Removal of Imidacloprid using Activated Carbon from Coconut Shells

Urbain Yao KOUAKOU , Ardjouma DEMBELE, Augustin Yao YOBOUET ,Albert TROKOUREY

UFR SSMT, Laboratoire de Chimie Physique, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire.

Laboratoire Central d'Agrochimie et d'Ecotoxicologie (LCAE), Abidjan, Côte d'Ivoire.

Ecole Normale Supérieure (ENS), Abidjan, Côte d'Ivoire.

UFR SSMT, Laboratoire de Chimie Physique, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire.

ABSTRACT:The main goal of this work was the study of imidacloprid adsorption onto activated carbon from coconut shells. For this purpose, two activated carbon from coconut shells were used. Adsorption kinetics was studied and the rate of sorption was found to conform to pseudo-first-order and pseudo-second-order kinetics with 90 min as equilibrium time. Langmuir, Freundlich and Temkin models were investigated and all of them were in good agreement but Freundlich model was better. In addition, Temkin model has proven that the adsorption process is exothermic. The maximum adsorption capacity calculated from Langmuir isotherm model were 31.15 mg.g^{-1} and 33.22 mg.g^{-1} from local activated carbon (CAS) and commercial activated carbon (NORIT PK 1-3) respectively. Adsorption process is physical. The effect of pH and activated carbon dose have been studied at 27ºC. Activated carbons properties have significantly influence onto adsorption of imidacloprid and parameters of solution such as pH. These activated carbons are found to be efficient material for imidacloprid removal from wastewater.

KEYWORDS: Activated carbon, Adsorption,Imidacloprid, pH, Water treatment.

I. INTRODUCTION

Environmental pollution concern all part of the world. Air, soil and water are regularly contaminated by many pollutants. This situation affects consequently ground and surface waters. However population increase with needs of water [1]. One of the important class of the pollutants is pesticides, substances used in agriculture, aquaculture, and households to control a large variety of insectivorous and herbaceous pests, or to eradicate vector-borne diseases. But, the toxicity of pesticides and their degradation products poses a potential hazard to environment [2].

The removal of pollutants from contaminated water has been attempted by several scientists employing a wide variety of techniques including precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange [3]. Of major interest, adsorption process, is recognized as the most efficient and promising fundamental approach in the wastewater treatment processes [4-5]. The main material commonly used in this technique is activated carbon. The advantages of this activated carbon derive from its large surface area, well-developed internal structure, large adsorption capacities and fast adsorption kinetics [6].

The purpose of the present study was to investigate the adsorption behavior of the pesticide imidacloprid 1-(6-chloro-3-pyridinylmethyl)-N-nitro-imidazolidin-2-ylideneamine (scheme 1) at the coconut shells activated carbon from aqueous solutions and thus the possibility to remove this pesticide from waters polluted by it.

To achieve our goal, Boehm titration, X-ray diffraction, ash content, pH and specific area were used to investigate activated carbon properties.Pseudo-first-order and pseudo-second-order kinetics models were adopted to examine the mechanism of the adsorption process of imidacloprid by activated carbon. The applicability of the isotherm models, that is, Langmuir isotherm, Freundlich isotherm and Temkim isotherm, was analyzed by comparing the correlation coefficients. In addition, the effect of pH solution and activated carbon dose were evaluated.
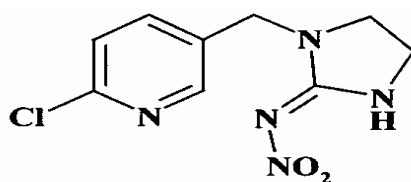
Scheme 1: Chemical structure of imidacloprid

II.   EXPERIMENTAL

A. ADSORBENTS

Two activated carbons from coconut shells were used as adsorbents: local activated carbon labeled in this study as CAS prepared by us in our laboratory and NORIT PK 1-3 supplied by Netherlands industry and produced. The only characteristics given for these adsorbents were particle sizes were 0.52-2.36 and 1.1-3.4 mm for CAC and NORIT PK 1-3 respectively. NORIT PK 1-3 was prepared by physical activation with CO_2 and CAC by chemical activation with orthophosphoric acid (H_3PO_4).

B. CHARACTERIZATION OF THE ACTIVATED CARBON

To assess the specific surface area of activated carbon acetic acid adsorption method as used [7-8]. For this, 20 mL of acetic acid concentrations ranging from 0.01 to 0.1 mol/L are placed into bottle. Then, 0.1 g of activated carbon is added. The mixtures were shaken for 60 min at 160 rpm to reach equilibrium. The obtained substrate was filtered, and titrated with NaOH (0.1M), using phenolphthalein indicator. The amount of adsorption q_e at time twas then calculated according to Equation (1):

$$q_e \ (mg/g) \ = \ \frac{(C_o \ -C_e)}{m} \times V \qquad \textbf{(1)}$$

whereC_0 and Ce are the concentrations of acetic acid at initial and equilibrium times respectively, V is the volume of the suspension and m is the mass of activated carbon used.

The use of Equation (2) (Langmuir equation) with Equation (3) will permit to have the specific surface:

$$q_e \ (mg/g) \ = \ \frac{(C_o \ -C_e)}{m} \times V \qquad \textbf{(2)}$$

$$S = \ q_m . s. N_A \qquad \textbf{(3)}$$

whereq_m (mol/g) is the maximum adsorption capacity of the activated carbon, s = 21Å^2, is the area for the acetic acid and $N_A = 6.2 \times 10^{23}$ mol^{-1}, Avogadro constant.

Quantitative determination of functional groups in activated carbons was made using the titration method of Boehm [9]. One gram of activated carbon was placed in 100 mL Erlenmeyer flasks and 50 mL of the 0.05 M solutions of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and hydrochloric acid (HCl) were added. The flasks were closed and agitated for 48 h at room temperature. After equilibration, HCl was used for titrations of the solutions of NaOH, Na_2CO_3 and $NaHCO_3$ and then the acidic surface function is obtained. Titration of HCl solution after equilibration provides the amount of basic surface character.

For pH determination, 3 g of each activated carbon were mixed with 60 mL of distilled water in a beaker. The covered beaker was heated gently to boil on a hot plate for 3 min. The solutions were filtered and allowed to cool at room temperature. Then pH of the solution was measured by pH-meter. The crystal structures were analyzed by an X-Ray diffractometer (D8 Advance Bruker, Germany) with a germanium detector for angle 2θ between 20–120^0 with scan rate of 0.01◦/s.

For the determination of ash contents, the samples were ground to pass through a 0.5 mm sieve. One gram of this sample in tarred porcelain dish was placed in a muffle furnace at 800°C for 2 h, then cooled at room temperature and reweighed.

C. STUDY OF IMIDACLOPRID ADSORPTION

1. KINETIC ADSORPTION STUDY

The study of the kinetics of adsorption of imidacloprid was carried out at room temperature on activated carbon. The aim is to determine the time required to reach equilibrium carbon adsorption and kinetic order. For kinetic adsorption study, 0.1 g of activated carbon was mixed with 20 mL of 5 ppm and 10 ppm standard imidacloprid solution in a 100 mL conical flask. These mixtures were shaken on magnetic agitator at 200 rpm for intervals time of 0, 0.25, 0.5, 0.75, 1, 1.25, 1.30, 2 and 3 hours. After each contact time solutions were filtered and the initial and final concentrations of imidacloprid were determined by HPLC. The amount of imidacloprid adsorbed onto carbon is calculated according to the following equation:

$$q_t \ = \ \frac{(C_o \ -C_t)}{m} \times V \quad (4)$$

where$q_t$is the amount of imidacloprid adsorbed by activated carbon (mg/g); C_0 and $C_t$are respectively the initial and the final concentration of imidacloprid at time after filtration $($ppm$)$; V is the initial solution volume (L); m is the mass of the activated carbon (g).

2. ADSORPTION ISOTHERMS

For equilibrium adsorption study, 0.1 g of activated carbon was mixed with 20 mL of different imidacloprid concentrations between 1.25 to 50 ppm in 100 mL conical flasks. Then reaction mixtures were shaken on magnetic agitator at 200 rpm for equilibrium time (90mn) at room temperature. After equilibrium time, samples were filtered and analyzed by HPLC. The amount of imidacloprid adsorbed per unit mass of coconut shell activated carbon at equilibrium, q_e, was calculated by:

$$q_e = \frac{(C_o - C_e)}{m} \times V \quad (5)$$

where C_0 and C_e are the concentrations of imidacloprid at initial and equilibrium times, respectively; V is the volume of the (L); and m is the mass of activated carbon used (g).

3. EFFECT OF PH

To study the effect of pH on imidacloprid adsorption on activated carbon, the experiments were mad with 20mL of imidacloprid 10 ppm mixed with 0,1g of activated carbon. The initial pH values were adjusted to 2; 3.4; 4.5; 5.3; 6.5, 8, 10 and 11.2 with 0.1M HCl or 0.1M NaOH. The suspensions were shaken using magnetic agitator (200 rpm) for equilibrium time (90mn) at room temperature and the amount of imidacloprid adsorbed determined by:

$$\% \text{ rétention} = \frac{(C_o - C_e)}{C_0} \times 100 \quad (6)$$

where C_0 and C_e are the concentrations of imidacloprid at initial and equilibrium times, respectively.

4. EFFECT OF ACTIVATED CARBON DOSE

The effect of sorbent dose on the uptake of imidacloprid was achieved using activated carbon mass of de 0.1g; 0.2g; 0.5g; 1g and 2g. The experiments were performed by shaking 20 mL 10 ppm of imidaclopridwith the above different sorbent mass to the equilibrium time (90 min) and the amount of imidaclopridadsorbed determined.

The concentration of imidacloprid was analyzed using on HPLC system Shimadzu Prominence LC-20A series (SHIMADZU, Japan) equipped with UV-Vis detector SPD -20A (set on 252 nm).

III. RESULTS AND DISCUSSION

A. PHYSICO-CHEMICAL CHARACTERISTICS OF THE ACTIVATED CARBON

1. SPECIFIC SURFACE AREA OF PREPARED ACTIVATED CARBON

The surface areas were measured using the adsorbed acetic acid method [7-8]. The Langmuir isotherms were plotted using (Figure 2). Values of isotherms and surface areas are summarized in Table 1. As displayed in this table, value of CAS local prepared activated carbon surface area are 721 m^2/g and for NORIT PK 1-3 the value is 754 m^2/g. So, both are similar surface area.
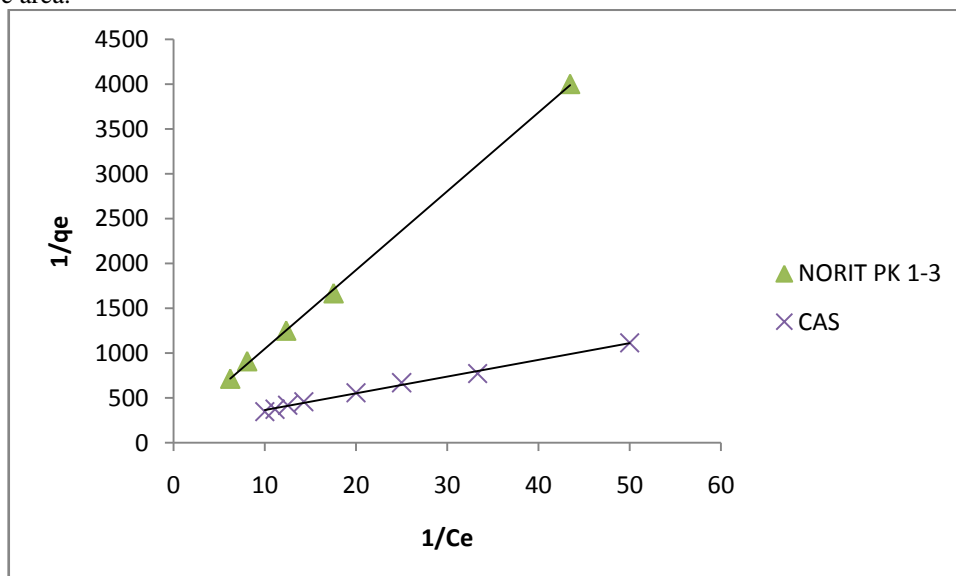

Figure 2. Langmuir plots for acetic acid adsorption onto CAS and NORIT PK 1-3

Table 1. Values of Langmuir isotherms parameters and surface area of carbons by adsorption of acetic acid

CARBON	R^2	q_m (mol/g)	Surface area (m^2/g)
NORIT PK 1-3	0.999	$5.963.10^{-3}$	754
CAS	0.995	$5.704.10^{-3}$	721

2. ADSORBENT SURFACE CHEMISTRY

The surface acidity and basicity is an important criterion to describe the surface chemistry of the carbon adsorbents [7], [10]. This criterion is investigated mixing 3 g of carbons with 60 mL of distilled water in a covered beaker and heated to boil on a hot plat for 3 min. The solutions were filtered and allowed to cool at room temperature. Then the pH of the solution was measured using pH-meter. As exhibited in Table 2, the pH values indicate basic character and neutral character for NORIT PK 1-3 and CAS respectively. The distribution of functional groups according to titration method of Boehm is consistent with the pH values. The same observation has been made by Yenisoy-Karakas [11]. NORIT PK 1-3 does not have any carboxyl groups and the acidity mainly comes from phenolic and lactonic groups. Acidity functions of CAS derived mainly from the oxygen-containing groups such as carboxylic and phenolic and also due to the chemical activation which increase carboxylic group [12]. The basic groups are higher in the NORIT PK 1-3 than in the CAS. The surface basicity could be due to the presence of oxygen-free Lewis sites and carbonyls, pyrone and chromene type structures at the edge of the carbon layers [13].

Table 2. Surface chemistry of carbons

	carboxylic (mmol/g)	Lactone (mmol/g)	Phenolic (mmol/g)	Total acidic sites (mmol/g)	Total basic sites (mmol/g)	pH
NORIT PK 1-3	0	0.80	0.42	1.22	1.90	9.34
CAS	0.29	0.21	0.64	1.14	1.65	7.2

3. X-RAY DIFFRACTION (XRD)

The crystalline structure of activated carbons was explored. Fig. 3 shows the typical XRD pattern of both NORIT PK 1-3 and CAS. As can be seen, a similar profile is obtained. The two diffractograms present broad peaks and absence of a sharp peak that revealed predominantly amorphous structure [14] However, the broad peaks around 26 and 46 for NORIT PK 1-3 and the same broad peak for CAS showed signs of formation of a crystalline carbonaceous structure resulting in better layer alignment [15] and amorphous structure. These carbons can be therefore identified as amorphous structure and could be a well adsorbent. This result is similar to those of Wimonrat [14].
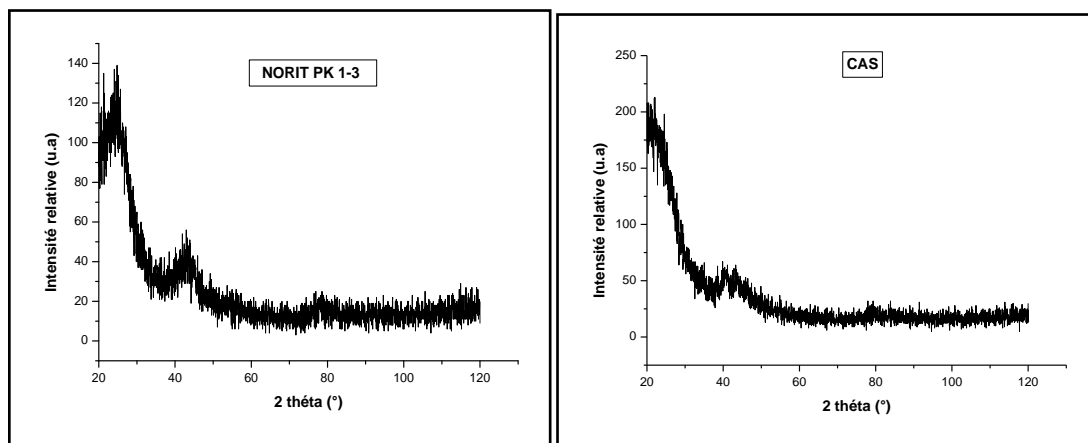

Figure 3. The X-ray diffraction profiles of NORIT PK 1-3 and CAS

B. KINETIC ADSORPTION STUDY

The study of the kinetics of adsorption of imidaclopridon NORIT PK 1-3 and CAS was carried out at room temperature with two different concentrations of imidacloprid solution.

Figure 4 shows the concentration versus time dataover an adsorption period of 200 min. As exhibited, the adsorption process is similar for the two activated carbon and can reach equilibrium at 90 min.
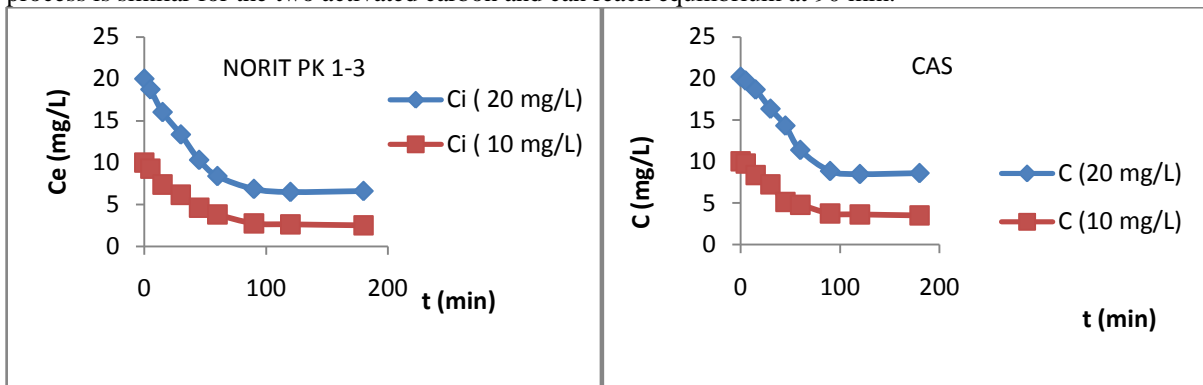

Figure 4. Adsorption kinetic of imidacloprid on NORIT PK 1-3 and CAS

To acquire the order of the imidacloprid adsorption kinetic, two kinetic models were used:

✓ pseudo-first order which can be formulated as

$$\ln C - \ln C_0 = -k_1 t \qquad (7)$$

✓ pseudo-second order which can be formulated as

$$1/C - 1/C_0 = k_2 t \qquad (8)$$

where q_t is the amount of imidacloprid adsorbed at any time, C_0 and C are the initial concentration and concentration of imidacloprid at any time respectively, t is time and k_i, k_1 and k_2 are rate constants for diffusion, pseudo-first order and pseudo-second order models, respectively.

The applicability of the two models was checked by plotting $\ln C$ versus t for pseudo-first order and $1/C$ versus t for pseudo-second order models. The rate constants k_1 and k_2 obtained from the slopes of corresponding linear plots are given in Table 4 and Table 5 together with correlation coefficients, R^2. The smallest correlation coefficients are obtained for the intraparticle diffusion model. All the correlation coefficients are higher than 0.96. So, the two models seem to be applicable.

Erol showed that adsorption of pesticides ametryn, diuron, aldicarb and dinoseb onto activated carbon-cloth could well be described by pseudo-first order and pseudo-second-order [17].

Table 4. Rate constants and correlation coefficients from imidacloprid adsorption onto CAS

Initial concentration	Kinetic model			
	Pseudo-first order		Pseudo-second order	
	k_1 (min^{-1})	R^2	k_2 (g.mg^{-1}.min^{-1})	R^2
20 ppm	$9.80.10^{-3}$	0.987	$5.01.10^{-3}$	0.985
10 ppm	$11.00.10^{-3}$	0.968	$6.13.10^{-3}$	0.991

Table 5. Rate constants and correlation coefficients from imidacloprid adsorption onto NORIT PK 1-3

Initial concentration	Kinetic model			
	Pseudo-first order		Pseudo-second order	
	k_1 (min^{-1})	R^2	k_2 (g.mg^{-1}.min^{-1})	R^2
20 ppm	$12.00.10^{-3}$	0.978	$2.93.10^{-3}$	0.995
10 ppm	$14.00.10^{-3}$	0.987	$2.76.10^{-3}$	0.995

C. EQUILIBRIUM ADSORPTION STUDY

These adsorption isotherm studies were conducted at 28°C with an equilibrium time of 90 min. Figure 5 shows the isotherms adsorption of imidacloprid onto coconut activated carbons. As displayed, the adsorbed amount of imidacloprid increases with the concentrations of imidacloprid at equilibrium. These adsorption of imidacloprid may therefore be classified as type I of IUPCA and may suggest that NORIT PK 1-3 and CAS have a goof affinity for imidacloprid due to their microporous structure [18]. However, imidacloprid is well adsorbed by NORIT PK 1-3.

The capacity of the adsorbent for the removal of organic or inorganic substances from aqueous solutions is commonly represented by two models, Langmuir and Freundlich [19] and often by Temkin model [19]. These equations are given below (Equation 9-11):

$$\text{Langmuir} \qquad \frac{1}{q_e} = \frac{1}{b\,q_m}\frac{1}{C_e} + \frac{1}{q_m} \qquad (9)$$

$$\text{Freundlich} \ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (10)$$

$$\text{Temkin} \; q_e = \frac{RT}{\Delta Q}\ln K_0 + \frac{RT}{\Delta Q}\ln C_e \qquad (11)$$

where C_e (mg.L^{-1}) and q_e (mg.g^{-1}) are the concentration of imidacloprid and the amount of imidacloprid adsorbed per unit mass of adsorbent at equilibrium respectively, b (L.mg^{-1}) is the Langmuir isotherm constants, q_m(mg.g^{-1}) is the maximum adsorption capacity of the adsorbent, K_F is the Freundlich constant (L^{-1}.mg), and 1/n is the heterogeneity factor, Temperature (K), K_0 is Temkin isotherm constants, R(8.314 J.mol^{-1}.K^{-1})is the universal gas constant and ΔQ is heat of adsorption.

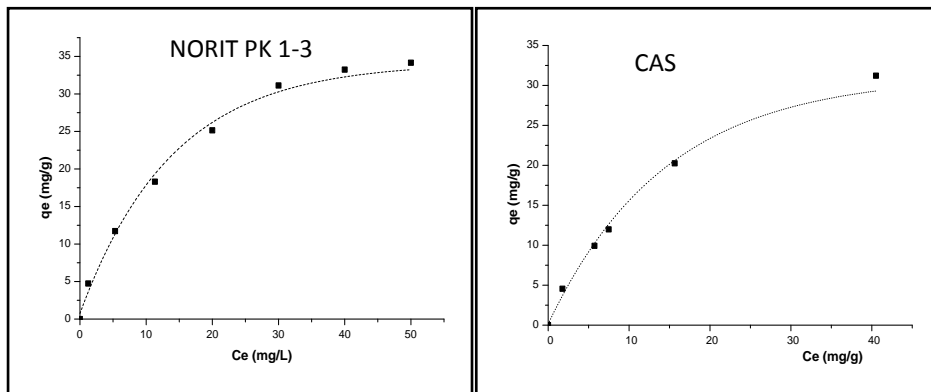**Figure 5**. Isotherm adsorption of imidacloprid onto coconut shells activated carbon

Plotting 1/qe against 1/Ce (Figure 6), a linear relationship between 1/qe and 1/Ce is obtained. It is therefore possible to obtain the value of Langmuir constant b and the maximum adsorption capacity of the adsorbent q_m related to Langmuir equation. The plot of ln(qe) versus Ce was employed to generate the intercept value of K_F and the slope 1/n (Figure 7)where 1/n is a measure of the deviation from linearity of the adsorption. By plotting q_e versus $\ln C_e$ (figure 8), it is also possible to obtain the heat energy (ΔQ). The Langmuir, Freundlich and Temkin isotherm parameters for the adsorption of imidacloprid onto AAC are listed in Table 6.
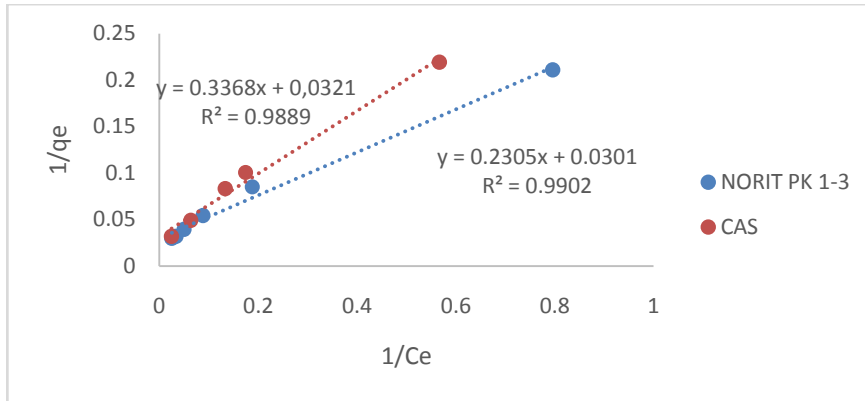
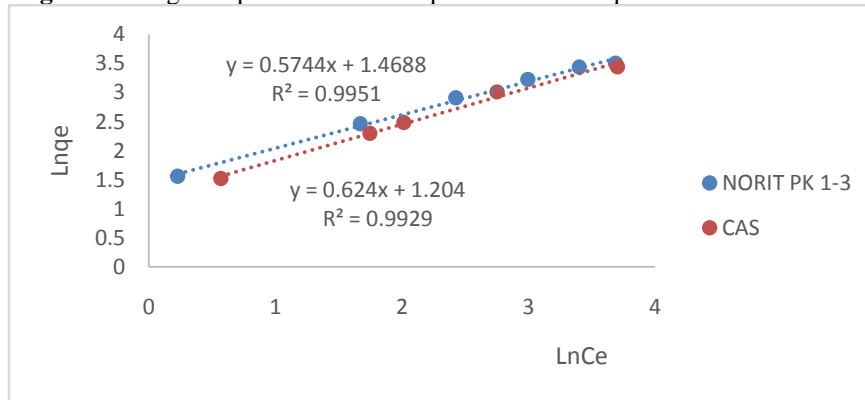**Figure 6**: Langmuir plots for the adsorption of imidacloprid onto NORIT PK 1-3 and CAS

Figure 7: Freundlich plots for the adsorption of imidacloprid onto NORIT PK 1-3 and CAS
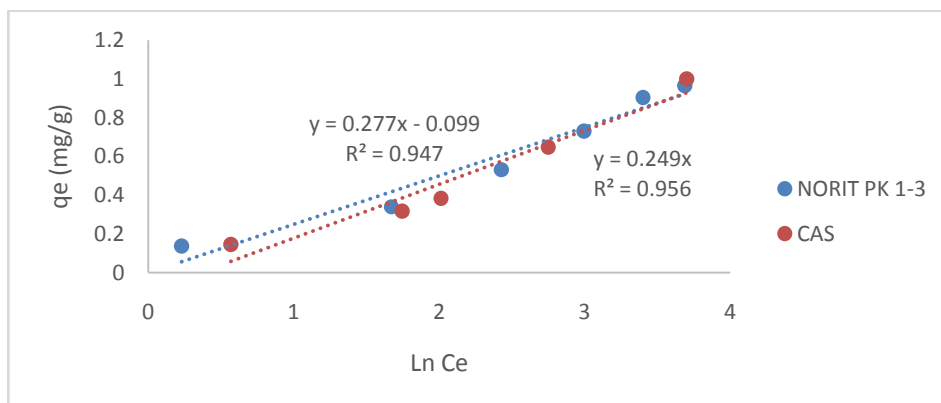

Figure 8: Temkin plots for the adsorption of imidacloprid onto NORIT PK 1-3 and CAS

According to the results displayed in Table 6, linear correlation R^2 values obtained from Freundlich and Langmuir models are greater than 0.98 suggesting that both Freundlich and Langmuir models fit well. The obtained values $1/n < 1$ and adsorption fitted well by Freundlich model implies that the adsorption process is physical [19-20]. The positive value of heat of adsorption find by model of Temkin (ΔQ) suggests that the adsorption process is exothermic [21].

Table 6. Equilibrium adsorption isotherm values for imidacloprid onto AAC

Model	Linear correlations (R^2)		q_m (mg/g)		b	
	Norit PK 1-3	CAS	Norit PK 1-3	CAS	Norit PK 1-3	CAS
Langmuir	0.990	0.989	33.22	31.15	0.124	0.095

Temkin	0.956	0.947	$\Delta Q = 10.02$ KJ/mol	$\Delta Q = 8.99$ KJ/mol	$K_0 = 1.016$	0.699
Freundlich			Ln k		1/n	
	0.995	0.9929	1.503	1.204	0.574	0.624

D. INFLUENCE OF pH SOLUTION ON IMIDACLOPRID ADSORPTION

Plotting amount of imidacloprid adsorbed versus pH, allow to study the influence of pH in imidacloprid adsorption onto coconut shell activated carbons. As shown in Figure 9, the adsorption of imidacloprid onto NORIT PK 1-3 is favorable at three pH (2.59; 4.25 and 7). But maximum adsorption is at pH =7. This result is similar of those of Daneshvar who obtained best adsorption at pH =7 by adsorption of imidacloprid onto activated carbon [21]. For adsorption of imidacloprid onto CAS, The best adsorption process is obtained at pH 3.84 suggesting that the pH affects significantly the adsorption process. The effect of pH may be attributed to the variation of surface charge of with pH [22] and the competition between imidacloprid and H^+ ions in acidic and with OH^- ions in basic solution [23].
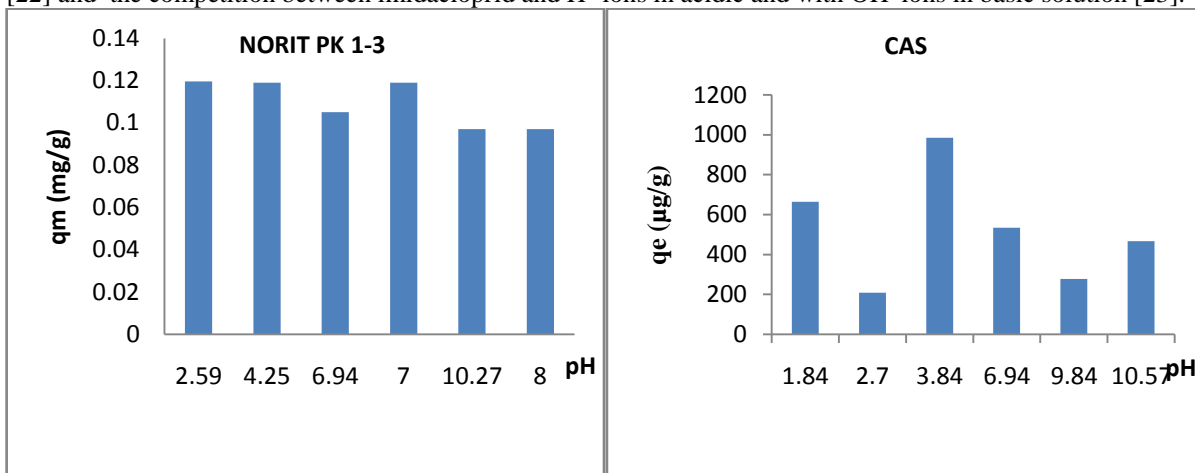

Figure 9: Plot of effect of pH on adsorption

E. INFLUENCE OF ADSORBENT DOSE ON IMIDACLOPRID ADSORPTION

The effect of sorbent dose on the uptake of imidacloprid was achieved using different massesof activated carbons. The results are shown in Figure 10. It is observed that the percentage removal of imidacloprid with activated carbons increases from 20 to 99 % when the adsorbent dose increases from 0.1 to 2 g per 100 mL. This result infers that 2g of NORIT PK 1-3 can be used as activated carbon to eliminate more than 99% of imidacloprid in waste water contain imidacloprid and local activated carbon prepared could well be used for the same aim but 2g of CAS can eliminate 93% of imidacloprid.
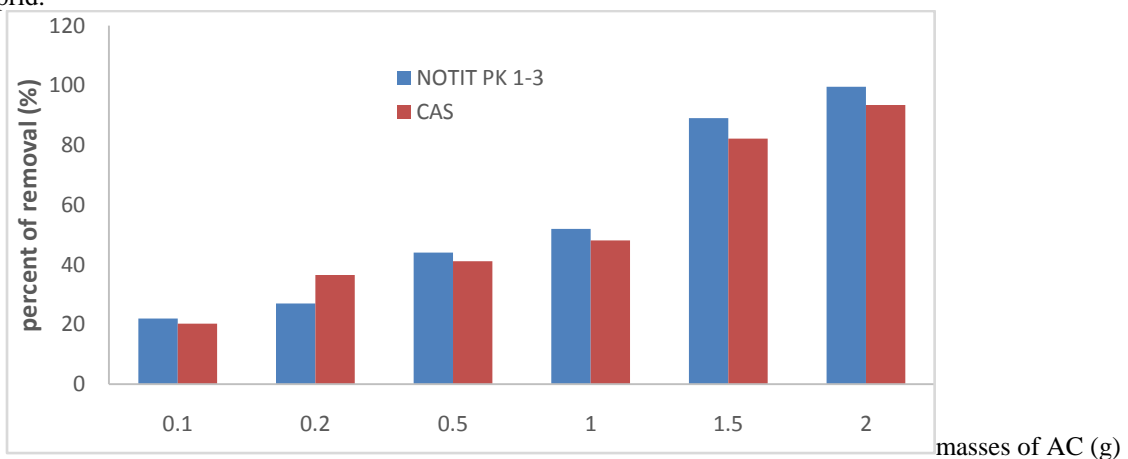

Figure 11: Plot of effect of adsorbent dose on adsorption

IV. CONCLUSION

In this work, activated carbons prepared from coconut shell have been used to remove imidacloprid. Local activated carbon (CAS) has 721 m^2/g as surface area so similar than commercial activated carbon (NORIT PK 1-3). Both are amorphous structure and many functions of surface, which show excellent adsorption properties.

These properties affect considerably adsorption of imidacloprid onto them. Imidacloprid is well adsorbed at pH acid onto CAS which surface is neutral and at neutral pH onto NORIT PK 1-3 which surface is basic.

In addition, it is found that more than 90 % of imidacloprid can be removed using the fabricated activated carbon and commercial carbon, that can help to fight against pollution and give quality of water.

The adsorption processes were found to follow the pseudo-second order and pseudo-first order kinetics over a period of 90 min. Also, the results have shown that the models of Langmuir and Freundlich are appropriate to describe the isotherms. However values of these model show that the process of adsorption is physical and exothermic.

REFERENCES

[1] Kouakou Y.U., Dembélé A., Ello A.S., Brou Y.S., Yao B.L., Trokourey A. "Study of adsorption of imidacloprid onto two different textures of soils", Int. J. Biol. Chem. Sci. vol. 9, pp. 472-482, 2015.

[2] Gu W., Sun C., Liu Q., Cui H. "Adsorption of avermectins on activated carbon: Equilibrium, kinetics, and UV-shielding", Trans. Nonferrous Met. Soc. China, vol. 19, pp. 845-850, 2009.

[3] Foo K.Y., Hameed B.H. "Detoxification of pesticide waste via activated carbon adsorption process", Journal of Hazardous Materials, vol. 175, pp.1-11, 2010.

[4] Foo K.Y., Hameed B.H." Recent developments in the preparation and regeneration of activated carbons by microwaves", Advances in Colloid and Interface Science, vol. 149, pp. 19-27, 2009.

[5] Gupta V.K., Suhas,"Application of low-cost adsorbents for dye removal- A review"; Journal of Environmental Management, vol. 90, pp. 2313-2342, 2009.

[6] Erol A., Numan H., "Adsorption of bentazon and propanil from aqueous solutions at the high area activated carbon-cloth", Chemosphere vol. 57, pp. 755-762, 2004.

[7]Hamouz A.E., Hilal H.S., Nashaat N., Zahi M.,"Solid olive waste in environmental cleanup: Oil recovery and carbon production for water purification", Journal of Environmental Management vol. 84, pp. 83-92, 2007.

[8]Avom J., Ketcha M.J., Matip M.R. "Adsorption isotherme de l'acide acétique par des charbons d'origine végétale",African Journal of Science and Technology (AJST). Science and Engineering Series, vol.2, pp.1-7, 2001.

[9] Boehm.H.P., "Surface oxides on carbon and their analysis: a critical assessment", Carbon, vol. 40, pp. 145-149, 2002.

[10] Foo K.Y., Hameed B. "Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K$_2$CO$_3$ activation", Bioresource Technology vol. 104, pp. 679-686, 2012.

[11]Yenisoy-Karakas S., Aygün A., Günes M. "Physical and chemical characteristics of polymer-based spherical activated carbon and its ability to adsorb organics", Carbon vol.42, pp. 477-484, 2004.

[12] Carlos M.C., Francisco C.M., Lopez-Ramon M.V., Miguel A.A.M."Chemical and physical activation of olive-mill waste water to produce activated carbons", Carbon vol. 39, pp. 1415-1420, 2001.

[13] El-Sheikh A.H., Hilal M.M.A., Sweileh, J.A."Bio-separation, speciation and determination of chromium in water using partially pyrolyzed olive pomace sorbent", Bioresource Technology vol. 102, pp. 5749-5756, 2011.

[14] Yu-bin T., Qiang L., Fang-yan C."Preparation and characterization of activated carbon from waste ramulusmori", Chemical Engineering Journal (2012), doi: http://dx.doi.org/10.1016/j.cej.2012.07.007

[15] Yang T., Lua A.C."Textural and chemical properties of zinc chloride activated carbons prepared from pistachio-nut shells", Mater. Chem. Phys., vol.100, pp.438-444, 2006.

[16] Paszko T."Sorptive behavior and kinetics of carben-dazim in mineral soils", Polish J. of Environ. Study, vol.15 pp. 449-456, 2006.

[17] Erol A., Numan H."Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth", Chemosphere vol. 60, pp. 1600-1607, 2005.

[18]Fadi A.M., Bernard L."Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 1. Equilibrium parameters", Journal of Hazardous Materials vol.170, pp.744-753, 2009

[19]OualidH., Naffrechoux E."Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two- parameter models and equations allowing determination of thermodynamic parameters", Journal of Hazardous Materials, Vol.147, pp.1-14, 2007.

[20] Gouli B.I.M, Yapo A.J., Ello AS, Diabaté D., Trokourey A., Adsorption of Acetic and Benzoic Acids from Aqueous Solutions on Activated Carbon. J. Soc. Ouest-Afr. Chim., vol. 26, pp.53-57, 2008.

[21]Nuray Y.R., Hülya K., Ayla C. "Adsorption of benzoic acid and hydroquinone by organically modified bentonites", Colloids and Surfaces A: Physicochem. Eng. Aspects, vol. 260, pp. 87-94, 2005.

[21] Daneshvar N., Aber S., Khani A. "Study of Imidaclopride removal aqueous solution by adsorption onto granular activated carbon using an on-line spectrophotometric analysis system", Journal of Hazardous Materials, vol.144, pp.47-5, 2007.

[22]Muhammad A.B., Shafi M.N., Syed T.H.S., Muhammad I.B., "Adsorption and Leaching Potential of Imidacloprid Pesticide through Alluvial Soil",American Journal of Analytical Chemistry, Vol.3, pp.604-611, 2012.

[23]Azza K., Ahmed El N., Amany El-S., Ola A."Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon", Desalination, Vol.238, pp.210-232, 2009.