isotherm equation assumes that the fall in the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy [46]. The Temkin isotherm has been applied in the following form:

$$q_e = \left(\frac{RT}{B}\right) \ln A + \left(\frac{RT}{B}\right) \ln C_e \quad (13)$$

Where A (L/g) and B (J/mol) are the Temkin constants. T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J/mol K). A and B are determined from the intercept and slope of plotting q_e versus $\ln C_e$, respectively.

The different adsorption isotherms of Ni(II) ions onto activated carbon are graphically illustrated in Fig. 9. It could be seen from the figure that the adsorption isotherm models fit the data in the following order: Freundlich > Langmuir > Temkin isotherm.

Table 2: Isotherm parameters for Ni(II) ions adsorption onto prepared activated carbon.

Langmuir model		Freundlich model		Temkin model	
Q_{max}	11.520	K_F	2.9340	A	4.0595
K_L	0.2632	$1/n$	0.4409	B	1149.3
R^2	0.9655	R^2	0.9938	R^2	0.9547

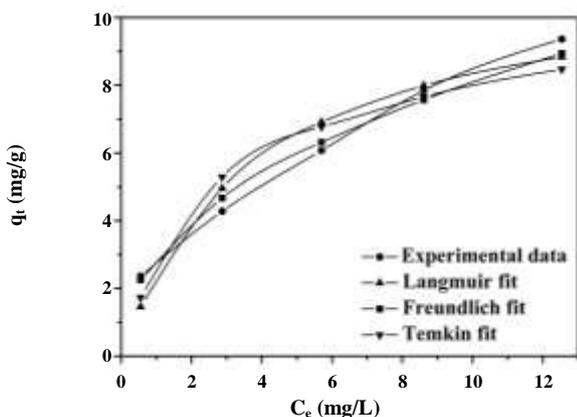


Fig. 9: Adsorption isotherms for Ni(II) ions adsorption by activated carbon.

The Langmuir, Freundlich and Temkin adsorption constants evaluated from the isotherms with the correlation coefficient (R^2) values for the three models are listed in Table 2. As it can be seen from the results, the Freundlich isotherm model has the highest value of the regression coefficient compared to the Langmuir and Temkin isotherms. This suggests that the adsorption on the activated carbon surface was a multilayer adsorption. The value of Freundlich constant ($n > 1$) indicates the feasibility of the adsorption process.

According to the Langmuir equation, the maximum uptake capacity for Ni(II) ions was 11.52 mg/g. The maximum adsorption capacities (Q_{max}) of Ni(II) ions of other adsorbents reported in the literature were compared with that of the present study and are presented in Table 3. It can be seen that the differences in Ni(II) adsorption capacities are dependent on the type of adsorbent, BET surface area and the range of initial Ni(II) concentration. Whereas we can note that the maximum adsorption capacities for all the adsorbents are in the same order. The comparison shows that the activated carbon used in this research exhibits favorable adsorption capacity if compared to the other adsorbents. The different performances of nickel uptake could be explained in term

of the following factors: (i) the heterogeneous nature and composition of raw materials; (ii) the properties of each adsorbent such as structure, functional groups, and their surface area.

Adsorption kinetic studies

Four kinetic models including pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion model are selected in this study for describing the adsorption process.

The pseudo-first order of Lagergren is given by the following equation [48]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (14)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first order. k_1 and q_e were calculated from the slope and intercept of the plot of $\ln(q_e - q_t)$ versus t , respectively.

The kinetic model of the pseudo-second-order [49] is described as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

Where k_2 (g/mg min) is the rate constant of the pseudo-second-order. The following expression denotes the initial adsorption rate h (mg/g min):

$$h = k_2 q_e^2 \quad (16)$$

The plot of (t/q_t) against t represents a linear relationship from which q_e and k_2 were determined from the slope and intercept of the plot, respectively.

The Elovich model is employed to describe chemisorption and is given by the equation [50]:

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

Where α and β are the Elovich constants. α (mg/g min) represents the initial adsorption rate and β (g/mg) is the desorption constant.

Table 3: Adsorption capacities of various adsorbents for nickel adsorption from aqueous solutions.

Adsorbents	S _{BET} (m ² /g)	C ₀ (mg/L)	Q _{max} (mg/g)	References
Scrap tire	–	0.1-40	25	[14]
Cashew nut shell	395	10-50	18.86	[15]
Rice husk	–	50-200	5.52	[16]
Sugarcane bagasse	–	10-200	2.32	[47]
Waste tea factory	0.39	50-300	18.42	[17]
Hazelnut shell	441	50-200	8.464	[18]
Sewage sludge	50.85	10-100	7.65	[41]
Sewage sludge	550	5-80	9.09	[20]
Sewage sludge	132.7	10-50	11.52	Present study

In general, the adsorption process may be described as a series of steps. To gain insight into the mechanisms and rate-controlling steps affecting the kinetics of adsorption, the intraparticle diffusion model proposed by *Weber* and *Morris* [51] is described by the following equation:

$$q_t = k_{id} t^{1/2} + C_i \quad (18)$$

Where k_{id} (mg/g min^{1/2}) is the intraparticle diffusion rate constant and C_i is the intercept at stage i , which k_{id} and C_i were calculated from the slope and intercept of the linear plot of q_t versus $t^{1/2}$, respectively.

The experimental results pertaining to the adsorption kinetics were compared to four kinetic models, allowing determining the parameters of these models (Table 4). Analysis of the correlation coefficients shows that the pseudo-second-order gave better fits compared to the pseudo-first order, Elovich, and intraparticle kinetics models. Indeed, the calculated equilibrium adsorption capacity value; q_e (cal.), is close to that determined by the experimental data; q_e (exp.). These findings are in agreement with the majority of reported works. It can be concluded that the rate-controlling step was the sharing or exchange of electrons between the Ni(II) ions and the activated carbon [52, 53]. The value of rate constant (k_2) and initial adsorption rate (h) are small if compared with other studies [14-16], which indicates that the kinetics of the adsorption process is slow. It could be attributed to the nature and properties of the adsorbent.

The intraparticle diffusion model indicates that two adsorption steps occurred in the process. The first sharper portion is the external surface adsorption or the

instantaneous adsorption. The second portion is the gradual adsorption stage where intraparticle diffusion was rate-limiting. The corresponding model parameters based on the above equation are listed in Table 4. We show that k_{id1} was higher than k_{id2} , this indicates that the removal rate of Ni(II) ions was higher in the beginning due to the available surface area of the activated carbon for the adsorption of Ni(II) ions. After the adsorbed material formed a thick layer and the uptake rate was controlled by the rate at which the adsorbate was transported from the exterior to the interior sites of the adsorbent particles.

Thermodynamic studies

The thermodynamic parameters: standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0), were calculated to evaluate the feasibility and nature of the adsorption process. The standard Gibbs free energy change ΔG^0 (kJ/mol) of the adsorption reaction can be determined from the following equation:

$$\Delta G^0 = -RT \ln K_c \quad (19)$$

Where T is the absolute temperature, R is the universal gas constant, and K_c is the thermodynamic equilibrium constant. The K_c value was calculated using the following equation:

$$K_c = \frac{C_a}{C_e} \quad (20)$$

Where C_a (mg/L) and C_e (mg/L) are the equilibrium concentrations of Ni(II) ions on the adsorbent and in the solution, respectively.

Table 4: Kinetics parameters of different models for Ni(II) ions adsorbed by activated carbon.

q_e (exp.) (mg/g)	Kinetic model	Parameters	values	
9.71	Pseudo-first order	q_e (cal.) (mg/g)	3.4570	
		k_1 (min^{-1})	0.0381	
		R^2	0.9918	
	Pseudo-second order	q_e (cal.) (mg/g)	9.8078	
		k_2 (g/mg min)	0.0218	
		h (mg/g min)	2.0950	
		R^2	0.9998	
	Elovich	q_e (cal.) (mg/g)	9.5606	
		α (mg/g min)	374.97	
		β (mg/g)	1.1340	
		R^2	0.9963	
	Intraparticle diffusion	First portion		
		k_{id1} (mg/g $\text{min}^{1/2}$)	C_1	$(R_1)^2$
		0.3875	6.1876	0.9949
Second portion				
k_{id2} (mg/g $\text{min}^{1/2}$)		C_2	$(R_2)^2$	
0.1909		7.4778	0.9989	

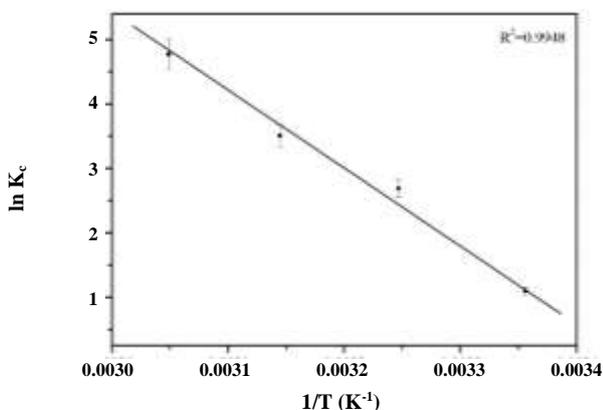


Fig. 10: Thermodynamic plot for Ni(II) ions adsorption onto activated carbon.

The relation between ΔG^0 , ΔH^0 and ΔS^0 can be expressed by the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (21)$$

$$\ln K_c = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (22)$$

Where ΔH^0 is the standard change in enthalpy (kJ/mol), ΔS^0 is the standard change in entropy (kJ/mol K). The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$, respectively (Fig. 10).

The values of obtained thermodynamic parameters in this study are presented in Table 5. The negative values of ΔG^0 indicate that the mechanism of Ni(II) adsorption from the aqueous solutions is feasible and show the spontaneous nature of the process. Results indicate that an increase in temperature is in favor of the adsorption process.

The positive value of ΔH^0 confirms the endothermic nature of the adsorption of Ni(II) onto activated carbon and the positive value of ΔS^0 reflects the affinity of activated carbon for Ni(II) and shows the increasing randomness at the solid-liquid interface during the adsorption process. Generally, the standard Gibbs free energy change (ΔG^0) for physisorption is usually between -20 and 0 kJ/mol, whereas that for chemisorption is often in the range of -80 to -400 kJ/mol. The ΔG^0 values obtained

Table 5: Thermodynamic parameters of Ni(II) ions adsorption onto activated carbon.

Temperature (K)	Thermodynamic parameters		
	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
298	-2.7113	96.389	0.3334
308	-6.8783		
318	-9.2639		
328	-13.011		

in this research indicate that the adsorption is a physisorption process. On the other hand, the heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1-20.9 kJ/mol, while the heats of chemisorption generally fall into a range of 80-200 kJ/mol. From Table 5, the obtained value of ΔH^0 indicates that the adsorption is chemisorption process. Which therefore indicates that nickel(II) adsorption onto activated carbon would be attributed to a physicochemical adsorption process rather than a purely physical or chemical adsorption process.

Desorption study

Desorption study helps to elucidate the mechanism of adsorption as well as to recover Ni(II) from the spent adsorbent apart from protecting the environment from solid waste disposal problems. Activated carbon saturated with Ni(II) desorption was performed at 25 °C by using 0.1 M HCl. The desorption efficiency of Ni(II) ions was almost total (100 %). The complete Ni(II) ions desorption shows that ion-exchange mechanism is operative in the adsorption process. The result clearly shows that the prepared activated carbon could be reused another time for nickel adsorption without significant effect on its adsorption capacity.

CONCLUSIONS

Batch adsorption studies for the removal of nickel(II) ions from aqueous solutions have been carried out using activated carbon prepared from sewage sludge by chemical activation using potassium hydroxide as the activation agent. The elaborated activated carbon had a favorable textural characteristics 132.7 m²/g of BET surface area, heterogeneous pore structure and it was found mesoporous in character. FTIR analysis revealed that the chemical functional groups such as hydroxyl, carbonyl, and carboxyl groups have been identified as potential adsorption sites to be responsible for binding Ni(II) ions to

the activated carbon. The optimized experimental parameters for Ni(II) ions adsorption were pH (8.0), adsorbent dose (4.0 g/L), contact time (90 min), initial concentration (50 mg/L) and temperature (55 °C). Equilibrium isotherm data were in good agreement with Freundlich than Langmuir and Temkin isotherms models. The maximum monolayer adsorption capacity, Q_{max} , of nickel (II) calculated from the Langmuir model, was found to be 11.52 mg/g at 25 °C. Adsorption kinetics studies revealed that the pseudo-second-order kinetic model better described the adsorption data. The thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 showed a favored, spontaneous, endothermic and physicochemical adsorption process. Desorption study with hydrochloric acid reagent indicated the good possibility of reusing the activated carbon. Based on the results of the present study, it can be concluded that the activated carbon prepared from sewage sludge by chemical activation with KOH was a cost-effective and a potential adsorbent for the removal of nickel(II) ions from aqueous solutions.

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