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Nitrogen Enrichment of Activated Carbon Made From Coconut Shell of Ivory Coast and its Application in Cd^{2+} Ions Removal

[1,2]**Kouakou Vianet Bossombra,** [1]**Tchirioua Ekou,** [1]**Lynda Ekou and** [2]**Trong-On Do**

[1]*Université Nangui Abrogoua, Laboratoire de Thermodynamique et de Physico-Chimie du Milieu (LTPCM) 02 Bp 801 Abidjan 02 – Côte d'ivoire*
[2]*Laval University, Department of Chemical Engineering, Québec, G1V 0A6, Canada*

Correspondence Author: Tchirioua Ekou, Université Nangui Abrogoua, Laboratoire de Thermodynamique et de Physico-Chimie du Milieu (LTPCM) 02 Bp 801 Abidjan 02 – Côte d'ivoire.
E-mail: tchiriouaekou@yahoo.fr

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Abstract

Urea was employed to modify activated carbons by KOH activation at high temperature from coconut shell from Ivory Coast. The urea-modified activated carbon was used to improve Cd2+ ions adsorption from aqueous solutions. The original activated carbon (AC) and urea-modified activated carbon (ACU) were characterized by N2 adsorption/desorption, Boehm's titration, SEM, FTIR,elemental analysis and XPS analysis. The Cd2+ ions removal capabilities of AC and ACU were evaluated by batch sorption experiments. The results of N2 adsorption/desorption demonstrated that the BET surface areas and total pore volumes of AC decreased after urea-modification. Nevertheless, the results of elemental analysis, Boehm's titration and FTIR showed that ACU contained more surface nitrogen functional groups than AC. Adsorption tests revealed that ACU had a higher adsorption capacity of Cd2+ than AC. Experimental adsorption data of Cd2+ ions on AC and ACU were better described by the Freundlich model.The main mechanisms for the adsorption of Cd2+ ions onto the carbons were supposed to be cation exchange and covalent bond formation.Kinetic study was performed,and the pseudo-second order model better described the adsorptions processes.

Key words: ActivatedCarbon, Nitrogen functional group, Urea, Cd^{2+} ions removal.

INTRODUCTION

Nowadays, an increase of discharge of heavy metal ions to natural sources by industrial activities is one of most serious environmental problems. Even at low concentrations, these metals can be toxic for organisms, including humans(Abdulkarim *et al.*, 2009).For example, the harmful effects of cadmium include several acute and chronic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy(Kadirvelu and Namasivayam, 2003). Many processes have been used to remove heavy metals from wastewater and contaminated soils. These are chemical precipitation, ion exchange, coagulation and flocculation, complexation, biosorption, adsorption and membrane processes(Ahn*et al.*, 2009)(Amuda*et al.*, 2007)(Aydiner*et al.*, 2006)(Bailey*et al.*, 1999)(Choi*et al.*, 2009)(Xiong*et al.*, 2009).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(Kannan and Rengasamy, 2005). To increase the capacity of activated carbons to absorb heavy metals,many methods of modifying the activated carbons surface have been introduced using chemical/physical treatment(Chen and Wu, 2004)(Mu and Tang, 2002)(Youssef*et al.*, 2004).

Recent studies have demonstrated that heteroatoms present in a carbon structure particularly nitrogen functionality while improving the basicity of the carbonaceous materials improve they heavy metal adsorption capacity(Mahaninia*et al.*, 2015). The main reason is that the nitrogen atom of nitrogen functional groups can bind to a proton or a metal ion following electron pair sharing. In addition, the electronegativity of oxygen is greater than that of nitrogen ; the donation of an electron pair isolated from nitrogen will be easier than that of the oxygen atom in the process of formation of the metal complex(Das et al., 2007). Nitrogen functionalities can be introduced in activated carbon by ammonia treatment or by using nitrogen rich precursors such as urea or melamine. From these viewpoints, surface modification of AC has been studied briskly to form nitrogen group-decorated surfaces.

Urea is an organic compound with a chemical formula $CO\ (NH_2)\ _2$ which contains two functional groups $-NH_2$ and a carbonyl (C = O). This compound has amino functional groups that can readily bind to heavy metals. Activated carbon modification with urea has been demonstrated to improve metal adsorption capacity of the carbons(Kong *et al.*, 2014).

In this study, activated carbon (AC) was produced by activating the virgin carbon of the coconut shell with KOH at high temperature. We attempted to improve the adsorption capacity of this activated carbon to adsorb the cadmium ions by modifying it. This Modified activated carbon (ACU) was prepared by mixing AC with urea and treating it at 450 ° C. The physicochemical properties and adsorption capacities of AC and ACU were then compared and the adsorption mechanism was briefly discussed.

MATERIALS AND METHODS

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.

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.

Surface modification of activated carbon:

To introduce nitrogen groups, the activated carbon AC (3 g) was treated with urea solution (2 g of urea in 10 ml of ethanol) and stirred at room temperature for 5 h. The mixture was then boiled at 120 °C to evaporate the alcohol and dried. Urea impregnated samples were calcined in a turbulent furnace at 450 ° C for 30 min at a rate of 5 $°C.min^{-1}$ under argon flow. After modification, the sample was washed with boilingwater to remove any excess decomposition products from urea. The activated carbon after modification is called ACU.To distinguish the effects of heat treatment (450 ° C) and the effects of incorporation of nitrogen groups on the chemical and textural properties of AC, an untreated activated carbon sample was heated under the same conditions as those used for the urea-impregnated samples.This sample was named AC-450.

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 N_2 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.

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 pHpzc.

Boehm titration:

The acidic and basic surface groups were determined according to the method of Boehm(Boehm, 1966). 0.5 gram ofcarbon 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.

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.

SEM, Elemental and XPS 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)).

Adsorption Experiments:

The adsorption experiments were carried in 50 ml conical flask containing 25 ml of aqueous Cd^{2+} 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 the adsorption temperature (35°C-55°C), adsorbent concentration (1g L^{-1} - 3.5 g L^{-1}) were studied. After equilibrium, the adsorbent was recovered by centrifugation and residual Cd^{2+}ions concentrations in the aqueous solutions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The adsorption capacity of Cd^{2+}ions (e.g., Qe) and the percentage of adsorption were calculated using equations 1 and 2 respectively(Zhang et al., 2014):

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

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

Where C_0 and C_e are the initial and equilibrium concentrations of Cd^{2+} 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 aqueoussamples were stirred at different time (0 - 300 min) and the concentrations of Cd^{2+} ions weremeasured. The amount of adsorption at time *t*, Q_t (mgg^{-1}), was calculated by:

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

Where C_t (mg L^{-1}) is the liquid-phase concentrations of Cd^{2+} ions at time *t*.

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 intraparticular diffusion model were used to understand adsorption kinetics. Table 1presents 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 (R^2_{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
Intraparticle diffusion model $Q_t = k_d . t^{1/2} + C$	Q_t versus t

RESULTS ET DISCUSSION

Textural and chemical characterization:

N_2 adsorption/desorption:

The textural characteristics of (AC)activated carbon and (ACU) modified activated carbon are shown in Table 2. The modification of AC by urea causes a slight decrease in the structural parameters of the activated carbon. Given that the temperature of the heat treatment during modification process was lower than the carbonization temperature, it is possible that the thermodynamically favorable reaction is the incorporation of nitrogen species at the edges of the layers of graphene. This suggests that even if the thermal treatment of the modified carbon after impregnation with urea affects the textural parameters, there is also a deposit of nitrogen species which block the accessibility of the pores by the nitrogen molecules used for thedetermination of textural characteristics(Bagreev*et al.*, 2004).

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

Samples	S_{BET} (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	1044	0.493	0.310	0.183	0.94

Boehm Titration:

The more detailed modifications of surface chemistry are observed from the Boehm titration results (Table 3). After modifications with urea, the number of acidic groups decreased while that of basic groups increased as expected. This increase can be related firstly by the reaction between urea and acidic oxygen groupsleading to the formation of nitrogen-containing functional groupsand then the creation of new basic oxygen sites such as pyrones or chromenes(Seredych*et al.*, 2008).

Table 3: Surface fonctionnal groups of the activated carbons.

Sample	Acidic groups (mmol/g)	Basic groups (mmol/g)	Total groups (mmol/g)	pHpzc
AC	1.5	1.45	2.74	9.65
AC-450	1.2	1.51	2.71	9
ACU	0.9	2.3	3.12	9.82

Zero point of charge:

As is clear from the data in Table 3, the zero pointscharge of AC and ACU were respectively 9.65 and 9.80, greater than 7 (in the basic range).The basic nature of AC can be attributedto the fact that the carbon has been activated with KOH at a very high temperature. About ACU,the reaction of urea with oxygen-containing functional groups leadto the formation of nitrogen functional groups which increase the basic character of the activated carbon(Seredych *et al.*, 2008).

SEM analysis:

The morphology of the different carbons (AC and ACU) was observed by electron microscopy and shown in Figure1. It appears that the modification by urea does not considerably modify the porous structure despite the treatment at 450 °Cnevertheless we notice a slight smoothing of the surface.

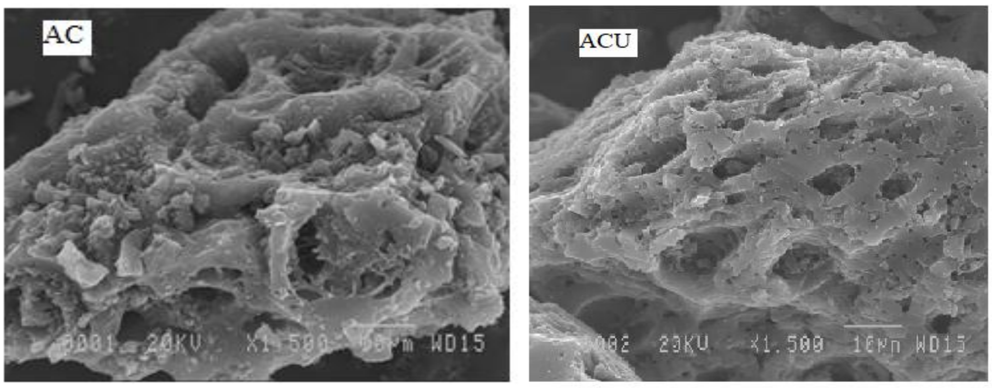

Fig. 1: SEM micrographs of (AC) Activated Carbon and (ACU) Urea-Modified activated carbon at magnification * 500

FTIR analysis:

The modified sample (ACU) has characteristic peaks substantially like those of AC(Figure2). The spectrum emerged at 1024 cm^{-1} is the C-O vibration in alcohols, ethers or acids,the peak at ~ 2900 represented the stretching C-H in the CH_2 group. The spectrum appearing at 1558 cm^{-1} is attributed to C = C vibrations in aromatic cycles(Johari *et al.*, 2016). The species $-NH_2$, -NH vibrate in the range of 3200 -3500 cm^{-1}, the characteristic stretch of their presence is effectively lost in the wide stretch band OH.

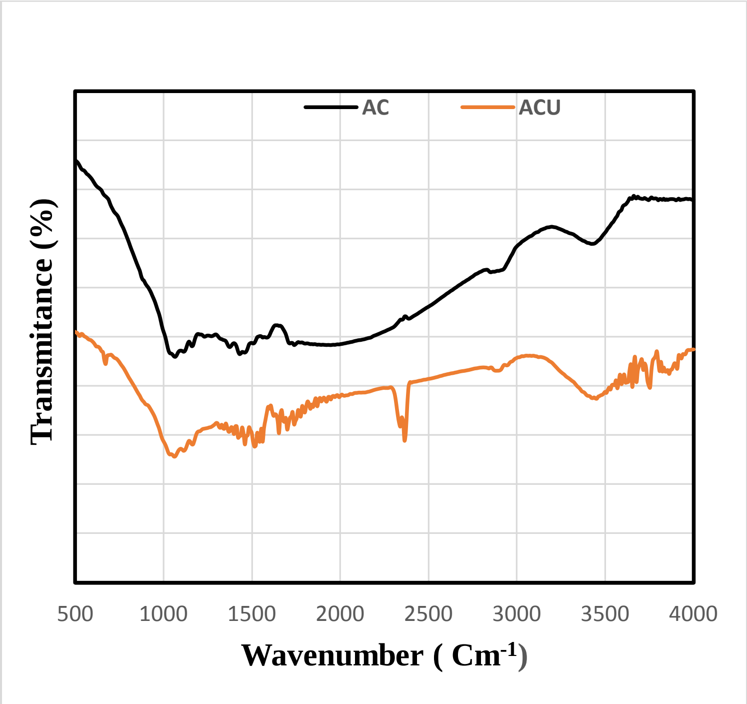

Fig. 2: The FTIR spectra of activated carbon (AC) and Melamine-modified activated carbon (ACU).

Elemental analysis:

The results obtained from the elemental analysis presented in Table 4 shows an increasein the nitrogen content of AC from 0.05 % to 2.12 % after modification withurea to obtain ACU.This confirms that the modification method adopted has allowed the incorporation of nitrogen-containing functional groups on the surface of our activated carbon.

Table 4: Elemental Analysis of Carbon Samples.

Sample	% C	% H	% N	% S
AC	85.87	0.65	0.05	0.03
AC-450	88.45	0.26	0.12	0.00
ACU	88.70	0.2	2.12	0.00

XPS analysis:

XPS analysis was performed to identify the different nitrogen functional groups that were introduced during the modification process. As shown on the XPS survey spectra of ACU (Figure3A). The peaks at 284.16 eV (C1s),532.16 eV (O1s) ,400.16 eV (N1s) and 560.16 eV (K2s) characterize the elements C, O, Nand K on the surface of ACU. The high-resolution spectrum of N 1s (Figure3B) gives us precisely the different nitrogen groups on the surface of ACU. The binding energies about 398.6eV; 400,1 eV and 403.1 eVcorrespond to the existence respectively of Pyridine,amide/amine or nitrile which were the main speciesand protonated pyrrole(Jansen and van Bekkum, 1995). The C1s spectrum (Figure3C) can be deconvoluted into five components. The weak peak at 283.6eV can be assigned to the carbon atoms chemically bonded to the metal atoms(Deniau *et al.*, 2006)probably potassium from potassium hydroxide used for activation of coal, the strong peaks at 284.8 eV and 285.1 eV is respectively attributed to the graphitic carbon and C-O for carbon in phenolic, alcohol and ester groups(Kong et al., 2014)(Kong et al., 2014), and the weakest peak at 288.8 eV corresponds to carbon in carbonyl group (O-C=O) In the case of O1s deconvolution (Figure3D), the binding energy about 531.1 eV, 532.4 eV and 534.1 eV that are assigned to the O=C (at 531.1 eV); carbonyl oxygen atoms in esters, anhydrides, hydroxyls or esters (at 532.4 eV) and the oxygen atom in carboxylic groups (at 534.1 eV)(Gao *et al.*, 2008).

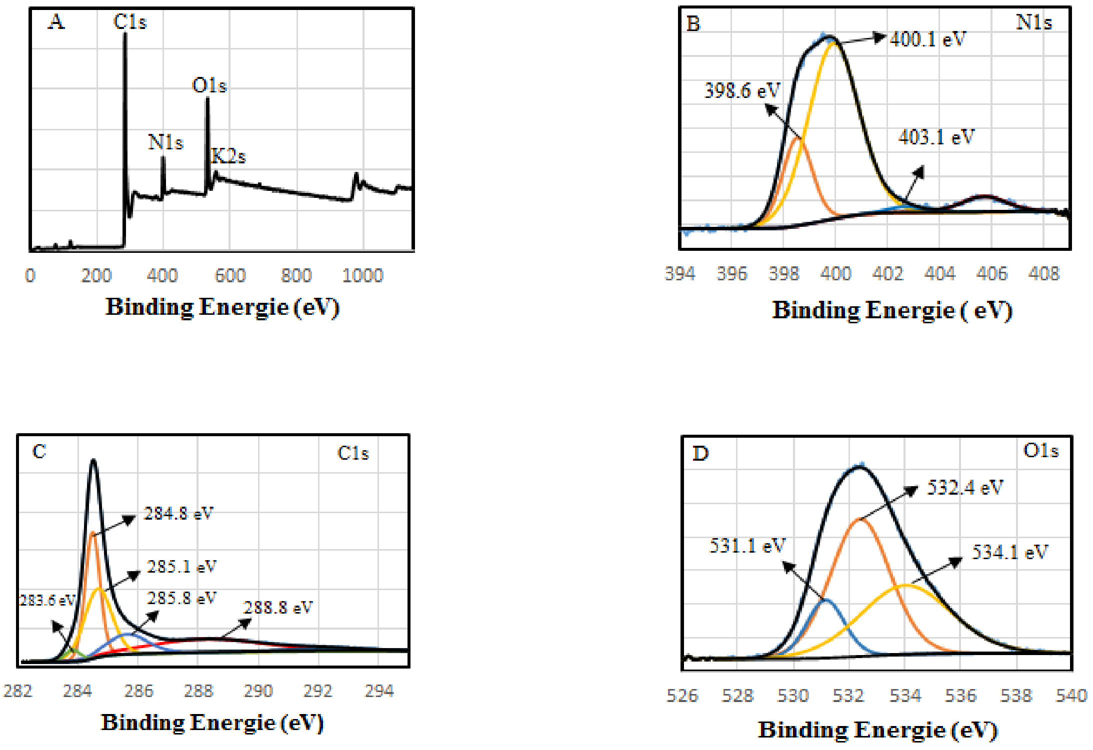

Fig. 3: XPS spectra of modified activated carbon (ACU) :(A) Survey spectra, (B) N1s spectra, (C) C1s spectra, (D) O1s spectra.

Adsorption study:

To evaluate the impact of the modification of activated carbon (AC) with urea on its maximum adsorption capacity, adsorption tests were carried out by varying the initial concentration of Cd^{2+} ions. It appears that when the initial concentration of metal ions was increased from 7.5 to 75 mg L^{-1}, the maximum adsorption capacity was increased from 15.96 mg g^{-1} for AC to 25.42 mg g^{-1} for ACU (Figure 4). It was clear that the maximum adsorption capacity of AC increased considerably, indicating that the nitrogen functional groups incorporated by the urea treatment improved the adsorption capacity with respect to Cd^{2+} ions.

The adsorption data were analyzed with the non-linear form of the Langmuir and Freundlich equations. The corresponding parameters of Freundlich (K_F and n) and Langmuir (Q_m and K_L) as well as the adjusted correlation coefficients are given in Table 4. The adjusted correlation coefficients (R^2_{adj}) of the Langmuir and Freundlich models are respectively 0, 98 and 0.99 for AC and 0.94 and 0.98 for ACU and the respective standard deviations are 0.67and0.5 or AC and 1.90 and 1.22. Based on the highest R^2_{adj} values and the lower SD value, it appears that the adsorption data of Cd^{2+} ions on AC and ACM were better simulated with the Freundlich model leading to the conclusion that the surface of the carbons (AC and ACU) is heterogeneous. Thus, adsorption has occurred on the surface with a diversity of energy(Kong et *al.*, 2014). However, the maximum adsorption capacities of AC and ACU given by the Langmuir model are closed to the values obtained experimentally. The values of the separation factors R_L were all between 0 and 1 and the Freundlich Coefficients "n" which are respectively 2.55 and 3.83 for AC and ACU satisfy the condition of 1 <n <10 for the favorable adsorption.

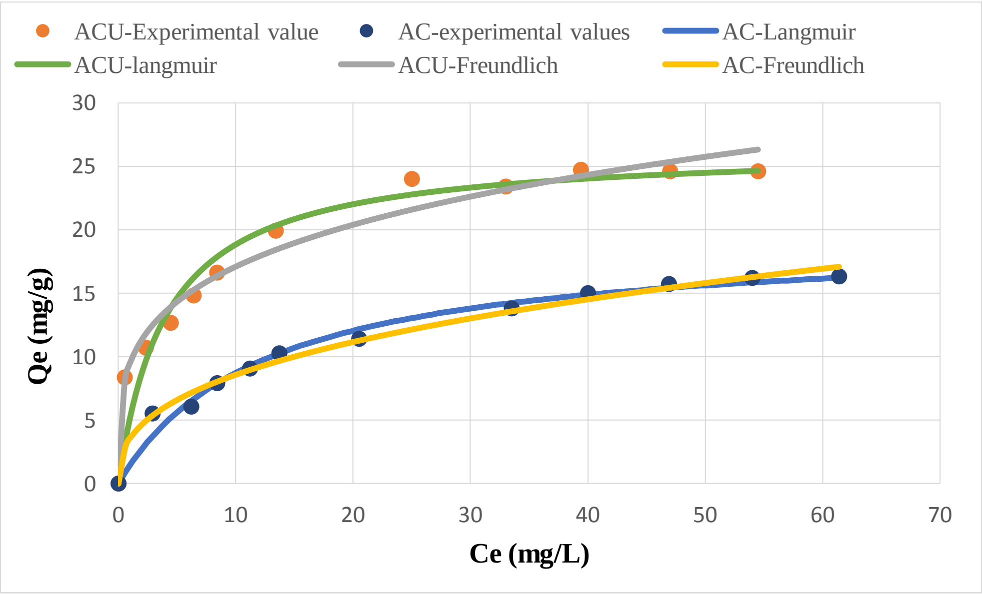

Fig. 4: Cd^{2+} adsorption isotherms onto AC and ACM (T = 25.0 °C; t = 24.0 h; pH = 5; adsorbents concentration = 1g L^{-1}).

Table 5: Langmuir and Freundlich isotherm constants.

Model	Langmuir				Freundlich			
parameters	Q_{SAT}	K_L	R^2_{adj}	SD	K_F	n	R^2_{adj}	SD
AC	19.46	0.08	0.98	0.67	3.58	2.63	0.99	0.5
ACU	26.58	0.25	0.94	1.90	9.52	3.93	0.98	1.22

Effect of pH:

The most important parameter governing the sorption of metal ions on different adsorbents is the pH of the adsorbate solutions. This is partly because the hydrogen ions themselves are a strong competitive adsorbate and partly because the pH of the solution influences the chemical speciation of the metal ions. The main form of Cadmium present in the pH range (between 2 and 8) studied was Cd^{2+}ions(Ahn *et al.*, 2009).The effect of pH on the adsorption of cadmium ions by AC and ACU is illustrated in Figure 5. As shown in this figure, at low pH (less than 4), the adsorption capacity is low for the two carbons. The low metal uptake can be attributed to the competition between Cd^{2+} and H^{+} ions. At the same time, protonation of the carbon surface causes electrostatic repulsion between metal ions and positively charged surface groups. The higher adsorption capacity of AC compared to ACU at low pH can be explained by the fact that AC had more acidic functional groups which constitute favorable sites for the exchange of H^{+}ions with Cd^{2+} ions on this pH range.The competition between H^{+} and Cd^{2+} decreases with increasing pH (from pH = 4 to pH = 6) due to the reduction of H^+ ion concentration in solution thus causing an increase in the adsorption of metal ions on the surface. Maximum adsorption of Cd^{2+}ions on both carbons occurred at pH 5.0. At pH values above 6, precipitation of the metal occurred, and the adsorption capacity decreased with the accumulation of metal ions(Torab-Mostaedi*et al*., 2010). Therefore, an optimal pH of 5.0 was chosen for other experiments.

Possible adsorption mechanisms between Cd^{2+} and carbons are ion exchange, covalent bond formation and electrostatic interaction with the surface. the maximum adsorption capacity of the two samples was reached at pH = 5, lower than the pHpzc of AC and ACM. The study of the pHpzc of AC and ACU showed us that these carbons have positively charged surfaces for a pH = 5 between 2 and 8, thus excluding an electrostatic interaction between the Cd^{2+} ions and the positively charged surface. Therefore

We suggest that the Cd^{2+} ions adsorption phenomenon on AC and ACU is governed mainly by ion exchange mechanisms between Cd^{2+} ions and surface acid functions and the mechanism of covalent bond formation between basic functional groups (oxygenated and nitrogenous) electron donors and Cd^{2+}ions electron acceptor.

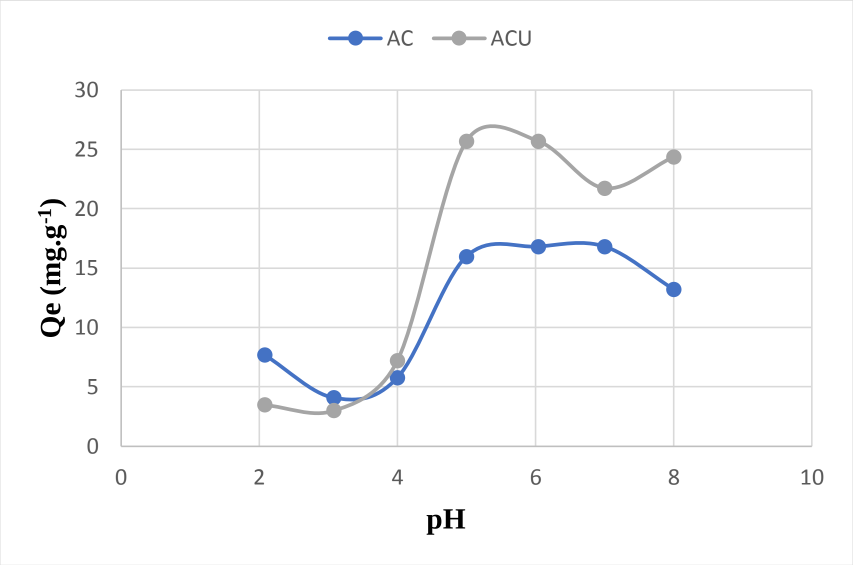

Fig. 5: Effect of initial pH on Cd^{2+} ions adsorption on AC and ACU (C_0=60.0mgL^{-1}; dosage 1.0 g L^{-1}; T = 25.0 ◦C; t = 24.0 h).

Effect of temperature:

To evaluate the effect of temperature on the adsorption of Cd^{2+} ions by AC and ACU. The experiments were carried out at a temperature ranging from 35 to 55 ± 1 ° C, while the initial concentrations of metals and pH were set at 60 mg. L^{-1} and 5, respectively. we note that the effect of temperature on the removal efficiency of Cd^{2+} ions was significant (Figure 6). It has been observed that the efficiency of removal of Cd^{2+} by AC and ACU increases with increasing temperature from 35 to 55 ± 1 ° C respectively from 36.66% to 50% for AC and 62% to 75%. % for ACU. The process is therefore endothermic. This trend could be attributed to the increase in kinetic energy of metal ions which increases the frequency of collisions between sorbent particles and metal particles. In addition, this increase in energy induced by the rise in temperature could break the repulsive forces that prevent adsorption.

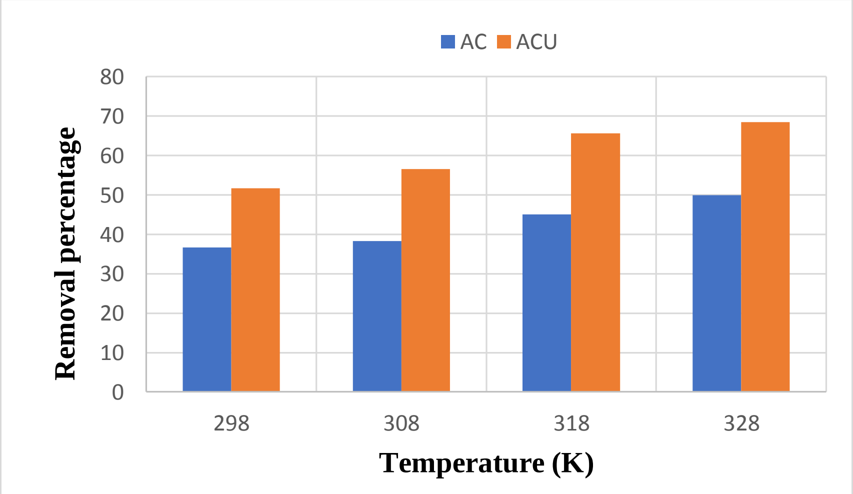

Fig. 6: Effect of Temperature on Cd^{2+} ions adsorption onto AC and ACU (C_0 = 60.0 mg L^{-1}; Adsorbents concentration = 1 g L^{-1}, t = 24 h, pH = 5)

Adsorption kinetic:

The study of sorption kinetics in wastewater treatment is very essential since it provides valuable insights into the adsorbent performances and the underlying sorption mechanism. It is an important parameter for the design of an appropriate adsorption process. The pseudo-first-order, pseudo-second-order and the intraparticle diffusion models were used to study the adsorption kinetic.The adsorption tests were carried out in a time interval between 10 min and 300 minwhile maintaining the other parametersconstant. As shown in Figure7, Cd^{2+}ionsadsorption on AC andACU reached maximum in the first 40 minutes, this is attributed to the vacancy and the availability of the adsorption sites. The increase in contact time beyond 40 min has no significant effect on adsorption efficiency.To investigate the adsorption mechanism and potential rate control steps,pseudo-firstorder kinetics,pseudo-second order kinetics(Figure 7) and intraparticlediffusion kineticsmodelswere usedto test experimental data. The kinetic parameters values, the adjusted correlation coefficients and the standard deviation for Cd^{2+} ions adsorption on AC and ACU were obtained using non-linear regression (Table 6). By comparing the values of the adjusted correlation coefficients and the standard deviationsof the two kinetic models used, we find that the pseudo-second-order model has the highest adjusted correlation coefficient and the lowest standard deviation in the two cases of Cd^{2+} adsorption on AC and ACU. Adsorption systems are therefore well described by the pseudo-second-order kinetic model, which has been developed assuming that the mechanism controlling adsorption is chemisorption(Boudrahem*et al*., 2011).

The Weber-Morris equation was used to describe the intraparticular scattering (Figure8). If the regression of q_t vs $t^{1/2}$ is linear and passes through the origin, intraparticular diffusion is the only speed limiting step(Mittal e*tal*., 2007).However, two stages of linearity are observed for the adsorption of Cd^{2+} to AC and ACU, indicating that two steps occur when adsorbing Cd^{2+}ions onto AC and ACU.The first step completed in a first step is the instantaneous adsorption which takes place on the external surface and the second part describes the step of progressive adsorption where the step which limits the rate of adsorption is the intraparticular diffusion. The linear part of the first step does not cross the origin, indicating that intraparticular diffusion is not the only mechanism controlling the adsorption process. Instead, other mechanisms such as covalent bond formation or ion exchange may partially control Cd^{2+}ions adsorption rate(Foo and Hameed, 2012).

Effect of adsorbent dosage:

Cd^{2+} ions removal was studied by varying the adsorbent concentration. It was observed that Cd^{2+} ions removal percentage increased from 22.16% to 79.95% for AC and from 39% to 99.5% for ACU when the adsorbent dose increased from 1 g L^{-1} to 3.5 g L^{-1}. The results therefore show that the percentage of heavy metals removal increased rapidly with the increase of the adsorbent dose in the solution (Figure 9). Indeed, the increase in the adsorbent dose generates more adsorption sites which promotes easier penetration and access of metal ions to the sorption sites due to the decrease in competition between Cd^{2+} and H^+ for adsorption sites.

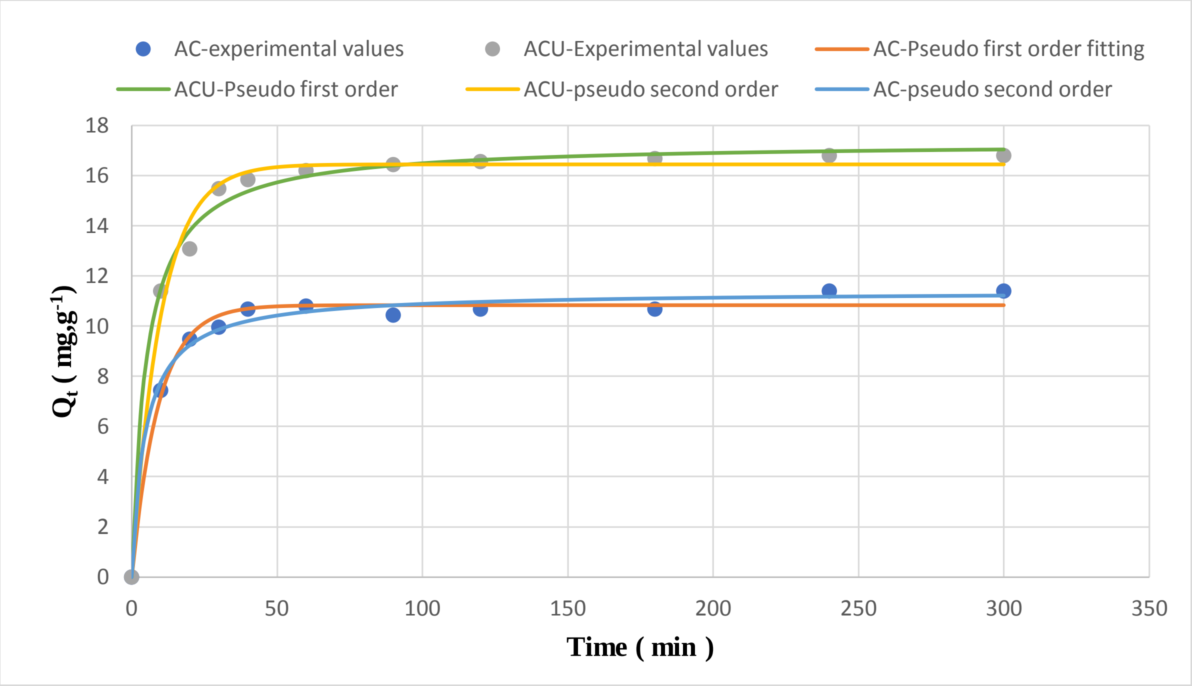

Fig. 7: Cd^{2+} ions adsorption kinetics onto AC and ACU (C_0 = 60.0 mg L^{-1}; adsorbents concentration = 1 g L^{-1}; T = 25.0 °C; pH=5).

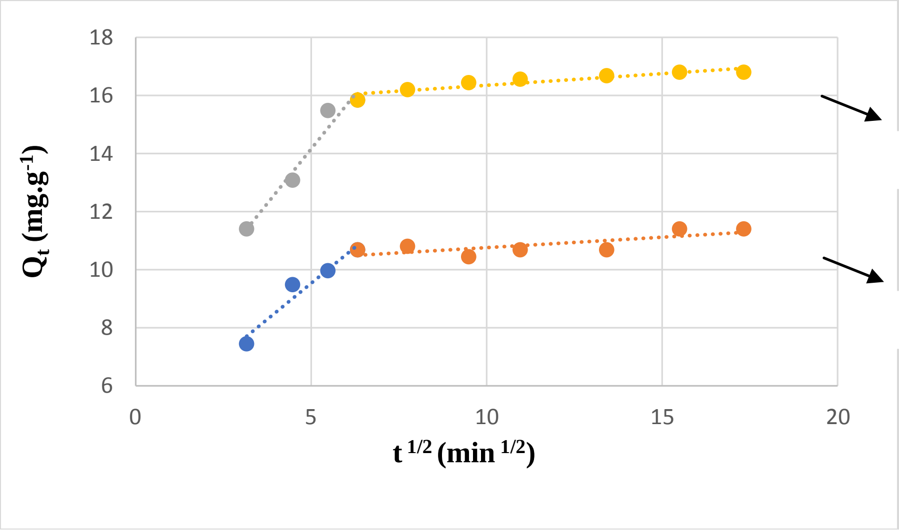

Fig. 8: Intraparticle diffusion plots for Cd^{2+} ions adsorption on AC and ACU.

Table 6: Pseudo-first-order, Pseudo-second-order model parameters.

Model		Pseudo-first order				Pseudo-second order			
parameters	Qe(exp)	Qe(cal)	k_1	R^2_{adj}	SD	Qe(cal)	k_2	R^2_{adj}	SD
AC	11.40	10.83	0.1	0.98	0.35	12.39	0.018	0.99	0.29
ACU	16.8	17.32	0.01	0.98	0.55	16.44	0.1	0.99	0.39

Table 7: Intraparticle kinetic model parameters.

Model	Intraparticle diffusion					
parameters	k_{D1}	k_{D2}	R_1^2	R_2^2	C_1	C_2
AC	0.99	0.07	0.94	0.58	4.56	10.4
ACU	1.5	0.08	0.95	0.86	6.67	15.54

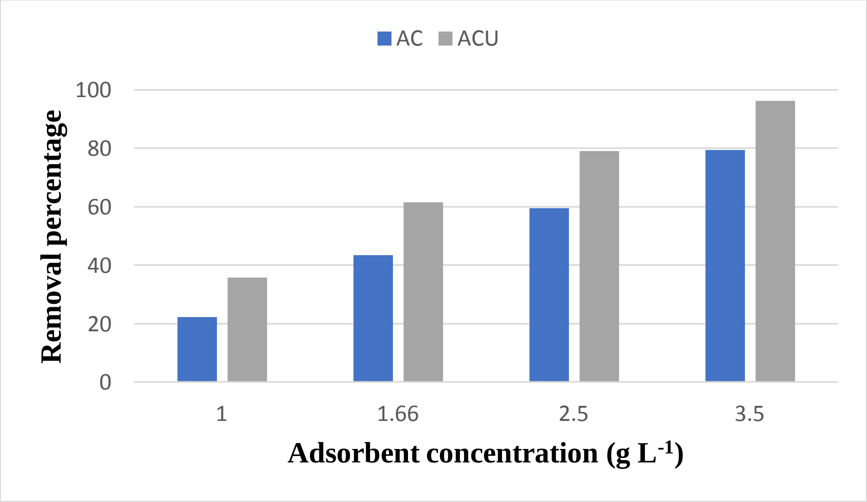

Fig. 9: Effect of adsorbents dosage on Cd^{2+}ions adsorption on AC and ACU (C_0=60.0mgL^{-1}; T = 25.0 ◦C; t = 8.0 h, pH = 5).

Conclusion:

In this study, activated carbon (AC) was synthesized from coconut shells collected in Ivory Coast. ACU was obtained by modification of AC with urea. The physical properties determined by N_2 adsorption / desorption, SEM analysis and chemical properties such as infrared spectroscopy, Boehm titration and elemental analysis of AC and ACU show that nitrogen functional groups have been loaded onto the AC surface.Comparative study of Cd^{2+}ions adsorption on AC and ACU shows that the maximum adsorption capacity of Cd^{2+} ions increased from 15.94 mg g^{-1} to 25.42 mg g^{-1} after treatment of AC with urea. The adsorption data were in good agreement with the Freundlich model suggesting that adsorption occurred on heterogeneous surfaces. The optimal adsorption pH was 5 below the pHpzc of both adsorbents. The main mechanisms proposed were ion exchange and covalent bonds formation. From a kinetic study, it is observed that the adsorption corresponds well to the kinetic model of pseudo-second order reflecting a chemical adsorption dominated by formation of covalent bond between the adsorbate and the functional groups of AC and ACUsurfaces.

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