Australian Journal of Basic and Applied Sciences
2018 Sept; 12(9): pages 10-19
DOI: 10.22587/ajbas.2018.12.9.2
Research Article
AENSI Publications
Journal home page: www.ajbasweb.com

# Enhancement of $Cd^{2+}$ Ionsremoval Bymelamine-Modified Activated Carbon Made From Coconut Shells

[1,2]Vianet Kouakou Bossombra, [2]Tchirioua Ekou, [2]Lynda Ekou, [1]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, Laval University, Department of Chemical Engineering, Québec, G1V 0A6, Canada
E-mail: tchirouaekou@yahoo.fr

**Received date:** 12 June 2018, **Accepted date:** 4 September 2018, **Online date:** 13 September 2018

## Abstract

Anactivated carbon (AC) prepared from the original coconut shell collected in Ivory Coast were modified with melamine (ACM) for the efficient removal of Cd2+ ions in aqueous solution. The resulting AC and ACM were characterized by different techniques including N2 adsorption/desorption isotherms, elemental analysis, XPS analysis, Boehm titration, spectroscopic methods (SEM, FTIR) and pH pzc determination. The adsorption capacities of AC and ACM with respect to Cd2+ ions were evaluated by batch sorption experiments and compared. The adsorption capacity was strongly influenced by the solution pH and the optimum pH was ~5. The adsorption capacity ofCd2+ ions for ACM is 75% higher than that for the no modified activated carbon(AC), due to the presence of nitrogen functional groups in the surface of the ACM material. adsorption isotherms and kinetic models were used to describe the adsorption process. The equilibrium data for AC and ACM fit well with the Freundlich model and the adsorption equilibrium can be reached after 4 h. The adsorption kinetics data were found to be better described by the pseudo-second-order model. The main mechanisms for the Cd2+ adsorption onto the activated carbons were proposed to be cation exchange, and coordination bond formation with basic functional groups of surfaces containing nitrogen or oxygen.

**Key words:** Activated Carbon, Nitrogen Functional Group, Melamine, Adsorption, Cd2+ Ions Removal

## INTRODUCTION

Current industrial development has led to an increase in dangerous substances particularly heavy metals in the environment. Especially cadmium comes mainly from anthropogenic sources, namely metal plating, manufacture and use of nickel-cadmium batteries, phosphate fertilizers, pigments, mining etc. (Kadirvelu and Namasivayam, 2003). Several studies have shown the toxicity of heavy metals to humans even at low concentrations(Abdulkarim and Abu Al-Rub, 2009). For example, diseases such as itai-itai, kidney damage, emphysema, hypertension and testicular atrophy have been reported to the consumption of water containing an excess of cadmium(González-Muñoz et *al.*, 2006). However, eliminating toxic heavy metals from the environment remains a challenge. Importantly, a heavy metal removal process must be simple, efficient and inexpensive. So far, several processes have been proposed to remove heavy metals from wastewater, including chemical processes(González-Muñoz *et al.*, 2006), membrane filtration processes(Kang and Cao, 2012), electrochemical processes(Liu, Yan*et al.*, 2013)and adsorption processes(Mohandas*et al.*, 2008).However, most of these methods have limitations such as high investment and operating costs, tolerance to pH change, incomplete metal removal and secondary waste(Mohandas *et al.*, 2008).Adsorption is considered a promising technique in terms of material reuse, low operating cost, improved selectivity for certain metals of interest and reduced operating time (Giri*et al.*, 2012). Activated carbons have been widely used as adsorbents, because of their developed porous structures, large internal surface area and their ability to be used for the adsorption of a wide range of species from gas or of liquid phases(Jia*et al.*, 2002). Importantly, it can be produced from cheaper and readily available resources like coke, peat, wood, sawdust, coconut shell(Nadeem*et al.*, 2009). The different mechanisms for the removal of heavy metals by activated carbon are electrostatic attraction between metallic species and activated carbon surface or chemical interaction between metal ions and various surface functional groups(Ahn*et al.*, 2009). Currently various modification methods have been introduced to improve the adsorption capacity of activated carbon. Recent studies have shown that the introduction of nitrogen into a carbon structure while increasing the basicity of carbonaceous materials improves the ability of heavy metals to attach to the activated carbon surface(Mahaninia*et al.*, 2015). This can be explained by the fact that nitrogen can easily share the pair of electrons to bind metal ions based on Lewis acid-base theory (Das*et al.*, 2007). Thus, the surface modification of AC by nitrogen introduction was studied (Tanada*et al.*, 1999). Melamine (2,4,6-triamino-1,3,5-triazine) is often used as a modification agent for nitrogen enrichment due to its high nitrogen content(Grondein and Bélanger, 2012).

The purpose of this study is to improve the adsorption capacity of an activated carbon (AC) by bringing nitrogen functional groups to its surface. The molecule used as a nitrogen source is melamine. The activated carbon obtained after modification (namely ACM) has been studied by multi-characterization techniques. The adsorption performance of ACM for the removal of $Cd^{2+}$ions in the liquid phase was studied and compared with that of the starting activated carbon (AC).The mechanism of$Cd^{2+}$ ions adsorption on AC and ACM was also discussed.

## MATERIALS AND METHODS

*Materials:*

The coconut shells were collectedin 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 melamine were purchased from Sigma Aldrich. The standard cadmium Cd (II) stock solution of 1 $gL^{-1}$was obtained by dissolving an 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 3/1/1.5 (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 and heated at 5 $°C.min^{-1}$ to 850 °C in air 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. During the washing step, the activated carbon (AC) 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 functional groups, the activated carbon AC (3 g) was treated with a melamine suspension (2 g of melamine 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. Melamine impregnated sample was calcined in a turbulent furnace at 450 ° C for 30 min at a rate of 5 °C / min under argon flow. After heat treatment, the sample was washed with boiling water to remove any excess decomposition products from the melamine and then dried. Activated carbon after modification is called ACM. 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 activated carbon sample without melamine was heated under the same conditions as those used for the sample treated with melamine. This sample was named AC-450.

*Textural properties:*

The textural properties of all samples were determined by nitrogen adsorption experiments at liquid nitrogen temperature (77 K) with a Quantachrom Autosorb 1. First, the samples were outgassed at 150°C for 6h under 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 of 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 ofa suspension of carbon sample in distilled water for 24 h. The initial pH of the suspensionwas 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 g 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, 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 followed by compression between the two stainless steel cylinders to form a thin transparent solid film. The spectrometer collected spectra in the range of 400–4000 $cm^{-1}$.

*SEM, Elemental and XPS analysis:*

Surface morphologies of these biosorbentswere observed by scanning electron microscopy (SEM) (JSM-840 scanning microscope).The elemental composition of the activated carbons was quantitatively determined by (EA 110, CHNS:Fisons). 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 carriedin 50 ml conical flask containing 25 ml of aqueous $Cd^{2+}$ solution. The adsorbents dose was first fixed at $1gL^{-1}$, 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 ($7.5\text{-}75mgL^{-1}$),initial pH (2-8) as well as the adsorption temperature (35°C-55°C), adsorbent concentration ($1gL^{-1}$ - 3.5 $gL^{-1}$)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 2respectively(Zhang*et al*, 2014):

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

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

Where $C_0$ 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 aqueous samples were stirred at different time (0 - 300 min)and the concentrations of $Cd^{2+}$ ions were measured. 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 $C_t$($mgL^{-1}$) 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<br>$Q_e = \frac{Q_m\, b\, C_e}{1 + b\, C_e}$ | $Q_e$ versus $C_e$ |
| Freundlich model<br>$Q_e = K_F\, C_e^{1/n}$ | $Q_e$ versus $C_e$ |
| Pseudo-first order model<br>$Q_t = Q_e\, [1 - \exp(-k_1 . t)]$ | $Q_t$ versus t |
| Pseudo-second order model<br>$Q_t = \frac{Q_e^2 k_2\, t}{k_2 (Q_e).t + 1}$ | $Q_t$ versus t |
| Intraparticle diffusion model<br>$Q_t = k_d . t^{1/2} + C$ | $Q_t$ versus t |

## RESULTS AND DISCUSSION

*Textural properties:*

The textural properties of activated carbon AC and melamine-modified activated carbon ACM are shown in Table 2. The modification of AC by melamine to obtain ACM causes a reduction in surface area, pore volume and average pore diameter of activated carbon. This could be due to pore obstruction by the decomposition products of melamine during heat treatment at 450 ° C for 30 min. To confirm this, the activated carbon AC without melamine loading was also treated under the same heat treatment conditions (called AC-450), no change in the texture properties was found.

The morphology of different steps of treatment to obtained ACM (precursor coal, activated carbon, modified activated carbon) was observed by scanning electron microscopy (SEM) and shown in Figure 1. It appears that the coal from the coconut shell had a rudimentary porosity that grew well in a random way after the high temperature KOH treatment step. Its modification with melamine did not fundamentally change the morphology after treatment at 450 ° C, whereas a slightly smoother surface was found.

**Table 2:** Specific surface area and pore volume of the carbons after different treatments.

| Samples | $S_{BET}$ ($m^2/g$) | $V_t$ ($Cm^3/g$) | $V_{mic}$ ($Cm^3/g$) | $V_{mes}$ ($Cm^3/g$) | $D_p$ (nm) |
|---|---|---|---|---|---|
| AC | 1074 | 0.626 | 0.316 | 0.310 | 1.16 |
| AC -450 | 1071 | 0.593 | 0.313 | 0.280 | 1.10 |
| ACM | 1000.4 | 0.456 | 0.306 | 0.150 | 0.91 |

AC: Activated carbon. AC-450: Activated carbontreated at 450 °C for 2h without melamine. ACM: Activated carbon impregnated with melamine and treated at 450°C for 2h.

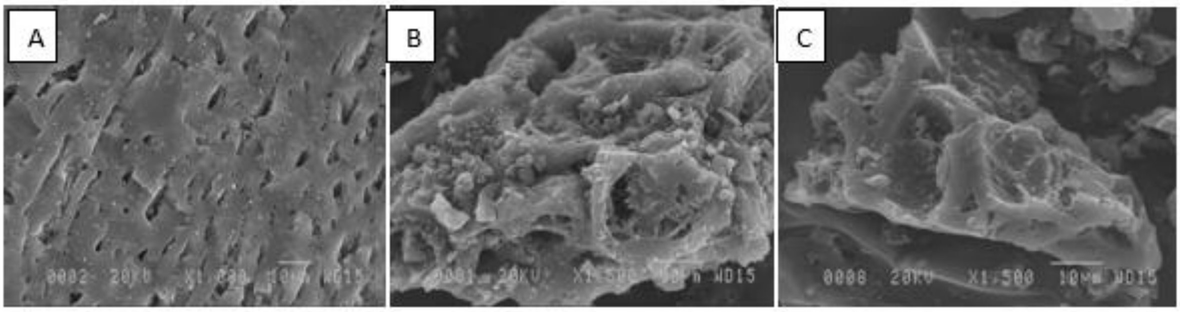

**Fig. 1:** SEM micrographs of Coal (A), Activated Carbon (B), Melamine-modified activated carbon (C) at magnification * 500.

*Surface chemistry of the activated carbons:*
*Bohem titration:*

Boehm titration was applied to determine AC's and ACM 's acidic and basic functional groups concentration (Table 3). Here we report only basic and acid groups concentration without distinction of carboxylic, lactonic or phenolic because certain nitrogenous groups can behave as base, weak acid (phenols) or strong acid (carboxylic acids) in the aqueous solution(Adib*et al.*, 2000). As shown in Table 3, after modification of AC with melamine leading to ACM, the surface chemistry of the ACM obtained was changed; the amount of basic sites increases as the amount of acidic groups decreases on ACM surface. However, the surface chemistry of the AC-450 sample was not significantly affected. Therefore, the change observed for ACM can be explained by the reaction between melamine and oxygenated acid groups such as carboxylic and phenolic groups during the calcination process at 450 ° C, resulting in the reduction of acid groups and the formation of nitrogen functional groups which are naturally basic.

*pH of zero-point charge:*

The pH of zero-point charge(denoted as pHpzc) determination of AC and ACM was 9.65 and 9.8, respectively. As seen in Table 3, the pH pzc of ACM is slightly higher than that of AC. However, both the materials have pHpzc greater than 7 (e.g., in the basic range). Thisis attributed to the coal activated with KOH at very high temperature (~850 °C) leading to a basic activated carbon (AC) and the introduction of nitrogen into the structure of this activated carbon by thermal treatment with melamine.

**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 | 2.95 | 9.65 |
| AC-450 | 1.2 | 1.51 | 2.71 | 9 |
| ACM | 0.45 | 2.41 | 2.86 | 9.8 |

*Fourier transform infrared spectroscopy:*

The surface nitrogen functional groups of the activated carbons were also investigated using FTIR analysis (Figure 2**)**. As seen in Figure 2, the AC and ACM samples exhibit similar FTIR peaks. In the both AC and ACM samples, a peakat~1465 $cm^{-1}$ corresponds to the aromatic ring stretching of C=C, and the peak at approximately 2900 $cm^{-1}$is assigned to the C-H stretching vibration(Cazetta *et al.*, 2011). The peak at 1058 $cm^{-1}$observed on the bothsamples can be attributed to the symmetrical angular deformation of the ethers.The broadbandat around 3500 $cm^{-1}$ is characteristic of N-H or O-H (from carboxyl, phenol or alcohol), this band is more intense for ACM(before melamine treatment) compared to that of AC. This more intense FTIR band of the modified activated carbon (ACM) can be attributed to the presence of-NH species which vibrate in the range of 3200- 3500 $cm^{-1}$.

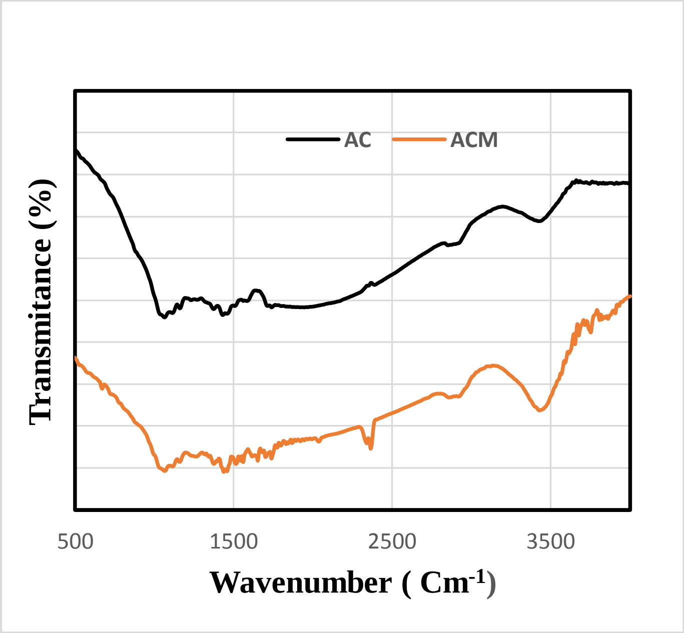

**Fig. 2:** The FTIR spectra of activated carbon (AC) and Melamine-modified activated carbon (ACM).

*Elemental analysis:*

The elemental analysesof AC, AC-450and ACM are summarizedin **Table 4**.The nitrogen content of the carbon increased from 0.05to 4.22 mole % after treatment of AC melamine to obtain ACM.This indicates that more nitrogen functional groups were incorporated into the carbon after the modification with melamine. The high amount of nitrogen (4.22 mole %) in ACM led to the increase of nitrogen functional groups as the adsorption site in ACM.

**Table 4:** Elemental Analysis of different activated 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 |
| ACM | 86.68 | 1.50 | 4.22 | 0.00 |

*XPS analysis:*

XPS analysis was performed to identify the different nitrogen functional groups that were formedafter the modification process. Figure3A shows the XPS survey spectrum of ACM. The peaks at 285.0 eV (C1s), 400 eV (N1s) and 531 eV (O1s) are attributed to C, O and N on the surface of ACM. The elemental composition determined by XPS analysis was 6.45, 2.08, 90.58 mole%, for nitrogen, oxygenand carbon respectively. The C1s XPS spectrum can be deconvoluted into five components(Figure3B). The weak peak at 283.5 eV can be assigned to the carbon atoms chemically bonded to the metal atoms(Deniau*et al.*, 2006), probably potassium from potassium hydroxide used for the activation of coal. The strong peaks at 284.6 eV and 284.7 eV are attributed to the graphitic (sp2 hybridized ) carbon. The peak at 285.3 eV is assigned to the carbons in the C–N and C–O bonds(Deniau *et al.*, 2006), and the very weak peak at 287 eV corresponds to carbon in the C=O bonds(Guo*et al.*, 2017). In the case of O1s deconvolution (Figure3C), the binding energiesat ~531.4 eV, 532.4 eV and 535.5 eV represent oxygen in C=O groups, C-OH/C-O-C groups and chemisorbed oxygen (carboxylic groups), respectively(Seredych*et al.*, 2008). The high-resolution spectrum of N 1s (Figure3D) shows the different nitrogen groups on the surface of ACM. As showninFigure3D,the N 1s spectrum exhibits three peaks. The binding energy peaks at~398.5 eV, 400 eV and 403.4eV correspond to the nitrogen of Pyridinic, pyrrolic/pyridonic and N-oxide groups, respectively(Guan *et al.*, 2015). The possible nitrogen species in the modified- activated carbon (ACM)is proposed inFigure4.

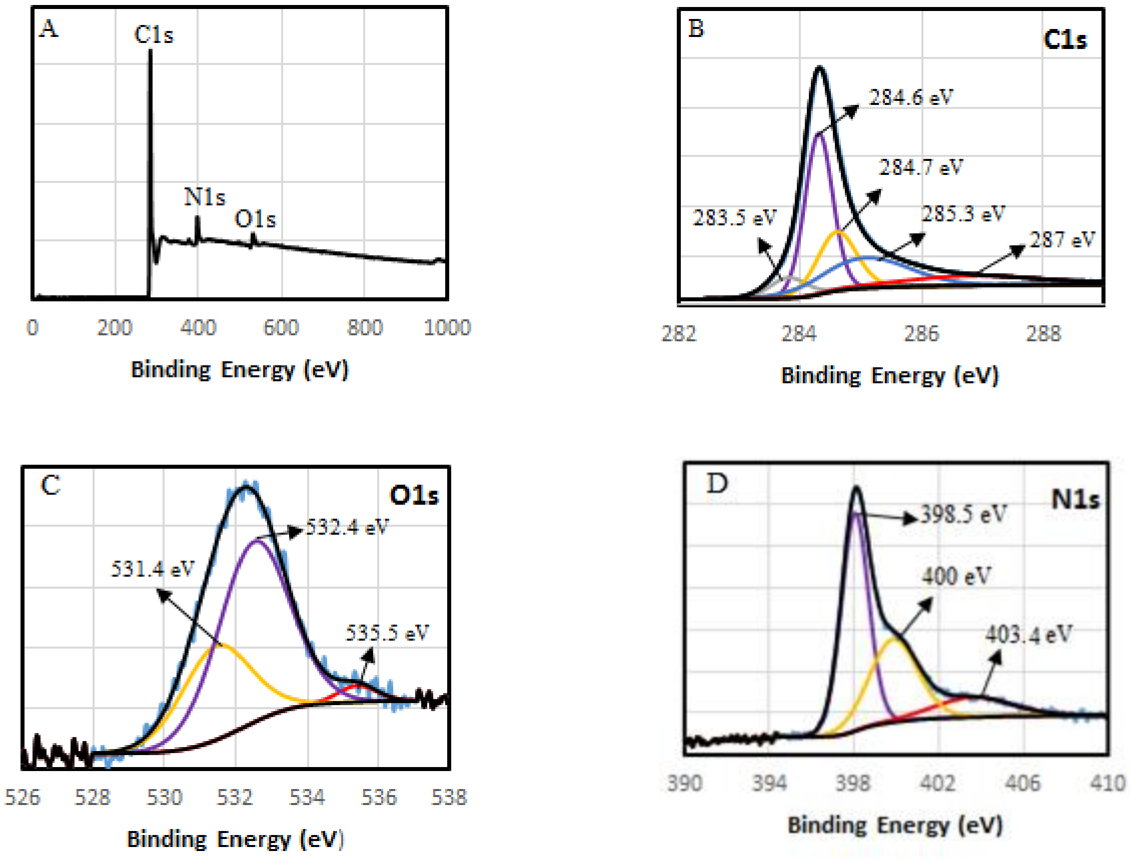

**Fig. 3:** XPS spectra of modified activated carbon (ACM) :(A) Survey XPS spectrum, (B) C1s and (C) O1s, (D) N1s spectra.

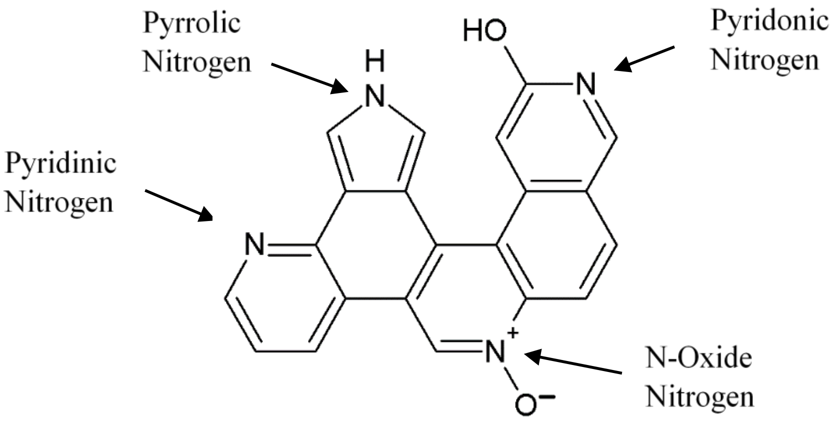

**Fig. 4:** The possible nitrogen species in the Melamine-modified activated carbon (ACM).

*Batch adsorption experiments:*
*Adsorption Isotherms:*

To study the adsorption capacity of AC and ACM as a function of $Cd^{2+}$ ions initial concentration, the experiments were carried out by varying $Cd^{2+}$ions initial concentration in aqueous solution from 7.5 to75 $mgL^{-1}$. The results revealed that the amount of adsorbed $Cd^{2+}$ ions per gram of AC and ACM increased with increasing initial $Cd^{2+}$ ions concentration (Figure 5).When the initial concentration of $Cd^{2+}$ ions increased from 7,5 to 75 mg $L^{-1}$, the adsorption capacity of AC increased from 2.9 mg $g^{-1}$ to 15.72 mg $g^{-1}$, while ACM's adsorption capacity increased from 9 mg $g^{-1}$ to 27.62 mg $g^{-1}$.Note that regardless of the initial $Cd^{2+}$ ion concentration, the adsorption capacity is much higher than that of AC. this indicates that the adsorption capacity of our resulting coconut activated carbon was improved by about 75% after the melamine treatment.

$Cd^{2+}$ ions adsorption isotherms on the carbons studied at 298 K show that $Cd^{2+}$ ions elimination by AC and ACM increases with $Cd^{2+}$ions concentration in solution and finally reaches an equilibrium value(Figure 5).The adsorption data were then analyzed with the nonlinear form of the Langmuirand Freundliche quations(Figure 5). The corresponding Freundlich ($K_F$ and n) and Langmuir ($Q_m$ and b) parameters, as well as the adjusted correlation coefficients ( $R^2_{Adj}$) and standard deviation (SD) are given in Table 5. Based on the highest $R^2_{adj}$ values and the lowest SD value, it appears that the Freundlich model was more suitable with the experimental data. This result suggests a heterogeneous distribution of active sites since the Freundlich equation assumes that the surface is heterogeneous. Therefore, the adsorption process could be carried out between the $Cd^{2+}$ ions and the various surface functional groups. Moreover, the Freundlich coefficients ‘n’ which are respectively 2.63 and 5.70 for AC and ACM satisfies the condition of $1 < n < 10$ for the favorable adsorption. The Langmuir parameter " b " for the adsorption of $Cd^{2+}$ ions on AC and ACM are 0.08 and 0.51 respectively. The estimated values " b " were used to calculate the dimensionless separation factor $R_L$, defined as $R_L = 1 / (1 + bC_0)$.The $R_L$ values are all between 0 and 1, indicating favorable adsorption $Cd^{2+}$ ions on AC and ACM. While the Freundlich model does not describe the saturation behavior of sorbents, the Langmuir constant $Q_m$, represents the equilibrium monolayer saturation or the monolayer adsorption capacity of the adsorbent. The monolayer adsorption capacity $Q_m$ predicted by Langmuir model were 19.46 $mgg^{-1}$ for AC and27.69 mg $g^{-1}$ for ACM.

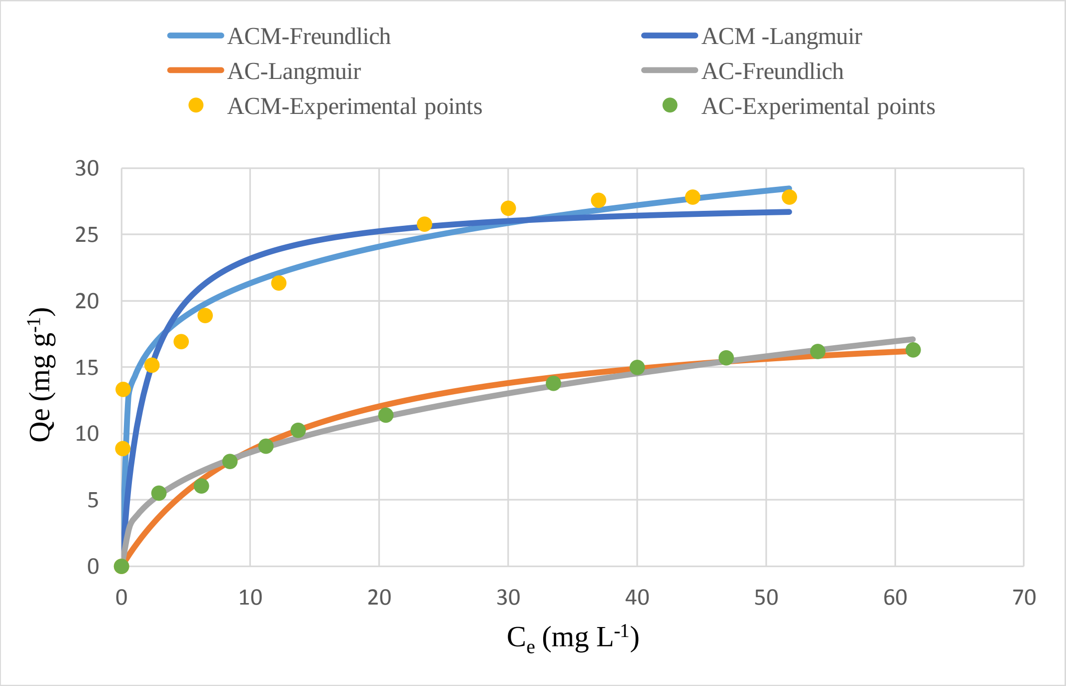

**Fig. 5**: $Cd^{2+}$ adsorption isotherms onto AC and ACM (T = 25.0 °C; t = 24.0 h; pH = 5; adsorbents concentration = 1g $L^{-1}$).

**Table 5:** Langmuir and Freundlich isotherm parameters.

| Model | Langmuir | | | | Freundlich | | | |
|---|---|---|---|---|---|---|---|---|
| parameters | $Q_m$ | b | $R^2_{adj}$ | 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 |
| ACM | 27.69 | 0.51 | 0.72 | 4.64 | 14.24 | 5.70 | 0.97 | 1.45 |

*Effect of pH:*

The pH of solution is one of the most important parameters that affects the metal ions adsorption. In this study, the $Cd^{2+}$ adsorption on AC and ACM was found to be dependent on pH (Figure6). At low pH (< 3.08), the adsorption capacity was low(7.48 $mgg^{-1}$ for AC and 5.92 $mgg^{-1}$ for ACM).As pH increased from 3.08 to 7, the adsorption increased and reached its maximum at pH 5-7 (Figure 6): 15.72 $mgg^{-1}$ and 27.6 $mgg^{-1}$for AC and ACM, respectively. Above pH = 7, $Cd^{2+}$ ions adsorption decreased. To understand the effect of pH on $Cd^{2+}$adsorption capacityon AC and ACM,the adsorption capacity of $Cd^{2+}$ions as a function of pH should be analyzed.At low pH (pH = 2-3, acidic medium), a competition between high concentration $H^+$ ions and $Cd^{2+}$ ions at the solid-solution interface for adsorption sites occurs and leads to the protonation of oxygen and nitrogen functional groups. Thus lessadsorption sites are available on the surface of ACM and AC(Barczak *et al.*, 2015).In addition,the electrostatic repulsion between the $Cd^{2+}$ions and the positively charged surface composed of protonated functional groups increases ($pH_{pzc}$ = 9.65 and 9.80 for AC and ACM, respectively). Both effects led to a decrease in $Cd^{2+}$ions adsorption at low pH on both ACM and AC.A slightly higher adsorption capacity of AC compared to that of ACM at low pH can be explained by the fact that AC had more acidic functional groups which provide more positive sites than ACM for $H^+$ exchange with $Cd^{2+}$ on this pH range. As the pH of the solution increases from 3 to 7, the competition between $H^+$ ions and $Cd^{2+}$ ions decreases, due to the decrease in $H^+$ ions concentration.Moreover, the deprotonation of oxygen and nitrogen groups occurs, leading to the enhancement of adsorption sites available on the surface thereby increasing the adsorption capacity of ACM and AC. Above pH = 7, the decrease of the adsorption capacity of both AC and ACM was found. This can be explained by the phenomenon of precipitation of $Cd^{2+}$ ions which occurs causing accumulation of metal ions(Torab-Mostaedi *et al.*, 2010).Therefore, the optimum pH=5was achieved despite the positively charged surface, and was selected for further experiments.

*Adsorption mechanism:*

The adsorption of metal cations on the activated carbons are largely governed by electrostatic attraction. In addition, in some systems, specific interactions such as coordination bond formation or ion exchange may also play an important role in the adsorption process.Noted that the pH of the adsorbate(e.g., metal ions) solutions has been identified as the most important parameter governing the nature of the interaction between the metal ions and the surface of the adsorbents because it determines not only the speciation of the adsorbate but also the charge density of the carbonaceous surface.

The distribution of cadmium species in the solution as a function of pH shows that the divalent cadmium cation ($Cd^{2+}$) is the most abundant at pH <8. Above pH=8, a hydrated precipitate of cadmium $Cd(OH)_2$ (s) can be formed. Therefore, in this work, the study of the pH effect was made in the pH range of 2 to 8.Moreover, the study of the pHpzc showed that the pHpzc of AC and ACM are respectively 9.65 and 9.8, which suggests that in the pH range (pH = 2-8), the surface of AC and ACM is positively charged. Thus, in the presence of $Cd^{2+}$ cations, adsorbate-adsorbent repulsive interactions exist,and only a low adsorption capacity of metals can be expected. However, the adsorption capacity of both samples was relatively high, and the maximum adsorption capacity was achieved at pH = 5, which is even below the pHpzc of AC and ACM.

Given that the pH range studied is lower than the pHpzc of the adsorbents, we suggest that there is a competition between electrostatic repulsion and specific interactions such as cation exchange and coordination bond formation. At pH= 3, the low adsorption capacity is due to the strong electrostatic repulsion between the $Cd^{2+}$ ions and the positively charged surface. Between pH = 5-7 this electrostatic repulsion still exists but is dominated by the interaction between $Cd^{2+}$ cations and the basic functions of nitrogen on the surface (Figure 4) or oxygen (pyrones and chromenes) according to Lewis acid-base theory leading to the formation of bonds coordination. Thus, the high adsorption capacity of ACM than AC can be attributed to the introduction of basic nitrogen functional groups providing more sites basiccapable to formcoordination bonds with $Cd^{2+}$ ions. Above pH = 7, the precipitation of $Cd^{2+}$ ions into $Cd(OH)_2$ (s) coupled with electrostatic repulsion leads to a decrease in the adsorption capacity of $Cd^{2+}$ ions.

**Citation:** Vianet Kouakou Bossombra, *et al.*, Enhancement of $Cd^{2+}$ Ionsremoval Bymelamine-Modified Activated Carbon Made From Coconut Shells. Australian Journal of Basic and Applied Sciences, 12(9): 10-19. DOI: 10.22587/ajbas.2018.12.9.2

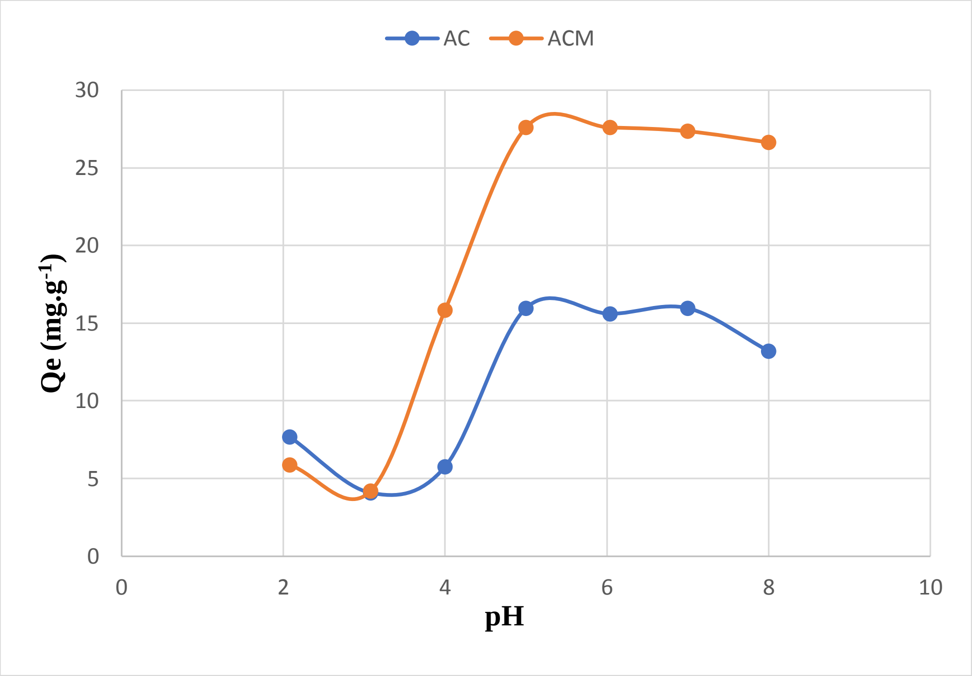

**Fig. 6:** Effect of initial pH on $Cd^{2+}$ ions adsorption onto AC and ACM ($C_0$ = 60.0 mg $L^{-1}$; adsorbents concentration = 1.0 g. $L^{-1}$; T = 25.0 °C; t = 24.0 h).

*Effect of temperature:*

The experiments were carried out at a temperature ranging from 35 to 55 ± 1 ° C, while initial metal concentrations and pH were set at 60 mg $L^{-1}$ and 5, respectively. The effect of temperature on the elimination efficiency of $Cd^{2+}$ ions was significant (Figure7). It was observed that the elimination efficiency of $Cd^{2+}$ ions by AC and ACM increased with increasing temperature from 35 to 55 ± 1 °C, from 36.65 %to 50 % for AC and 56.5 % to 68.5 % for ACM, respectively. This trend could be attributed to the increase in the kinetic energy of metal ions causing an increase in the frequency of collisions between adsorbent particles and metal ions (Sekar*et al.*, 2004).

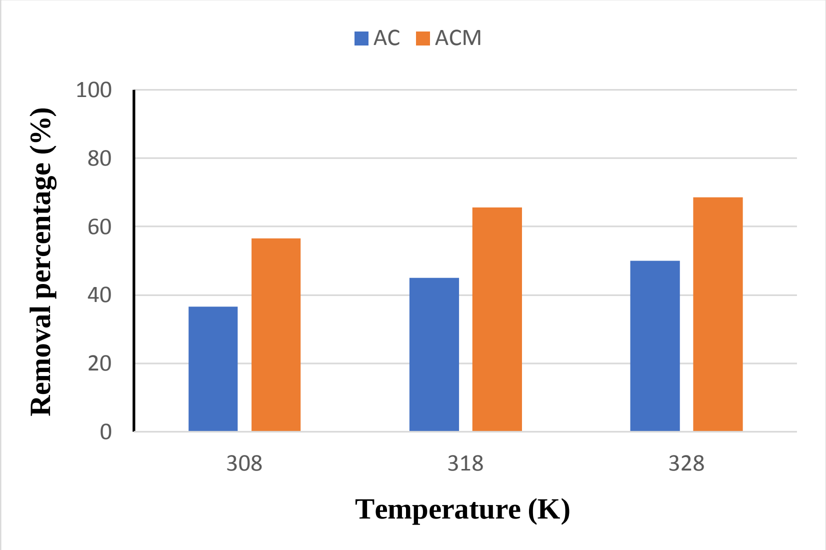

**Fig. 7:** Effect of Temperature on $Cd^{2+}$ ions adsorption onto AC and ACM ($C_0$ = 60.0 mg $L^{-1}$; Adsorbents concentration = 1 g $L^{-1}$, t = 24 h, pH = 5).

*Adsorption kinetics:*

Equilibrium time is one of the most important operational parameters for the effectiveness of treatment. This is the contact time required for the adsorption process to be effective and efficient. The adsorption of $Cd^{2+}$ ions by AC and ACM was studied as a function of time. As shown in Figure 8, the modification of the activated carbon with melamine has no remarkable effect on the adsorption rate but rather on the adsorption capacity $Q_t$ at a time t. Adsorption of $Cd^{2+}$ ions was rapid for AC and ACM in the first 40 minutes because the adsorption sites are vacant and available. After 40 minutes, the adsorption sites become unavailable, the remaining vacant surface sites are difficult to be occupied due to repulsive force between the solute molecules on the solid and bulk phases, therefore the adsorption of $Cd^{2+}$ ions continue but slowly until reaching equilibrium.

To investigate the adsorption mechanism,adsorption kinetics experimental data were analyzed with nonlinear adjustment of two different kinetic models namely pseudo-first order and pseudo-second order **(**Figue 8**)**.Kinetic parameter values (Qe (cal) and k) as well as the adjusted correlation coefficient($R^2_{Adj}$) and standard deviation (SD) for $Cd^{2+}$ions adsorption on AC and ACM were obtained using nonlinear regression(Table 6). Based on the fact that the model with the largest value of $R^2_{adj}$ and the smallest value of SD is the best fit(Lima and Adebayo, 2015), it appears that the second-order kinetic model better describes the experimental data than the first-order kinetic model, this suggests that the sorption process could be the formation of a covalent bond between the surface fonctional groups of the adsorbent and the adsorbate(Lima and Adebayo, 2015).

To describe the diffusion mechanism, the intraparticle diffusion model based on the theory proposed by Weber and Morris was used(Figure9). According to this theory, If the regression of $Q_t$vs $t^{1/2}$ is linear and passes through the origin, intra particle diffusion is the only speed limiting step(Mittal*et al*, 2007). However, two stages of linearity are observed for the adsorption of $Cd^{2+}$ onto AC and ACM, indicating that two steps occur when adsorbing $Cd^{2+}$ ions. The first part completed in the first 40 minutes is the instantaneous adsorption (external surface adsorption) and the second part describes the step of progressive adsorption where intraparticule diffusion is the speed limitation step. The linear part of the first step does not cross the origin, indicating that it is not only the intraparticle diffusion that limits the adsorption process, but other mechanisms such as coordination bond formation or ion exchange can control partially the adsorption rate of $Cd^{2+}$ ions(Foo and Hameed, 2012).

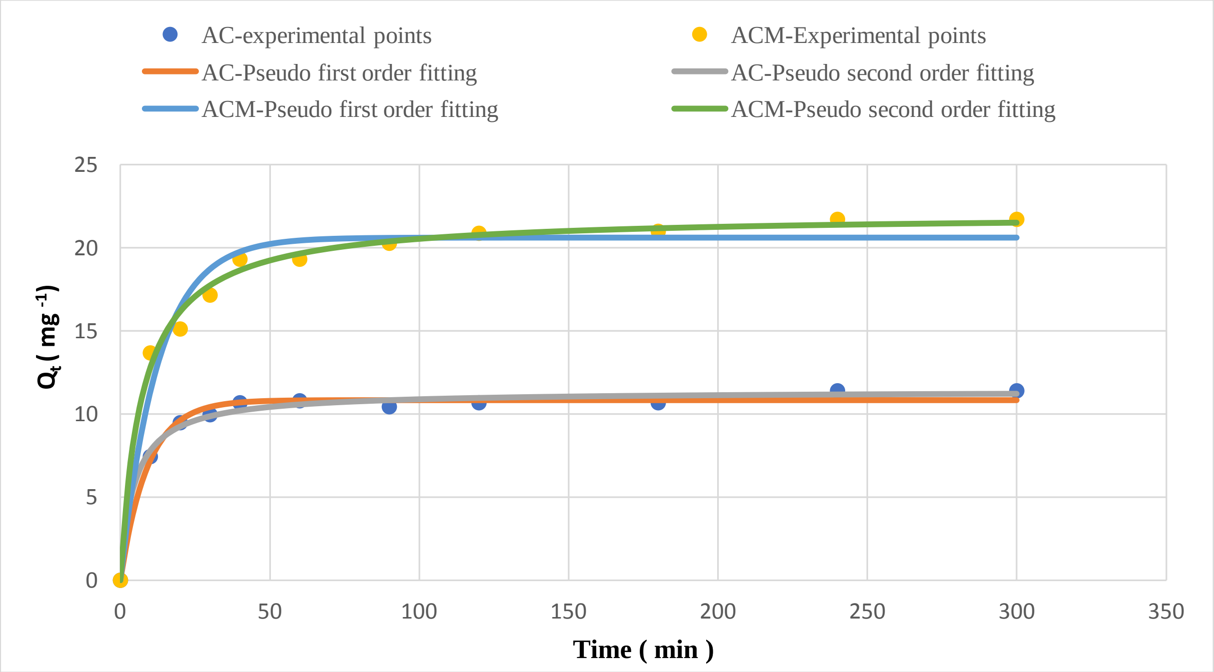

**Fig. 8:** $Cd^{2+}$ ions adsorption kinetics onto AC and ACM ($C_0$ = 60.0 mg $L^{-1}$; adsorbents concentration = 1 g $L^{-1}$; T = 25.0 °C; pH=5).

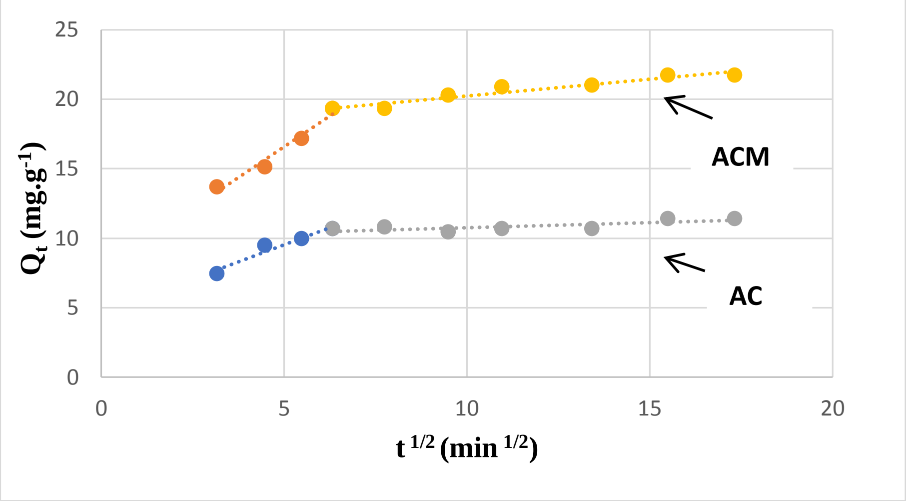

**Fig. 9:** Weber-Morris intraparticle diffusion kinetics adsorption curve of $Cd^{2+}$ onto AC and ACM ($C_0$ = 60.0 mg $L^{-1}$; adsorbents concentration = 1 g $L^{-1}$; T = 25.0 °C; pH=5).

**Table 6:** Pseudo-first-order and Pseudo-second-order kinetics models 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 | 21.72 | 20.60 | 0.079 | 0.96 | 1.24 | 22.03 | 0.006 | 0.99 | 0.58 |

**Table 7:** Intraparticle diffusion 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 | 1.774 | 0.224 | 0.97 | 0.93 | 7.701 | 17.84 |

*Effect of adsorbent dosage:*

The removal of $Cd^{2+}$ ions as a function of the adsorbent concentration was carried out. The results revealed that the percentage of removal of heavy metals increased rapidly with increasing dose of the adsorbent (Figure 10). It was observed that the percentage removal of $Cd^{2+}$ ions increased from 22.16% to 79.95% for AC and from 39 % to 100% for ACM when the adsorbent dose increases from 1 $gL^{-1}$ to 3.5 $gL^{-1}$. This is due to the availability of more adsorption sites and therefore to easier penetration and access of the metal ions to the adsorption sites. Thus, a higher dose of adsorbent may have a positive effect on the initial rate of removal of $Cd^{2+}$ ions.

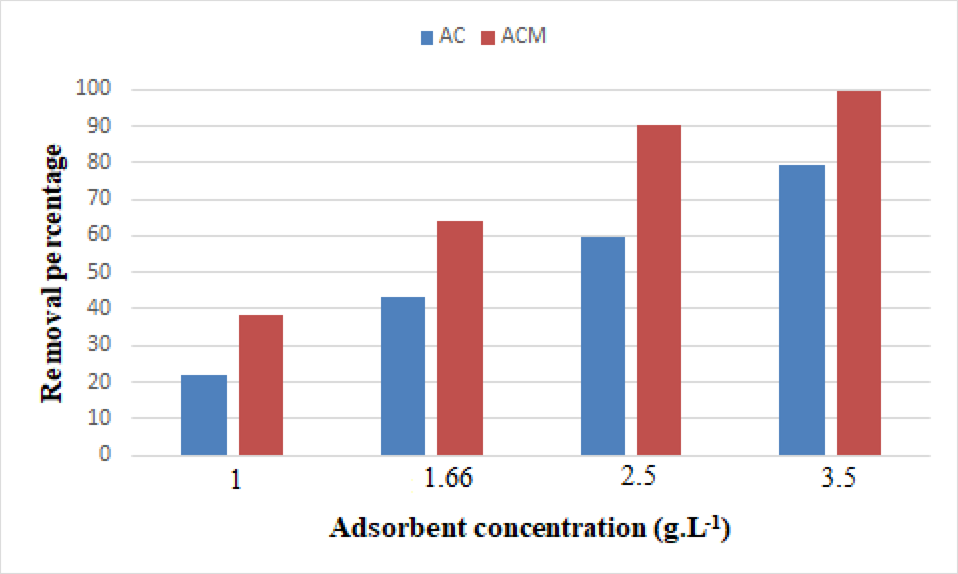

**Fig. 10:** Effect of adsorbents concentration (AC, ACM) on $Cd^{2+}$ ions removal ($C_0$ =60.0 mg $L^{-1}$; T = 25.0°C; t = 8.0 h; pH = 5).

*Conclusion:*

In this study, activated carbon (AC) made from the original coconut shell of Ivory Coast was modified by nitrogen functional group input using melamine as a nitrogen source for the efficient removal of $Cd^{2+}$ ions from aqueous solution .The chemical and textural properties determined by $N_2$ adsorption/desorption, Boehm titration, FTIR, elemental analysis and XPS showed that nitrogen-containing functional groups such as pyridine, pyrrole andpyridonic nitrogen were loaded onto the AC surface after the treatment with melamine. The adsorption tests on AC and ACM reveal that the adsorption capacity of AC with respect to $Cd^{2+}$ ions has risen from 15.72 mg $g^{-1}$ to 27.60 mg $g^{-1}$ (a 75% improvement).The adsorption capacity was strongly influenced by the pH of solution and the optimum pH was ~5. The equilibrium data of AC and ACM fit well with the Freundlich model, and the adsorption equilibrium can be reachedafter 4 h. The adsorption kinetics data were found to be better described by the pseudo-second-order model. It can be concluded that the surface modification method using melamine as the nitrogen functional group sourcecan be used to enhance the adsorption capacity of activated carbon to adsorb cationic heavy metal ions. Melamine-modified activated carbons derived from the original coconut shell is low-cost, making them promising materials for industrial wastewater treatment applications.

## ACKNOWLEDGEMENTS

The Ministry of Higher Education and Scientific Research of Ivory coast for its financial support for this research. We are also grateful to Prof. Trong-on Do and his team at the Laboratory of Catalysis and Nanomaterials at Laval University for their availability.

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