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Study of adsorption of imidacloprid onto two different textures of soils

Yao Urbain KOUAKOU[1*], Ardjouma DEMBELE[2], Aimé Serge ELLO[1],
Yapi Serge BROU[1], Brou Lazare YAO[2] and Albert TROKOUREY[1*]

[1]UFR SSMT, Laboratoire de Chimie Physique, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire.
[2]Laboratoire Central d'Agrochimie et d'Ecotoxicologie (LCAE), Abidjan, Côte d'Ivoire.
[*]Corresponding author, E-mail: urbainyk@gmail.com, 21 BP 1639 Abidjan 21 Côte d'Ivoire. Tel.: +225 08 01 96 97

ABSTRACT

The main goal of this research is to evaluate the potential for imidacloprid to contaminate water and ground water. For this purpose, the adsorption of imidacloprid on two different soils is investigated. Physicochemical properties such as texture, organic matter, pH of the two soils are investigated. Both soils have high organic matter and the same pH but different textures. The kinetic study of adsorption on these soils over 90 days yielded a mean half-life of 60 days. Furthermore, adsorption kinetics of imidacloprid was studied and the rate of sorption was found to conform to pseudo-second-order kinetics with 3.10 mg/g/h and 10.204 mg/g/h for soils of banana field and cocoa field respectively. Equilibrium isotherm data were analyzed according to Langmuir, Freundlich and Redlich–Peterson equations. The Redlich–Peterson isotherm gave the best correlation for the adsorption of imidacloprid adsorption on soils. The maximum adsorption capacities were determined to be 4.139 mg/g and 5.74 mg/g of soils from banana field and cocoa field respectively.The differences in adsorption capacities may be due to the effect of soils textures.

Keywords: Imidacloprid, soils textures, adsorption, Redlich-Peterson model, Freundlich model, HPLC.

INTRODUCTION

Earth is called blue planet because it contains 72% of water, or 1,360 billion km^3. However, only 2.3% is fresh water available for human needs. Almost all of this freshwater is in ground and basement and, a small percentage in lakes, marshes, atmosphere and water courses (Perrier et al., 2005). But these resources of water are highly threatened by pollution of all kinds of species, especially pesticides. Although pesticides are known to increase production yields, protect food supply, protect against disease vectors and parasites toxin producers (Ayranci et al., 2004; Carvalho, 2006; FAO, 2012). The population growth in contradiction with the needs of human being or the surfaces of available arable land increases more and more the use of pesticides. Unfortunately, once ejected, pesticides undergo several physical, biological and chemical process including volatilization, infiltration, retention and degradation which can be harmful to the environment. It is estimated that during spraying pesticides, 25 to 75% is waste in the atmosphere, leading to the contamination of the air, mist and rain. A significant fraction streams then infiltrate to reach and contaminate the surface water and the ground water (Margni et al., 2002). Even, some

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pesticides can contaminate the food through various mechanisms.

Imidacloprid or 1-(6-chloro-3-pyridinylmethyl)-N-nitro-imidazolidin-2-ylideneamine (Figure 1), like most pesticides, is a systemic insecticide which can spread throughout the body of the plant. This character leads to the presence of these insecticides in the nectar and the pollen of the flowers of treated crops (Bonmatin et al., 2005; Stokstad, 2012). As they are powerful neurotoxic to insects, this kind of diffusing insecticides is unfortunately most used in the world (Charvet, 2004). A recent study about leaching of imidacloprid up to 60 cm depth showed that its concentration decreased with depth (Muhammad et al., 2012). However, according to a report from the Ministry of Environment of Quebec, imidacloprid was detected in 35% of groundwater samples collected near potato crops (Giroux, 2003). Moreover, it is very stable in water and hardly degradable in the pH range between 4 and 9. This character leads to its classification as persistent in Soil by ARP (Agency Regulation of Pest). According to Canadian council of the environmental minister (CCEM), the half-life typical DT_{50} of imidacloprid is estimated to be 40 days to 2 years (CCEM, 2007.). Furthermore, the adsorption is one of the important phenomena in the process of degradation, which itself depends on several parameters such as physico-chemical properties of the soil, the contact time and the method used to assess the adsorption. The mobility of imidacloprid in soil, taking account the pH, or the structure of the soil has been the subject of extensive investigation (Sabbagh et al., 2002; Papiernik et al., 2006). However, no work on the influence of the soil type on the adsorption of imidacloprid has been conducted yet. The present work aims at studying the adsorption of imidacloprid on two different textures of soil, mainly in order to know the favorable soil for the degradation of imidacloprid. For this, we used a fast reliable and inexpensive extraction method based on solid-liquid extraction. This study is important in order to minimize the risk of water contamination for country such as Ivory Coast (Côte d'Ivoire), where imidacloprid constitutes more than 50% of insecticide used in agriculture (MINAGRI, 2012).

MATERIALS AND METHODS

Materials

Imidacloprid standard high purity (98%) was provided by Dr. Ehrenstorfer GmbH (Germany) and used to have calibration data for HPLC analysis and Commercial imidacloprid solution called CAO-NET 30 SC with concentration 30 g/L manufactured by SOFACO AF- CHEM purchased from local market (Abidjan, Côte d'Ivoire) used as pesticide which will be study. The concentration of imidaclopid was analyzed using on HPLC system Shimadzu Prominence LC-20A series equipped with UV-Vis detector SPD -20 A (set on 252 nm), Shimadzu interchrom ODS C18 (250 x 4.6 mm) and a computer system to check solvent gradient. Sieves with different pores for soil texture, a muffle furnace (Nabertherm West Germany) preheated to the 375 °C for determination of organic matter and a pH-meter (multipara-meter HQ 40d) were also used.

Methods

Study Area

Two types of fields were selected for the study. The first field is used for the cultivation of bananas located in Attinguié, North of Abidjan (soil A) and the second field is for the cultivation of cocoa located in Azaguié, east of Abidjan (soil B). Both fields underwent treatment with imidacloprid.

Simple preparation

Standards solutions from high purity of imidacloprid and those prepared with commercial solution were prepared following the same simple protocol. Indeed 2 mL of stock solution were taken and dissolved in distilled water to obtain new solutions at lower concentrations and detectable by high performance liquid chromatography (HPLC) analysis. Acetic acid was used to prepare 0.01% solution of acetic acid in water for HPLC analysis. The other reagents have not undergone pretreatment.

Characterization of soils

For the soil texture, 10 g of soil were used and separated with different sieves (2 mm, until 0.002 mm pores). So, the sizes of the soil which sieve are higher than 2 mm correspond to sand and under 0.002 mm to clay (Ben Hassine H, 2006). A muffle furnace (Nabertherm West Germany) preheated to the 375 °C was used to obtain organic matter by Walkley-Black method (Moreno et al., 2001).

Extraction of soil

The samples from the different soils were dried at room temperature for 48 hours to have total dryness. 10 g of dry soil were mixed with 20 mL of acetonitrile in a screw cap tube of 50 mL, and then the mixture is placed on a magnetic agitator for 30 minutes at a speed of 160 rpm. After decantation, 10 mL of the supernatant are transferred to a flask and evaporated to dryness on rotavapor. The residue is taken up in 5 mL of acetonitrile solution and then analyzed by HPLC to determine the concentration.

Conditions of chromatography analysis

Mobile phase was acetonitrile /0.01% acetic acid-water (40:60, v/v) at a flow rate of 1.0 mL min^{-1}, the volume injected was 20 µL. The recording of peaks for samples with different surfaces was realized with microprocessor-assisted software SHIMADZU. Under this operating condition, the retention time of imidacloprid was 5.33 min.

Statistical method used

In this work, the obtained graphs are the average calculated using $\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$ (each test is done three times), the standard deviation is obtained from $SD = \sqrt{\frac{1}{n-1}\left(\sum_{i=1}^{n}(X_i - \overline{X})^2\right)}$ and the relative standard deviation is performed by $\mathrm{RSD} = 100\,\frac{\mathrm{SD}}{\overline{X}}$.

Limit of detection (LOD)= 3×RSD×concentration (lowest). The limit of quantification (LOQ) defined as the lowest measured quantity above which the analyte can be quantified was obtained by LOQ = 3.3 x LOD (Shrivastava, 2011).

RESULTS AND DISCUSSION

Physicochemical properties of soil

As the physicochemical properties such as pH, texture, organic matter and electrical conductivity of the soil can significantly affect the transfer of the pesticide through the different compartments of environment, these parameters are investigated. The results are shown in Table 1. It can be seen that both soils are acidic. So they would be more favorable for the adsorption of the pesticides such as imidacloprid (Paszko, 2006; Ping, 2010). On the other hand, the values of the organics matters of the soils suggest that the textures of soils can influence adsorption of imidacloprid onto these soils (Madrigal-Monarez, 2004). However, the lower electrical conductivity value of these soils indicates that the contact-time of adsorption would be reduced (Muhammad, 2012).The soil of banana field has higher percentage of sand and a bit of clay (2.6%), but the soil of cocoa field contains an important proportion of clay (18.18). Pesticides could infiltrate the first soil (banana field). As imidacloprid is a polar substance (log Kow = 0.57), it might be retained on soil of cocoa field which has the best proportion of clay and slit (Sheng et al., 2001).

Evolution of imidacloprid on soils

Method performance

The parameters of the extraction method were evaluated. The quality of the extraction is performed by Percent Recovery like this: blank soil of 10 g weight was spiked with 3 different concentrations (0.1, 0.5 and 1 ppm) of imidacloprid standard solutions. The mixture was vigorously vortexed for 12 hours at a speed of 300 rpm to distribute completely the pesticide. The mixture was dried at room temperature. Then the result of the 10 g was mixed with 20 mL of acetonitrile in a screw cap tube of 50 mL, and then the mixture is placed on a magnetic agitator for 30 minutes at a speed of 160 rpm. After decantation, 10 mL of the supernatant are transferred to a flask and evaporated to dryness on rotavapor. The residue is taken up in 5 mL of acetonitrile solution and then analyzed by HPLC to determine the concentration. The recovered percentage of imidacloprid in soil A and B are given in Table 2. The recoveries were found to be 74% for the soil A and 81.12% for the soil B. The percent recovery is higher than 70%. Considering the recent EU guidelines for method validation which mention acceptability criteria of recovery to be between 70 and 120%, these results are in good agreement (Melo et al., 2005; Walorczyk, 2007). So this method could be accepted for imidacloprid extraction onto soils.

Furthermore, the LOD and LOQ are determined and given in Table 2. These values are good and lower than those found by some researchers. LOQ is below imidacloprid MRL estimated to 0.1 mg/Kg (Concha-Grañan et al., 2010; Pizzutti et al., 2007). Retention time is 5.33 min. All these values show that the extraction and the analysis method of imidacloprid are good.

Residual concentrations of imidacloprid in soils

The evolution of imidacloprid concentration on the soils is studied. The results are shown in Table 3. As shown, the concentration of imidacloprid decreases slowly. This slow decrease in concentration suggests that the imadacloprid does not adsorb significantly on this soils. However, compared with adsorption of imidacloprid on each soil it seems that the adsorption is better and quicker on the soil B. The calculated DT$_{50}$ is found to be around 60 days for the soil B while the DT$_{50}$ for the soil A is between 60 and 90 days which are in concordance with the previous work (Sabbagh et al., 2002). This concordance in these results may be due to the pesticide formulation which is SC (Suspension Concentrated) and characteristics of the soils (Sheng et al., 2001; Madrigal-Monarez, 2004; Muhammad et al., 2012). After 90 days, the concentration of imidacloprid in these soils is higher than 0.3 ppm (mg/L) suggesting that this pesticide is persistent.

Kinetic study of the imidacloprid adsorption

The study of the kinetics of the imidacloprid adsorption on the soils was carried out at room temperature. For this study, 1 g of the soil was mixed with 20 ml of 10 ppm of 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, 05, 0.45, 1, 2, 3, 5, 6 and 8 hours. After each contact time, the solutions were filtered and the initial and final concentrations of imidacloprid were determined by HPLC. The amount of imidacloprid adsorbed onto the soil is calculated according to the equation (1):

$$q_t = \frac{(C_0 - C_t)}{m} \times V (1)$$

where q_t is the amount of adsorbed imidacloprid on the soil sample (mg/g), C_0 and C_t are the initial and the final concentration of imidacloprid at time after filtration (mg/L)respectively, V is the initial solution volume (L) and m the mass of the soil sample (g).

Figure 2 shows the kinetic adsorption curves. As displayed, a rapid adsorption until 2 hours followed by a slow adsorption and finally reach equilibrium time at 6 hours can be observed. The rapid adsorption of imidacloprid should be due to the vacant sites which are initially available in the soil, while the observed slow adsorption could be due to a slow migration and diffusion of imidacloprid molecules in soil after the saturation of vacant sites (Paszko, 2006).The equilibrium time found is similar to those reported in literature (Kumar et al., 2006; Pizzutti et al., 2007; Muhammad et al., 2012). This behavior does not depend on the type of soil may but be due the fact that both soils contain the same amount of organic matter.

Besides, the curves of Figure 2 are those of pseudo second order model. Regression coefficients higher than 0.99 are obtained. The adsorption could be a bimolecular process in which a collision between one imidacloprid molecule and one adsorption site occurs. Therefore, this adsorption is chemisorption (Kumar et al., 2006; Fernandez-Bayo et al., 2008). However, the rate constant values are 3.10 mg/g/h and 10.204 mg/g/h for soils A and B respectively confirming thus, the relative slowness of adsorption.

Modeling of adsorption isotherms

The adsorption isotherm indicates the adsorption molecules distribution between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. For this study, 5 g of soil was mixed with 100 mL of different imidacloprid concentrations as 1 ppm, 5 ppm, 10 ppm, 20 ppm et 30 ppm in a 250 ml conical flasks. The reaction mixtures were shaken on magnetic agitator at 200 rpm for equilibrium time (6 hours) at room temperature. After equilibrium, the samples were filtered and analyzed with HPLC. The amount of imidacloprid adsorbed per unit of mass of the soil at equilibrium, q_e, was calculated by:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \qquad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the concentrations of imidacloprid at initial and equilibrium times respectively, V (L) is the volume of the initial solution, and m (g) is the mass of the soil sample. .

Adsorption equilibrium data of imidacloprid on soils were fitted by applying Langmuir, Freundlich and Redlich - Peterson isotherm models, respectively.

Langmuir Isotherm Model

The expression of the Langmuir model is given by: $q_e = \frac{q_m b C_e}{1+bC_e}$ (3) where q_e (mg/g) and C_e (mg/L) represent the amount of adsorbed imidacloprid per unit of mass of soil and imidacloprid concentration at equilibrium, respectively, q_m (mg/g) is the maximum adsorption capacity of the soil and b is a constant related to the affinity of binding sites.

The linear expression of Langmuir model $\frac{1}{q_e} = f(\frac{1}{C_e})$ gives the plots of Figure 3 and parameters in Tables 4 and 5. Correlation coefficients were below 0.95 and the calculated q_m were not appropriated to use as maximum capacity of imidacloprid adsorption onto these soils suggesting that the adsorption of imidacloprid did not obey Langmuir isotherm. So soils were therefore not homogeneous.

Freundlich Isotherm Model

The relation between the amount of adsorbed solute q_e (mg/g) and his concentration at equilibrium C_e (mg/L) for Freundlich adsorption isotherm is given by equation (4):

$$q_e = K_F C_e^{1/n} \qquad (4)$$

Where K_F[(mg/g)(L/mg)$^{\frac{1}{n}}$] is a constant related to adsorption capacity and n is a measure of surface heterogeneity (Hamdaoui and Naffrechoux, 2007).

The plots of $\ln q_e = f(\ln C_e)$ is given in Figure 4 and parameters of this model in Tables 4 and 5. The correlation coefficients, R^2 are higher than 0.96 then, this model may obeyed the sorption of imidacloprid. The value of n is 1.518 and 1.439 for the soil A and B respectively. As $1 < n < 10$ suggests that the adsorption process may be favorable, so the soils are heterogeneous (Al-Mutairi, 2010).

Redlich - Peterson Isotherm Model

Redlich–Peterson isotherm is an empirical model that incorporates features of the Langmuir and the Freundlich isotherm models to represent equilibrium data by:

$$\mathrm{Ln}\left(\frac{q_m K_L C_e}{q_e} - 1\right) = n\mathrm{Ln}C_e + \mathrm{Ln}K_L \qquad (5)$$

Where K_L (L/mg) and q_m (mg/g) are constant at equilibrium of Langmuir and maximum amount of imidacloprid, respectively and n like « n » of Freundlich ranging from 0 to 1 (Hamdaoui and Naffrechoux, 2007).

The plots obtained by application of this model are shown in Figure 5 and model parameters are given in Tables 4 and 5. This adsorption isotherm with $R^2 > 0.99$ describes better than the previous isotherms. Therefore, the adsorption of imidacloprid on both soils is less multilayer with non- uniform distribution of adsorption heat and affinities (Samiey, 2010). This can explain why these soils retain weakly imidacloprid. However, adsorption capacities of these soils are higher than those of many of soils studied by adsorption of organic pollutants onto them (Pizzutti et al., 2007; Muhammad et al., 2012).

Table 1: Physicochemical properties of the soil.

Soils Parameters	Banana field	Cocoa field
pH	5.33	5.11
Electrical Conductivity (µS/cm)	0.11	0.12
Organic Matter (%)	9.98	10.16
Clay (%)	2.6	18.18
Sand (%)	91.17	64.32
Slit (%)	6.23	27.52
Classification	Sandy	Sandy Loam

Table 2: Recoveries, LOD and LOQ of method.

Parameter	value	
	Soil A	Soil B
Percent recovery (%)	74% ± 1.02	81.12 ±1.04
LOD (µg/Kg)	0.013± 0.00027	0.012± 0.00018
LOQ (µg/Kg)	0.042± 0.0009	0.039± 0.0006

Table 3: Evolution of imidacloprid on soils.

Time (day)	Soil of cocoa field		Soil of banana field	
	Concentration (mg/L)	Percent of remain (%)	Concentration (mg/L)	Percent of remain (%)
1st	1.43125	0	1.19832	0
3rd	1.36421	4.68	1.18567	1.06
7th	1.30135	9.05	1.04007	13.20
10th	1.20136	16.06	0.89777	25.08
15th	0.93757	34.49	0.72423	39.56
30th	0.84453	40.99	0,69737	41.80
60th	0.72145	49.59	0.58668	51.04
90th	0.30456	78.72	0.21132	82.36

Table 4: Equilibrium adsorption isotherm values for imidacloprid: a) onto soil A.

Soil A	Model	Parameter	Value
	Langmuir	q_m (mg/g)	13.532
		b	0.327
		R^2	0.9238
	Freundlich	K	27.816
		n	1.518
		R^2	0.984
	Redlich-Péterson	q_m (mg/g)	4.139
		K_L	1.069
		n	0.364
		R^2	0.9948

Table 5: Equilibrium adsorption isotherm values for imidacloprid: b) onto soil B.

Soil B	Model	Parameter	Value
	Langmuir	q_m (mg/g)	14.701
		b	0.340
		R^2	0.904
	Freundlich	K	31.047
		n	1.439
		R^2	0.965
	Redlich-Péterson	q_m (mg/g)	5.741
		K_L	1.543
		n	0.3587
		R^2	0.9978

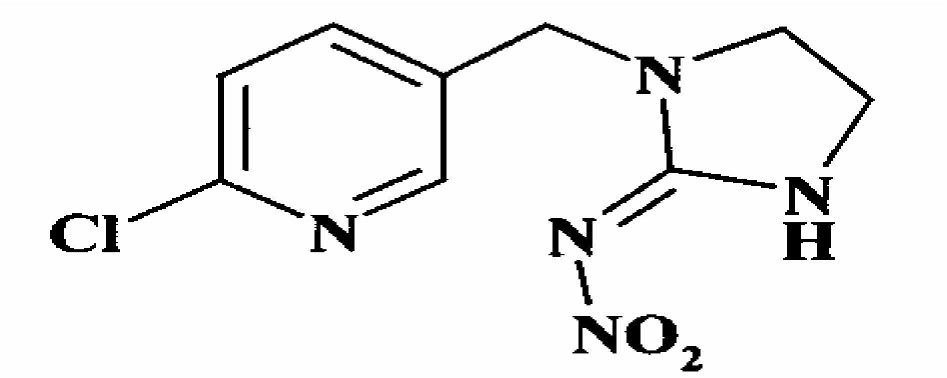
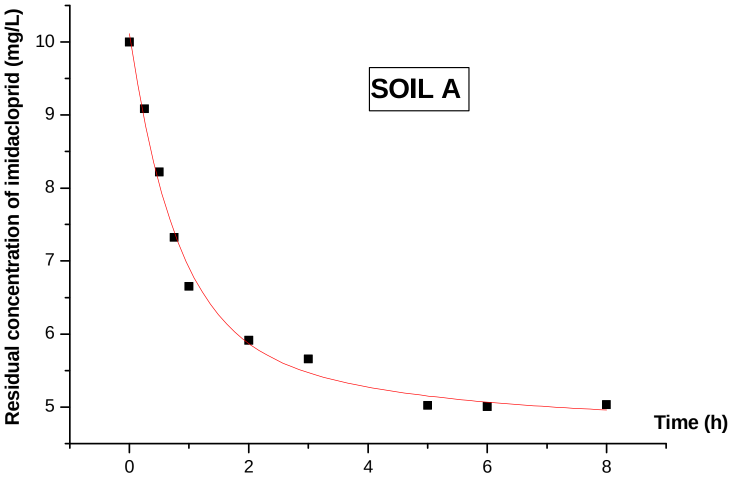


Figure 1: Chemical structure of imidacloprid.



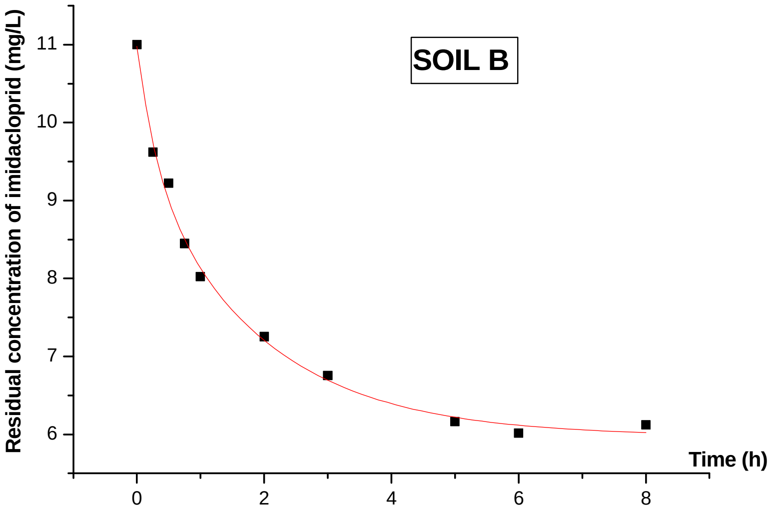


Figure 2: Adsorption kinetic of imidacloprid on soils A and B.

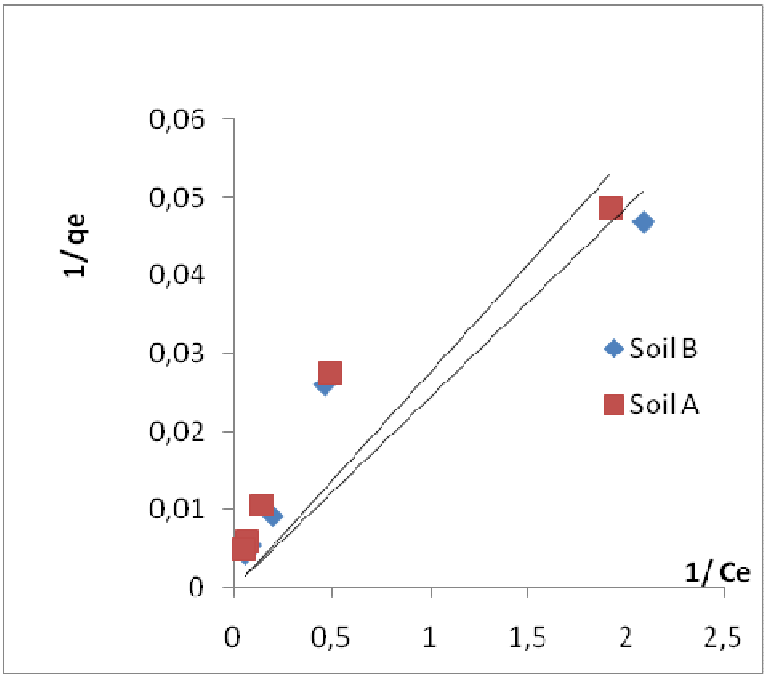


Figure 3: Linear form of Langmuir isotherm for imidacloprid adsorption on soils.

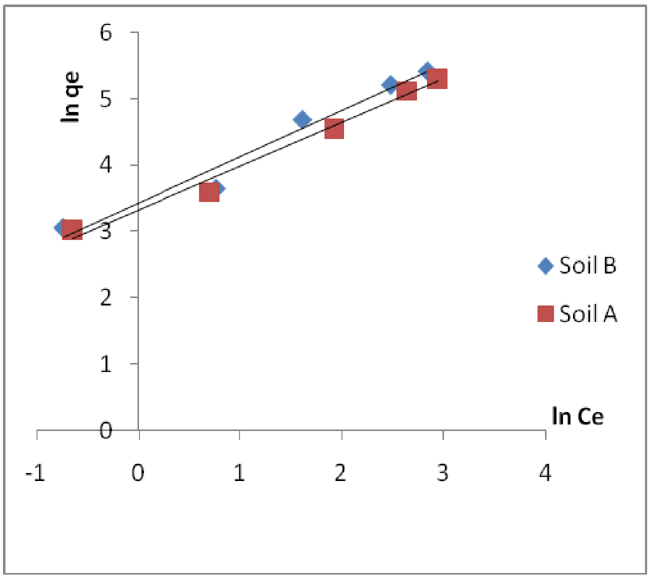


Figure 4: Linear form of Freundlich isotherm for imidacloprid adsorption on soils.

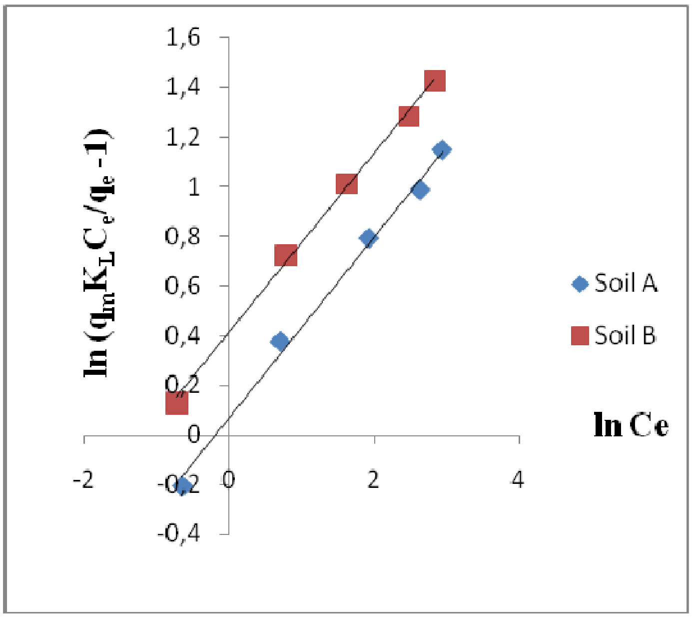


Figure 5: Linear form of Redlich-Peterson isotherm for imidacloprid adsorption on soils.

Conclusion

A very fast and easy method has been developed to determine imidacloprid onto soils using only acetonitrile as solvent. Comparison of imidacloprid adsorption performance onto two different soils revealed that adsorption isotherms are best fitted by Redlich-Peterson and Freundlich models. The adsorption processes were found to follow the pseudo-second order kinetics over a period of 6 hours. It was demonstrated that the surfaces of the soils are heterogeneous and adsorption process is chemisorption.

Soils have high organic matter but different textures. Due to high clay, adsorption is better onto Sandy Loam in cocoa field than Sandy in banana field. The soils do not retain very well imidacloprid and may be potential candidates against diffusion or significant leaching.

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