

Comparison of Two Processes of Activated Carbon Modification Based on Nitrogen Incorporation in Order to Improve its Adsorption Capacity of Cd²⁺

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Abstract

In this study activated charcoal synthesized from coconut shell was modified by adding nitrogenous functions from urea following two methods (M1 and M2). To detect the presence of nitrogen functional groups on the surface of ACU-1 and ACU-2, the resulting AC, ACU-1 and ACU-2 were characterized by different techniques including N₂ adsorption/desorption isotherms, elemental analysis, Boehm titration, spectroscopic methods (SEM, FTIR) and pH_{zpc} determination. It appears after characterization that the modification methods employed leading to ACU-1 and ACU-2 respectively allow the incorporation of 2.15 and 0.26% of nitrogen. A comparative study of Cd²⁺ ions adsorption carried out on the supports obtained shows that the first modification improves the adsorption capacity of activated carbon from 15.96 to 25.42 mg g⁻¹ while a slight decrease from 15.96 to 13.92 mg g⁻¹ was noted following the second modification. The adsorption capacity was strongly influenced by the solution pH and the optimum pH was ~5. The modeling of the adsorption data through the nonlinear Langmuir and Freundlich equations showed us that the equilibrium data for AC, ACU-1 and ACU-2 is well adapted to the Freundlich model. The adsorption kinetic study shows that the equilibrium can be reached after 4 hours and that the data is better described by the pseudo-second-order model.

Keywords: Activated Carbon, Nitrogen functional group, Urea, Cd²⁺ ions removal

1. Introduction

The presence of heavy metals in the environment even at low concentrations can be detrimental to a variety of living species including human[1]. The removal of heavy metals from water is therefore important for human health. Various methods including chemical precipitation, membrane filtration, ion exchange and adsorption have been proposed for the removal of heavy metals, each having advantages and limitations[2]. In the present study, we focus on the adsorption process using activated carbon, because this process is widely applicable, efficient, and creates relatively little sludge. Particularly, Adsorption using activated carbon made from biomass appears to be a promising method given its lower cost for developing countries such as Ivory Coast. The ability of activated carbons to absorb heavy metals can be improved by using many modification methods. These modifications consist of a chemical and / or physical treatment aimed at modifying the surface chemistry[3][4]. Recent studies on the modification of activated carbon by treatment with urea have shown that the presence of nitrogen functional groups in a carbonaceous structure improves its adsorption capacity[5][6]. The main reason mentioned is that the nitrogen atom of nitrogen functional groups compared to oxygen can easily bind to a proton or a metal ion through electron pair sharing due to its weak electronegativity.

In this study, activated carbon (AC) was produced by activating the virgin carbon of the coconut shell with KOH at high temperature. We have tried to improve the cadmium ions adsorption capacity of this activated carbon by modifying it. During the modification of this activated carbon two methods of treatment using urea to provide nitrogen functional groups on the surface of AC were studied. The physicochemical properties of the adsorbents obtained from each method as well as their adsorption capacity were then compared.

2. Materials and Methods

2.1. Materials

The coconut shells were collected in Ivory Coast. After being washed with distilled water, the precursors were dried in an oven for 24 h. The activating and modifying agents respectively KOH and urea were purchased from sigma Aldrich. All the chemicals used in this study were analytical reagents, and deionized water was used as the experimental water. The standard cadmium stock solution of 1 gL⁻¹ was obtained by dissolving appropriate amount of cadmium chloride in deionized water. The working solutions were obtained by diluting the stock solution to desired concentrations with distilled water.

2.2. Preparation of the Activated Carbon

The washed and dried coconut shells were charred at 550°C for one hour under air in an oven at a rate of 5°C.min⁻¹. The coal obtained is ground to have coal of a size smaller than 250 µm. An amount of coal was mixed with KOH and distilled water at a mass ratio of 3/1/1.25 (KOH / CHAR/ distilled water) in a rectangular crucible. The mixture was dried in an oven at 110 °C for 24 h. The dry mixture is placed in a closed turbulent furnace heated at 5 °C.min⁻¹ to 850 °C and maintained for 2 h. After cooling, the resulting carbon was washed with a 0.1 M HCl solution followed by hot distilled water up to pH 6.5 to remove the activating agent residues and other inorganic species formed during the process. In the washing step, the activated carbon was separated using 0.45 µm membrane filters. The resulting carbon was dried at 105 °C for 24 h and held in hermetically sealed bottles for further analysis.

2.3. Surface Modification of Activated Carbon

- The first modification method adopted to introduce the nitrogen functional groups on the surface of activated carbon from urea as nitrogen source is the following: 3g of activated carbon AC was mixed with a suspension of urea (2 g of urea in 10 ml of ethanol) and stirred at room temperature for 5 h. The whole is then dried at 120 ° C. and then calcined in a tubular oven at 450 ° C. for 30 minutes at a temperature rise rate of 5 ° C./min under an argon flow. After heat treatment, the sample was washed with boiling water to remove decomposition products of excess urea and then dried. The activated carbon obtained is called ACU-1.
- The second modification method using urea consists in impregnating 3 g of activated carbon in a suspension of urea (2 g of urea in 10 ml of ethanol) and stirred at ambient temperature for 5 h. The mixture was then dried at 110 ° C. the coal recovered after evaporation of the ethanol was washed several times and then dried. The resulting activated carbon was named ACU-2.

2.4. Porosity Properties

The textural parameters of all samples were determined by nitrogen adsorption experiments at liquid nitrogen temperature (77 K) with a Quantachrom Autosorb 1 instrument. First, the samples were outgassed at 150°C for 6h under the vacuum prior to the N₂ adsorption/desorption tests. The surface areas were calculated by applying the BET (Brunauer–Emmet–Teller) equation on the first part of the isotherms. Micropore analysis was made by the t-method. The total pore volume in each sample was evaluated from the amount of nitrogen adsorbed at the highest relative pressure examined.

2.5. Point of Zero Charge Measurements

Point of zero charge for produced carbons was measured according to the method suggested by Noh and Schwarz (Reymond and Kolenda, 1999), which requires recording of the equilibrium pH after shaking of suspensions of carbon samples in distilled water for 24 h. The initial pH of the suspensions was selected in the range of 2–11. The fixed equilibrium value of pH was taken as the pH_{pzc}.

2.6. Boehm Titration

The acidic and basic surface groups were determined according to the method of Boehm [8]. 0.5 gram of carbon sample was placed in 50 ml of 0.1 N solutions of either sodium hydroxide or hydrochloric acid. The vials were sealed and shaken for 48 h and then 20 ml of each filtrate was pipetted, and the excess of base or acid was titrated with 0.1N HCl or 0.1N NaOH, as required. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes all acidic groups (carboxylic, phenolic and lactonic groups) and HCl reacts with all basic groups.

2.7. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were taken using a Perkin Elmer spectrophotometer instrument. Data's acquisition was performed automatically using an interfaced computer and a standard software package. The dried samples first were, ground with KBr salt followed by compression between two stainless steel cylinders to form a thin transparent solid film. The spectrometer collected a spectrum in the range of 400–4000/cm.

2.8. SEM and Elemental Analysis

Surface morphologies of these biosorbents were detected by scanning electron microscopy (SEM) (JSM-840 scanning microscope). The elemental composition of carbons was quantitatively determined by (EA 1108, CHNS: Fisons) and the functional groups on the surfaces of modified activated carbon (ACM) were qualitatively determined using X-ray photoelectron spectroscopy (Axis-Ultra system spectrometer from Kratos (UK)).

2.9. Adsorption Experiments

The adsorption experiments were carried in 50 ml conical flask containing 25 ml of aqueous Cd²⁺ solution. The adsorbents dose was first fixed at 1g L⁻¹, the initial pH was adjusted to the desired pH values by addition of 0.1 N of HCl or NaOH. The suspensions were stirred at room temperature. The effects of initial metal concentration (7.5 - 75 mg L⁻¹), initial pH (2-8) as well as adsorbent concentration (1g L⁻¹ - 3.5 g L⁻¹) were studied. After equilibrium, the adsorbent was recovered by centrifugation and residual Cd²⁺ ions concentrations in the aqueous solutions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The adsorption capacity of Cd²⁺ ions (e.g., Q_e) and the percentage of adsorption were calculated using equations 1 and 2 respectively[9]:

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \tag{1}$$

$$R (\%) = \frac{(C_0 - C_e) \times 100}{C_0} \tag{2}$$

Where C₀ and C_e are the initial and equilibrium concentrations of Cd²⁺ ions (mgL⁻¹), M is the mass of adsorbent (g), and V is the volume of solution (L).

The procedure of kinetic tests was identical to those of equilibrium tests. The aqueous samples were stirred at different time (0 - 300 min) and the concentrations of Cd²⁺ ions were measured. The amount of adsorption at time *t*, Q_t (mgg⁻¹), was calculated by:

Where C_t (mg L⁻¹) is the liquid-phase concentrations of Cd²⁺ ions at time *t*.

$$Q_t = \frac{(C_0 - C_t) \times V}{M}$$

2.10. Adsorption Isotherm and Kinetic Models

The application of adsorption isotherms is very useful for describing the interaction between the adsorbate and the adsorbent. There are several models for analyzing experimental adsorption equilibrium data. The Langmuir and Freundlich models are the most widely used surface adsorption models for single-solute systems. In this study, these two-parameter models (Langmuir and Freundlich) were applied. Kinetic models such as pseudo-first order, pseudo-second order, and intraparticle diffusion model were used to understand adsorption kinetics. Table 1 presents the equations and parameters of these adsorption isotherms and kinetic models. The adsorption isotherms, pseudo-first and pseudo-second order kinetic models were adjusted by applying the nonlinear fitting method, using the Origin 8.0 software. The most appropriate theoretical models describing the experimental data were selected considering the adjusted correlation coefficient (R²_{Adj}) and the standard deviation (SD).

Table 1: Isotherm and kinetic adsorption models

Isotherm and kinetic model	Plot
Langmuir model $Q_e = \frac{Q_m b C_e}{1 + b C_e}$	Q _e versus C _e
Freundlich model $Q_e = K_F C_e^{1/n}$	Q _e versus C _e
Pseudo-first order model $Q_t = Q_e [1 - \exp(-k_1 t)]$	Q _t versus t

Pseudo-second order model $Q_t = \frac{Q_e^2 k_2 t}{k_2(Q_e).t + 1}$	Q_t versus t
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3. Results and Discussion

3.1. Textural and Chemical Characterization

3.1.1. N₂ adsorption/Desorption

The measurement of the specific surface area by nitrogen adsorption is the most frequently used method for the characterization of porous materials. The N₂ adsorption-desorption isotherm (Figure 1) gives important information about the porosity of the carbon samples. Incorporation of nitrogen functional groups on the AC surface was investigated by measuring the specific surfaces of AC, ACU-1 and ACU-2 (Table 2). It appears a decrease in the specific surface area of AC depending on the modification method adopted. The characteristics of the control sample AC-450 (AC treated at 450 ° C. for 30 min without impregnation in a solution of urea) show us that this reduction is not caused by the heat treatment involved in the modification process leading to ACU-1 but rather by the formation of nitrogen-containing functional groups resulting from the decomposition of the urea at 450 ° C obstructing certain mesopores and / or micropores, thus preventing them from adsorbing N₂ during the measurement of the surface specific[10]. Compared with ACU-1, the most remarkable decrease of the ACU-2 surface may be due to the size of the urea molecule which, according to modification method 2, should be grafted onto the surface of AC after reaction with the oxygenated surface acid groups further clogging the mesopores and / or micropores.

Figure 1: Adsorption isotherm of different activated carbons

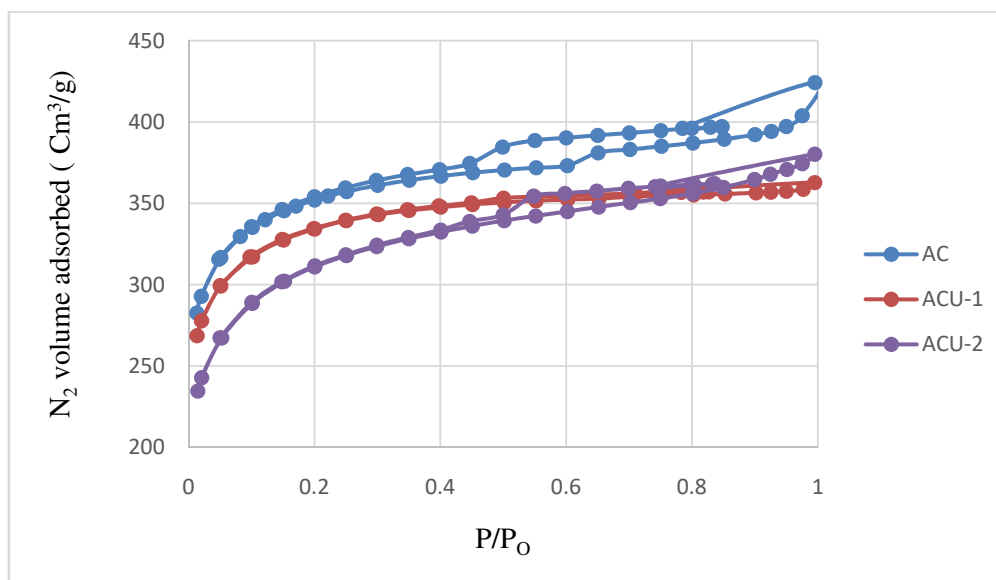


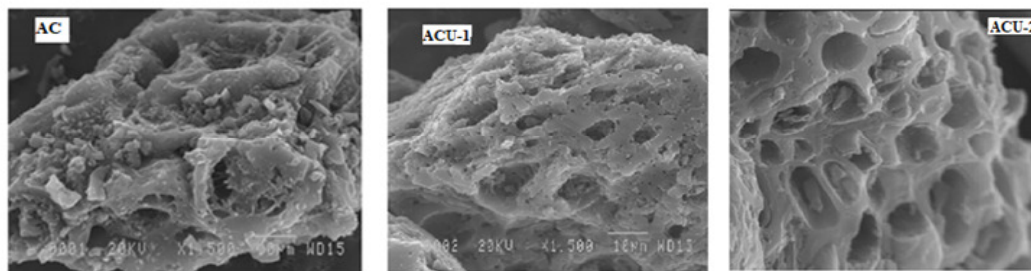
Table 2: Surface area and pore volume parameters of the carbons

Samples	SBET(m ² /g)	Vt(Cm ³ /g)	Vmic(Cm ³ /g)	Vmes(Cm ³ /g)	Dp(nm)
AC	1074	0.626	0.316	0.310	1.16
AC -450	1071	0.593	0.313	0.280	1.10
ACU-1	1044	0.493	0.310	0.183	0.94
ACU-2	972	0.553	0.345	0.208	1.12

3.1.2. SEM Analysis

Scanning electron microscopy (SEM) was used to observe the morphology of the various synthesized carbons (AC, ACU-1 and ACU-2), no notable transformation is observed for the porous structure except that the AC surface has become less rough.

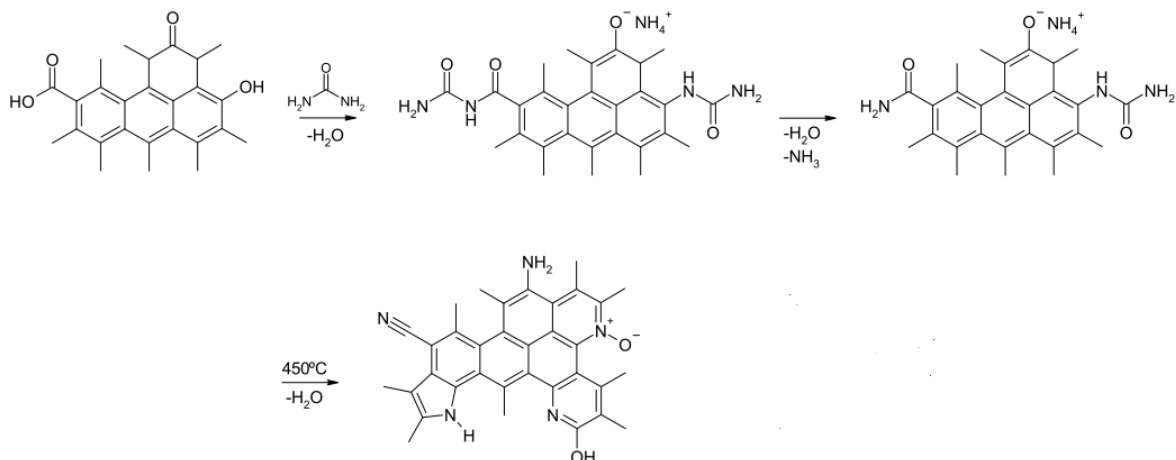
Figure2: SEM micrographs of AC, ACU-1 and ACU-2 at magnification * 500



3.1.3. Boehm Titration and pH_{pzc} Determination

The Boehm titration was applied to observe the influence of the modification methods used on the surface chemistry of activated carbon (Table 3). Only the overall concentrations in basic and acidic groups are presented without distinction of carboxylic, lactonic or phenolic because certain naturally basic nitrogenous groups can behave like acids, weak acids or strong acids in the aqueous solution. As shown in Table 2, the modification method leading to ACU-2 only slightly altered the surface of AC. This can be attributed to the difficult access of the active sites in the pores by the urea molecule during the impregnation following the fixation of some of the molecules obstructing the entry of the pores. However, the surface chemistry of ACU-1 described by Boehm titration shows a considerable change in the composition of surface functional groups of AC. This change is reflected in the increase of basic functional groups concentration (from 1.45 mmol g⁻¹ to 2.3 mmol g⁻¹) and the decrease in acid functional groups concentration (of 1.55 mmol g⁻¹ to 0.9 mmol g⁻¹). The observed change can be explained by the reaction between the surface oxygenated acid groups first with urea during the impregnation step and then with the decomposition products of urea during heat treatment at 450 °C; which leads to the reduction of the oxygenated acid groups and the formation of basic nitrogen functional groups according to the mechanism (Figure. 3) given by Mykola Seredych et al[11]. This is confirmed by the fact that when AC is treated at 450 without being previously impregnated in urea no noticeable change was observed concerning its surface chemistry.

The results obtained during the pH_{pzc} study are presented in the table. It appears that the pH_{pzc} of ACU-1 is slightly higher than that of AC while the pH_{pzc} of ACU-2 has slightly decreased. However, all materials have a pH_{pzc} greater than 7 (in the base range). This can be partly attributed to the fact that the method used for the activation of the original coal (impregnation in a KOH solution followed by a heat treatment at ~ 850 °C) leads to a basic activated carbon (pH_{pzc} greater than 7) and secondly to the incorporation of surface nitrogen functions.

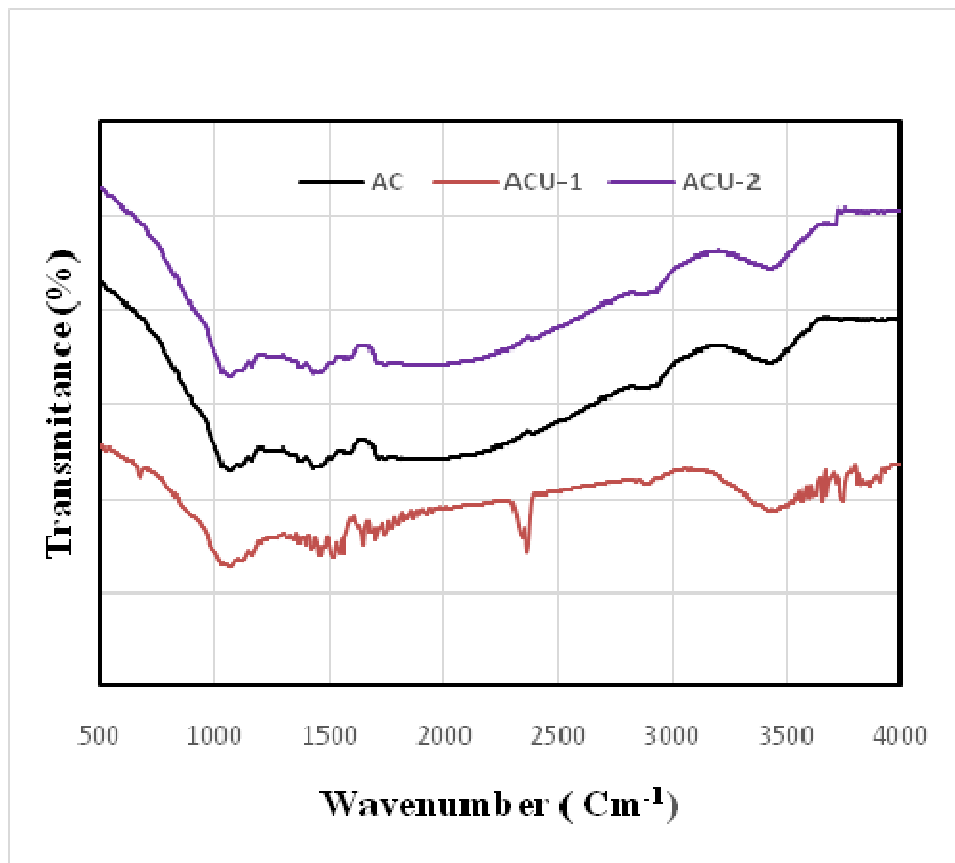
Figure 3: Possible chemical reactions of urea with surface functional groups and thermal transformations**Table 3:** Surface fonctionnal groups of the activated carbons

Echantillons	Fonctions Acides (mmol/g)	Fonctions Basiques (mmol/g)	Fonctions totales (mmol/g)	PHpzc
AC	1.5	1.45	2.74	9.65
AC-450	1.2	1.51	2.71	9
ACU-1	0.9	2.3	3.12	9.82
ACU-2	1.04	1.56	2.60	9

3.1.4. FTIR Analysis

Nitrogen functional groups on the surface of activated carbons were also studied using FTIR analysis (Figure 4). As shown in Figure 4, the FTIR spectra of ACU-1 and ACU-2 samples show FTIR peaks like those of the AC spectrum. The peaks at 1024 cm^{-1} , 1465 cm^{-1} and about 2900 cm^{-1} observed in the three samples can be attributed respectively to C-O stretching, the stretching of the aromatic ring C=C and C-H stretching. The wide band at around 3500 cm^{-1} , which is the characteristic of the OH stretch (of carboxyl, phenol or alcohol), also materializes the presence of the desired functions -NH₂, -NH (Adib et al., 2000). Therefore, The characteristic stretch of their presence is probably lost in the wide stretching band -OH of the ACU-1 and ACU-2 spectra.

Figure4: The FTIR spectra of activated carbon (AC) and Urea-modified activated carbon (ACU-1 and ACU-2)



3.1.5. Elemental Analysis

The elemental analyzes of AC, AC-450, ACU-1 and ACU-2 are summarized in Table4. The nitrogen content of the activated carbon AC increased from 0.05 % to 2.12% and 0.26 % respectively for ACU-1 and ACU-2. This indicates that a quantity of nitrogen functional group was introduced on AC surface with both modification methods used. The elevated nitrogen amount of ACU-1 (2.12 %) than that of ACU-2 (0.26 %) can be attributed to the additional heat treatment (450 ° C for 30 min) involved in the modification leading to ACU-1. Indeed, in the modification protocol leading to ACU-1, after evaporation of the ethanol, the urea particles that have not reacted with the acid functions on the surface of AC in the solution during the impregnation, melt at 135 ° C during heat treatment at 450 ° C thus causing additional interactions between the product of urea decomposition and oxygenated acid functional groups on AC surface.

Table 4: Elemental Analysis of Carbon Samples

ECHANTILLON	% C	% H	% N	% S
AC	85.87	0.65	0.05	0.03
AC-450	88.45	0.26	0.12	0.00
ACU-1	88.70	0.2	2.12	0.00
ACU-2	88.66	0.42	0.26	0.00

3.1.6. Adsorption Study

To study the influence of the two modification methods used on the adsorption capacity of AC, adsorption tests were carried out by varying Cd^{2+} ions initial concentration of an aqueous solution from 7.5 to 75 mg L^{-1} . It appears that the amount of adsorbed Cd^{2+} ions per gram of ACU-1 and ACU-2 increases with the increase of the initial concentration of Cd^{2+} ions (Figure 5). Comparison of Cd^{2+} ions adsorption isotherms on the various adsorbents (AC, ACU-1 and ACU-2) shows us an improvement of the adsorption capacity of AC with the modification leading to ACU-1 and a slight decrease of the adsorption capacity with that leading to ACU-2. This can be explained by the fact that the first modification method allowed to incorporate a larger quantity of nitrogen (2.12%) on the surface of AC, unlike the second modification method, which allowed only the incorporation of 0, 26% of nitrogen. The modeling of Cd^{2+} ions adsorption experimental values using the Langmuir and Freundlich model is presented in Figure 5. The resulting model parameters, the standard deviations and the adjusted correlation coefficients are summarized in Table 5. Since the best model is the one with the highest adjusted correlation coefficient and the lowest standard deviation, it is clear that the Freundlich model better describes the adsorption phenomenon of Cd^{2+} ions on the various supports (AC, ACU-1, ACU-2). This therefore reflects the heterogeneity of the surface of the different supports. The Cd^{2+} ions are therefore adsorbed on the surface of these materials with different energies.

Figure 5: Cd^{2+} adsorption isotherms onto AC, ACU-1 and ACU-2 ($T = 25.0\text{ }^{\circ}\text{C}$; $t = 24.0\text{ h}$; $\text{pH} = 5$; adsorbents concentration = 1 g L^{-1})

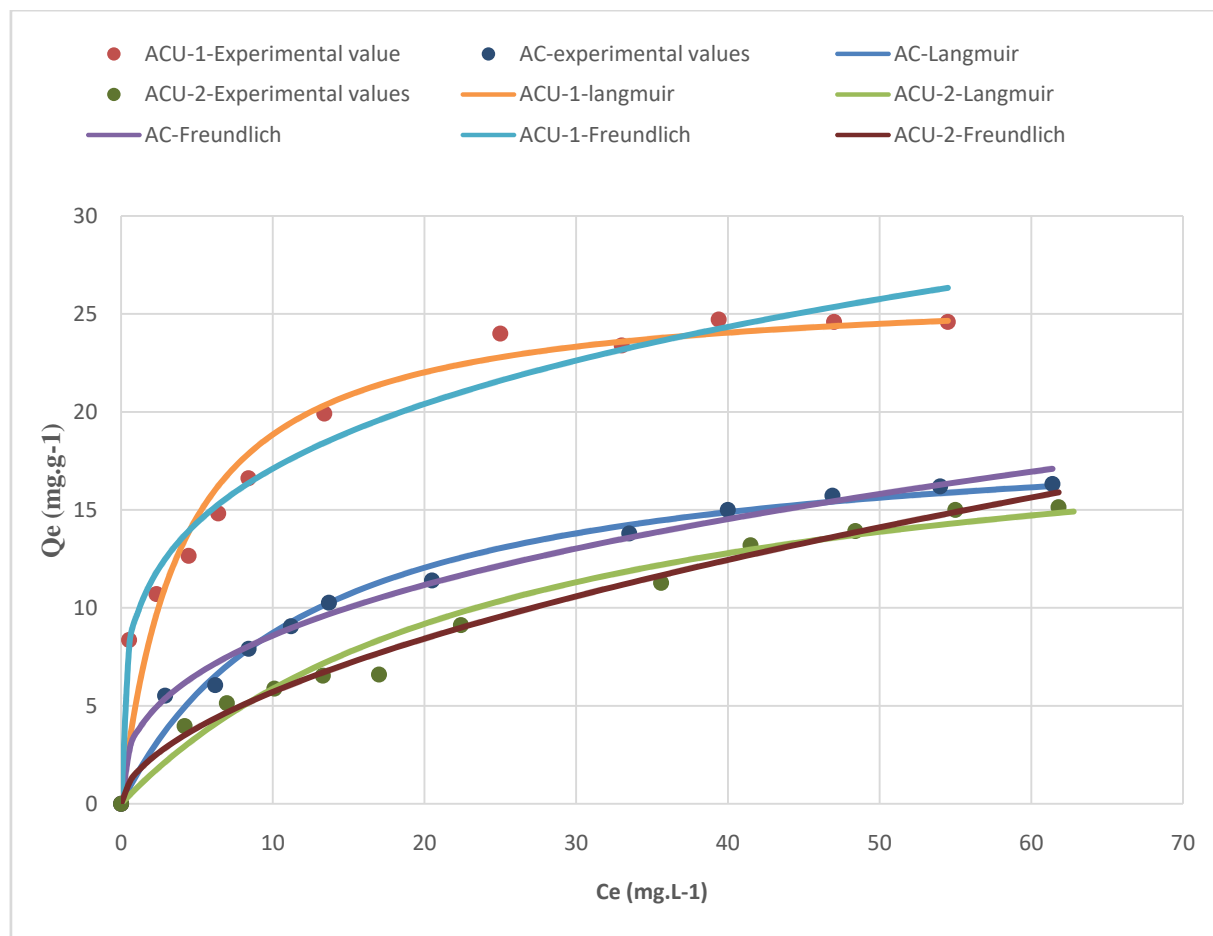
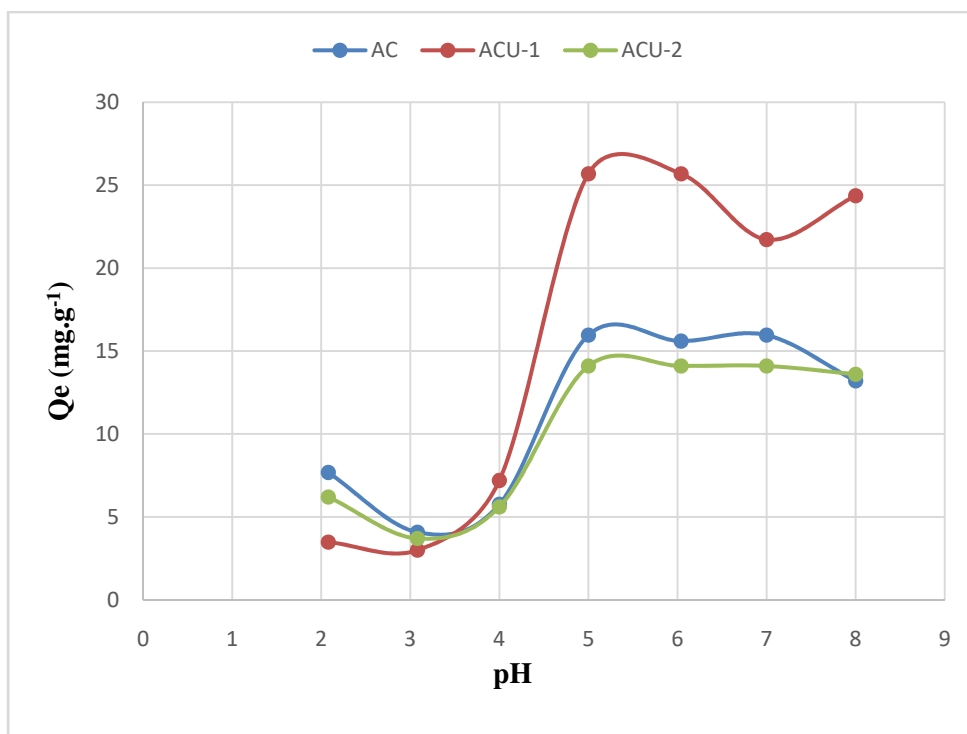


Table 5: Langmuir and Freundlich isotherm constants

Model	Langmuir				Freundlich			
	Q _{SAT}	K _L	R ² _{ADJ}	SD	K _F	n	R ² _{adi}	SD
AC	19.46	0.08	0.98	0.67	3.58	2.63	0.99	0.50
ACU-1	26.48	0.25	0.94	1.90	9.52	3.93	0.98	1.22
ACU-2	20.05	0.038	0.97	0.77	1.56	1.77	0.99	0.45

3.1.7. Effect of pH on Cd²⁺ ions Adsorption onto AC, ACU-1 and ACU-2

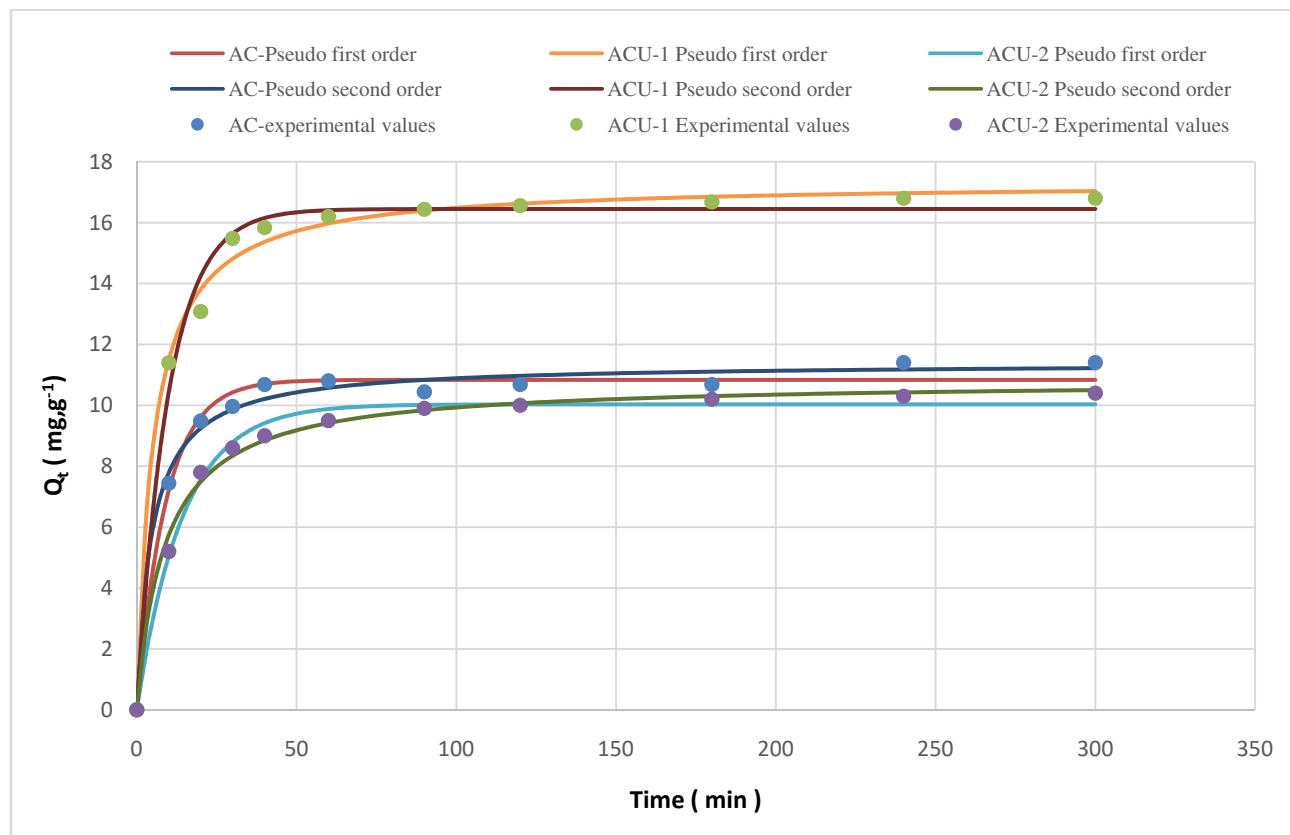
Figure 6: Effect of initial pH on Cd²⁺ ions adsorption onto AC, ACU-1 and ACU-2 (C₀= 60.0 mg L⁻¹; dosage 1.0 g L⁻¹; T = 25.0 °C; t = 24.0 h).



During an adsorption phenomenon, pH is one of the most important factors. This parameter influences not only the dissociation of the sites on the adsorbents surface but also the speciation of the heavy metals in solution. Figure 6 shows the effect of the initial pH on the removal of Cd²⁺ ions by AC, ACU-1 and ACU-2. The optimal pH of Cd²⁺ ions adsorption on AC, ACU-1 and ACU-2 is 5. Below this pH (pH = 5) adsorption was found to be quite low. The higher adsorption capacity of AC and ACU-2 compared to ACU-1 at low pH (2 ≤ pH ≤ 3) can be explained by the fact that according to the Boehm titration, AC and ACU-2 have more acidic functional groups than ACU-1, thus providing more ion exchange sites between H⁺ ions and Cd²⁺ metal ions (Kong et al., 2014). Above pH = 7, Cd²⁺ ions precipitate as Cd (OH)₂, therefore, the adsorption capacity of our different adsorbents decreases.

3.1.8. Adsorption Kinetics

Figure 7: Cd^{2+} ions adsorption kinetics onto AC, ACU-1, ACU-2 ($C_0 = 60.0 \text{ mg L}^{-1}$; adsorbents concentration = 1 g L^{-1} ; $T = 25.0 \text{ }^\circ\text{C}$; $\text{pH}=5$)



The adsorption kinetics is defined by the evolution of the adsorbed quantity as a function of the adsorbent / adsorbate contact time. The study of the contact time effect was carried out in a time interval between 0 and 300 min at room temperature. The initial pH of the cadmium solution was ~ 5 . The adsorbent concentration was 1 g L^{-1} and the initial Cd^{2+} concentration was 60 mg L^{-1} . Figure 7 shows that generally the adsorption kinetics was initially very fast during the first 40 minutes because of the availability of the active sites on the surface of the various adsorbents [12], then it becomes slower until it reaches equilibrium because of the contact surface reduction after occupation of the active sites.

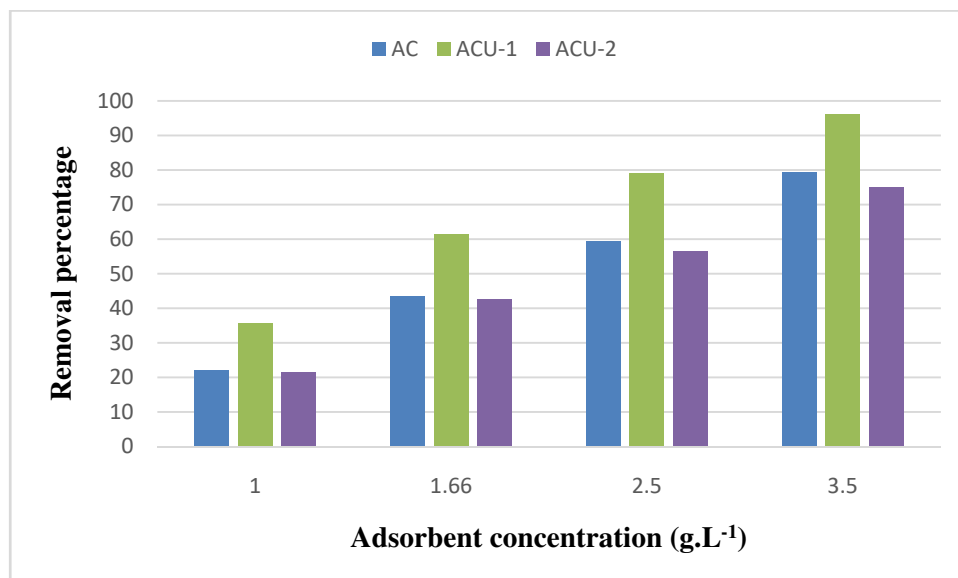
Experimental values of cadmium sorption kinetics by different adsorbents are modeled by pseudo-first-order and pseudo-second-order nonlinear equations (Figures 7). The adjusted correlation coefficients, the standard deviations and the different models parameters are collated in the Table 6. Through the comparison of the adjusted correlation coefficients and the standard deviations of the two models it appears that the second-order model better describes the Cd^{2+} adsorption phenomenon on the various adsorbents (AC, ACU-1, ACU-2). This suggests that the Cd^{2+} ions are adsorbed on the adsorbents surfaces by covalent bond formation with (O and N) basic surface functional groups of different adsorbents [13].

Table 6: kinetics parameters

Model		Pseudo-first order				Pseudo-second order			
Parameters	$Q_e(\text{exp})$	$Q_e(\text{cal})$	k_1	R^2_{adi}	SD	$Q_e(\text{cal})$	k_2	R^2_{adi}	SD
AC	11.40	10.83	0.10	0.98	0.35	12.39	0.018	0.99	0.29
ACU-1	16.8	17.32	0.01	0.98	0.55	16.44	0.1	0.99	0.39
ACU-2	10.4	10.35	0.01	0.98	0.28	10.81	0.014	0.99	0.23

3.1.9. Effect of Adsorbent Concentration

Figure 8: Effect of adsorbents concentration on Cd²⁺ ions adsorption on AC and ACU (C₀=60.0mgL⁻¹; T = 25.0 °C; t = 8.0 h, pH = 5)



The removal of Cd²⁺ ions was also studied by varying the concentration of adsorbents from 1 g L⁻¹ to 3.5 g L⁻¹. The results show us that the removal percentage of heavy metals increases rapidly with the increase of the adsorbent concentration in the solution (Figure 9). Indeed, the increase in the adsorbent dose generates more adsorption sites which promotes easier access of metal ions to sorption sites. When the adsorbent concentration reaches 3.5 g L⁻¹, ACU-1 removes almost all of the Cd²⁺ ions in solution while ACU-2 removes only 75% of the Cd²⁺ ions in solution. The modification leading to ACU-1 therefore increases the efficiency of AC.

4. Conclusion

The aim of this study was to compare two activated carbon modification methods using urea as a nitrogen source to improve the adsorption capacity of activated carbon. For this purpose, AC was synthesized from coconut shells collected in Ivory Coast. ACU-1 was obtained by impregnation of AC with a solution of urea followed by a heat treatment at 450 ° C. ACU-2 was obtained by impregnation of AC with a solution of urea followed by drying at 110 ° C. The physical properties determined by N₂ adsorption / desorption, SEM analysis and chemical properties such as infrared spectroscopy, Boehm titration and elemental analysis of AC and ACU show a nitrogen supply of approximately 2.12% with ACU-1 and 0.26% with ACU-2. A comparative study of adsorption of Cd²⁺ ions on AC, ACU-1 and ACU-2 shows an improvement in the maximum adsorption capacity from 15.92 mg g⁻¹ to 25.42 mg g⁻¹ with ACU-1 and a slight decrease of this one with ACU-2. Experimental adsorption data were better described with the Freundlich model suggesting that adsorption occurred on heterogeneous surfaces. The optimal adsorption pH was 5. The kinetic study shows that the adsorption corresponds well to the kinetic model of pseudo-second order reflecting a chemical adsorption dominated by the formation of a covalent bond between the adsorbate and basics surface functional groups of AC, ACU-1, ACU-2. The study of the effect of the adsorbent concentration shows us an improvement in the efficiency of AC with the modification method leading to ACU-1 because 3.5 g.L⁻¹ of ACU-1 are sufficient to eliminate all the Cd²⁺ ions.

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