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Soil speciation and residue analysis for decontamination of imidacloprid: a sustainable resource management model for cotton crop

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ABSTRACT

Cotton is an important commercial fiber crop in the world. Its production is limited by various factors among which pest infestation causes deterioration in lint quality and 10–40% losses in production. To overcome the losses, pesticides are irrationally applied, that in turn; deteriorate the soil quality through residue accumulation. The research is an attempt to present a decontamination model for removal of imidacloprid using soil (as sustainable resource). For this purpose, three composite samples each of soil and field water were analyzed for physicochemical parameters. Soil was sequentially extracted for background concentration of metal species prior to selection of the soil type for adsorption process. Composite soil (KCF2) depicted higher concentration of species bound to organic matter due to low K_{oc}. Residue concentration and degradation pattern was analyzed on GC–MS. Series of batch adsorption experiments were conducted at varying pH as a function of time. Results revealed attainment of adsorbent–adsorbate equilibrium in 45 min following a zigzag pattern and are reasonably approximated by an instantaneous and closed-system equilibrium. Soil provides effective resource management by removing 99.5% of imidacloprid at optimum pH 7. The good fit of Freundlich equation (0.969) approximates for heterogeneous surface energies and exponential distribution of active sites.

Keywords: Residue analysis; Speciation; Adsorption; Imidacloprid; Sustainable approach

1. Introduction

Cotton crop is the lifeline of Pakistan's economy as it accounts for more than 60% of export earnings and about 85% of domestic oil production. It is an occupation of more than 1.5 million farming families and a source of livelihood for several million of labor in the cities and towns. The sale of cotton products accounts as much as 40% of income of rural household.

Pakistan is the land of cotton and on a global basis it is the fourth largest cotton producing country of the world after China, India, and USA. It is third largest consumer, third largest yarn producer with 9%,

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second largest yarn exporter with 26%, third largest cloth producer with 7%, and third largest cloth exporter with 14% of world cotton production [1].

Pakistan's share of total world cotton production in 2004–2005 stood at 9.47%. Its production rose steadily over the years with increase in area from 1.23 to 3.10 million hectares and concurrent production from 1.1 to 14.6 million bales. This phenomenal growth in production is attributed to introduction of high-yielding varieties having better fiber quality characteristics, heat tolerant, wider adaptability, and introduction of improved cotton production technologies across the cotton belt. The soil of the cotton fields in Pakistan has varietal potential and favorable agro-climatic conditions for exploitation of full yield of the present commercial varieties under irrigated.

Cotton crop is mainly grown in Punjab and Sind provinces in Pakistan contributing 81 and 17% in cotton production, respectively. Khyber Pakhtoonkhwa and Baluchistan provinces have potential for cotton production, and it has been identified as most suitable area for organic cotton cultivation.

Pakistan's "Cotton belt" area is known to produce the finest cotton in the World and the major cities representing cotton belt are Khanewal, Multan, Dera Ghazi Khan, Vehari, Faisalabad, and Rahim Yar Khan. However, cotton is considered the world's "dirtiest" crop due to its heavy use of insecticides. Cotton uses 16% of the world's insecticides, more than any other single major crop [2]. The residual and persistent nature of chlorinated pesticides and indiscriminate use lead to many adverse effects, such as, poisoning of the human beings and animals, bioaccumulation, pesticide residues, and destruction of environment.

Pesticides upon application in the field interact through their functional moieties with metal ions present in soils via donor–acceptor mode. In addition, inorganic fertilizers supplement micronutrients such as Zn for optimum crop production [3]. The translocation of pesticides in soil is influenced by the organic matter, clay minerals, hydroxy-oxides constituent, and pH effects. It is known that soil composition drives the pesticide mobilization in a soil matrix. Furthermore, a specific portion of the soil interacts to a contaminant, as well as the time of contact between them [4] is also important.

It is reported that many pesticides are transported to a depth of up to one meter and beyond [5–7] thereby posing a risk to groundwater reservoirs. Available literature showed that in Pakistan, limited scientific data are available for the residual concentration in soil and groundwater.

A large number of studies [8,9] on biological control of pests have been carried out. Still, the synthetic chemicals (pesticides) are considered as a common and reliable source. Furthermore, formulation of imidacloprid is officially recommended in Punjab (Pakistan) cotton belt to be applied as a seed coating for controlling aphids and thrips on cotton plants.

A preliminary survey was conducted for determining the mostly used pesticides in cotton fields. On the basis of survey-data, imidacloprid was selected owing to its popularity in the farmer field. For the present investigation, top soil rich in organic fraction is selected for decontamination of the imidacloprid and its residue. Top soil was also analyzed for chemical speciation of metal to assess the feasibility of soil adsorbent in terms of background concentration of six metal species.

The aim of this study, therefore, was to investigate the residue of the applied pesticide in soil and groundwater to determine long-term effect of the use of these pesticides on farmlands in relation to soil metal content and associated groundwater risk assessment. Furthermore, transport of pesticides through soil by leaching with infiltrating water was also assessed to devise an adsorption decontamination model for sustainable resource management.

2. Experimental

The present study includes extraction of applied imidacloprid on cotton fields and groundwater. Residue concentration and degradation pattern was analyzed on GC–MS. The soil was characterized for its physicochemical parameters ad background concentration of metal species of Pb, Ni, Cd, Cr, Zn, and Cu. Series of batch experiments were conducted at variable pH as a function of time to study the adsorption behavior of imidacloprid.

2.1. Sampling

For the study of total metal and chemical speciation of six trace elements, soil samples were collected from Khanewal city of Punjab. Top soil samples (4–5") were collected from different fields of cotton. A total of 30 sub soil samples were collected in X-pattern from at least three different fields. Composite sample prepared by thorough mixing and blending of 30 sub soil samples representative of whole field was used for the further study and experimental work. The field temperature and pH of the samples were also noted.

Groundwater samples were collected in plastic bottles in triplicate from hand pumps close to cotton fields of Khanewal. Each sample was spiked with

1 mL dichloromethane on-site in order to avoid biological degradation. The sealed bottles were immediately transported and stored in an air-conditioned room till further use.

2.2. General procedure for extraction of imidacloprid

GC–MS is one of the most effective methods to determine pesticide residues [10–13].

2.2.1. Extraction from water

Water sample (250 ml) containing 5–20 μg/L of imidacloprid was mixed and stirred with 0.4 g of NaOH. Mixture was heated in water bath at 85˚C for 15 min, cooled, neutralized with hydrochloric acid, and extracted in chloroform repeatedly.

The extracts were mixed, dehydrated with anhydrous sodium sulfate, filtered, and concentrated to a few milliliters in a rotary vacuum evaporator and injected to GC–MS system. Calibration graph was constructed using solutions of imidacloprid of known concentrations.

2.2.2. Extraction from soil

Soil sample (50 g) and 100 ml of deionized water were treated in an ultrasonic bath for 15 min. Mixture was filtered and chloroform was added for extraction.

2.3. Physicochemical characterization of soil and water samples

For soil and water samples characterization, selected physical and chemical properties were determined using the well-established laboratory procedures.

Potential for hydrogen ion (pH) and electrical conductivity (EC) was measured using the pH (720, inolab, Germany) and EC meter (CyberScan Con 500, Singapore). Bulk density and soil moisture content were determined by the standard procedures. The soil moisture content was calculated with the help of the following formula:

$$\text{Soil moisture content} = \frac{\text{Wet soil} - \text{Dry soil}}{\text{Dry soil}} \times 100$$

Soil organic matter was determined by Walkley Black method [14]. The percentage of organic matter was calculated by using the following formula:

$$\%\ \text{Organic matter} = \frac{\text{Total C} \times 1.72}{0.58}$$

The % total carbon was calculated from:

$$\%\ C = \frac{(B - S) \times \text{M of Fe}^{2+} \times 12 \times 100}{\text{g of soil} \times 4{,}000}$$

where B is the ml of Fe^{2+} solution used to titrate blank, S is the ml of Fe^{2+} solution used to titrate sample. 12/4,000 = milli-equivalent weight of C in g.

Nitrate concentration was determined by using the UV–visible spectrophotometer (UV-1601, Shimadzu) at wavelengths 430 nm. The chlorides were calculated by multiplying the volume of the acid used (HCl) with 354.3.

Cotton field water samples were run on calibrated COD meter for measurement of chemical oxygen demand.

2.4. Metal speciation procedure

Chemical species content for six selective trace-metals, that is, Zn, Pb, Ni, Cd, Cu, and Cr was experimentally determined through sequential extraction into filtrate A and residue A; filtrate B and residue B; filtrate C and residue C; and filtrate D and residue D. The extracted filtrates A–D were analyzed for the determination of concentration of exchangeable, carbonate bound, Fe/Mn oxide bound, and organic matter bound chemical species [15], respectively, in the soil samples for six elements with the help of the flame atomic absorption spectrophotometer (SpectrAA220, Varian, Australia).

2.5. Batch experiment

The batch experiments were designed to determine the adsorption capacity of the cotton field soil samples toward the selected pesticide. Composite soil sample of KCF2 was further applied as adsorbent due to relatively higher organic content and low K_{oc} in comparison with other two soil samples. Batch studies were conducted with commercial imidacloprid; however, pesticide standard obtained from (Ali Akbar Group, Pakistan) was used for the calibration. The active ingredient (3.17%) in commercial pesticide was determined experimentally from calibration curve of the standard pesticide.

Three separate sets of batch experiments were conducted for the adsorption studies at variable pH of 4, 7, and 10. For each batch, sample was extracted at regular intervals of two minutes till the equilibrium is attained. Each extract was run on the pre-calibrated UV–visible spectrophotometer (UV-1601, Shimadzu, Japan) at 270 nm ($\lambda_{\max}$ for pesticide) and absorbance was noted. Concentration of each extract was determined from the standard calibration curve.

The K_d values were calculated with the help of following formula:

K_d = amount of pesticide in adsorbent/amount of pesticide in solution $\times 1/S$

The K_{oc} values were calculated as:

$$K_{oc} = K_d/OC \times 100$$

2.6. Adsorption isotherms

Adsorption equilibrium models of Langmuir [16] and Freundlich [17] were applied on adsorption data. The best fitting isotherm was evaluated by linear regression, and the parameters [18] obtained from the intercept and slope of the linear plots of these models.

3. Results and discussion

The present research is planned to cover three aspects: (a) to detect the residual concentration of imidacloprid in water and soil samples collected from cotton fields of Khanewal using GC–MS, (b) determination of physicochemical parameters and concentration of metal species in soil on FAAS, (c) batch adsorption experiment for decontamination of applied imidacloprid with natural material soil as adsorbent.

The objective of the study is to suggest a resource managed decontamination model for the soil loaded with pesticide residues using same soil as adsorbent.

3.1. Residue analysis

Soil and water samples run on GC–MS for residue analysis of imidacloprid depicted different fragments identified on the basis of mass to charge (m/z) and relative intensity of each peak. Fragmentation pattern of soil shows imidacloprid primarily breakdown into imidacloprid urea (m/z 211) and 6-hydrooxynicotinic acid (m/z 139) which then results in the formation of CO_2 (m/z 44) also reported [19,20].

On the other hand, imidacloprid urea was detected as the only and most significant metabolite in water samples. The results are comparable to study conducted by Zheng and Liu [21] identifying one metabolite via hydrolysis. The lower residual concentrations of imidacloprid fragments in soil may be attributed to low K_{oc}.

The present study depicts that lower is the K_{oc}, less is the residual fragments following sequence KCF2 (202) through KCF3 (292) to KCF1 (309). On the other hand, residual fractions in water were found higher. It may be related to higher COD values in three field water sample as KCF1 (920 mg/L), KCF3 (600 mg/L), KCF2 (280 mg/L). COD of water revealed an inverse relation with organic matter content in soil samples (see Table 1).

The residual analysis concludes that soil can serve as a better degradation agent, as soil has a low potential for bioaccumulation [22] of imidacloprid. It was selected as decontamination adsorbent material.

3.2. Physicochemical analysis

Three composite samples of soil and three field water samples were collected from three different cotton fields of Khanewal (KCF1, KCF2, and KCF3). Each composite sample was analyzed for physicochemical parameters to determine the pH, extent of organic matter, and chemical oxygen demand as important aspects affecting the adsorption process. Results are summarized in Table 1.

pH of soil samples is found relatively higher than field water samples. The arid and semi-arid environments (such as in Pakistan) have soils rich in cations (Ca^{+2}, Mg^{+2}) and soluble carbonates and bicarbonates, making soil alkaline [23]. The results of present study are comparable to soil samples collected from agricultural fields (pH 7.52–7.84) [24].

Table 1
Physicochemical characteristics of soil and field water samples

Sample codes	KCF1	KCF2	KCF3
Soil samples			
pH	7.90	7.97	7.92
EC (mS/cm)	6.76	4.74	6.66
Bulk density (g/cm^3)	1.25	1.31	1.28
Moisture content (%)	0.19	0.16	0.13
Organic matter (%)	4.74	4.98	4.78
Nitrates (mg/kg)	28.6	10.4	14.8
Chlorides (mg/kg)	1806.93	1257.76	1877.79
Field water samples			
pH	6.73	6.55	6.37
EC (µS/cm)	315	310	316
Turbidity (NTU)	3.3	8.5	20
TDS (mg/L)	189	186.3	189.7
COD (mg/L)	920	280	600
Chlorides (mg/L)	188	181	195
Nitrates (mg/L)	18.05	10.2	15.12

It is clear that parameters did not exhibit intra-sample variations. It may be attributed to the fact that cotton fields of same city are selected. However, the results contributed to selection of sample (KCF2) for further adsorption studies owing to relatively higher organic matter and less COD in comparison with other two samples (KCF1 and KCF3).

3.3. Soil metal speciation

Residual soil was also characterized for chemical species of six metals, as metals are known to bind to form larger and stable complex with imidacloprid and thus resist to degradation. Speciation of Cd, Cr, Cu, Ni, Pb, and Zn was subjected through sequential extraction procedure.

Speciation of metals into chemical fractions identified in the soil samples of Khanewal is shown in Fig. 1. The presence of cadmium in exchangeable, carbonate bound, Fe–Mn oxide, and organic bound species average values favors its prevalence in carbonate bound fraction. Nickel species shows more concentration range from 0.06 to 1.92 mg kg^{-1} than other species and order followed is Fe–Mn oxide > carbonate bound > organic bound > exchangeable.

Cr species shows significant variation of species concentration in three different soil samples that may be due variable contributing sources of Cr to soil [25]. Relatively higher fraction of Fe–Mn oxide, chromium is reported due to its labile nature through water and other supporting systems [26].

Lead Fe–Mn oxide fraction shows significantly higher concentration followed by carbonate bound, exchangeable and organic bound, respectively. It has been investigated that Pb either co-precipitates with metal oxides or is adsorbed at metal oxide surface, thus retaining this chemical species into soil as long-term source of contamination [27].

The metal speciation analysis shows that zinc follows the same order as that of lead with (Fe–Mn oxide) fraction to the extent of 40% followed by carbonate 36% confirming the fact that Zn-oxides in soil are easily transformed mainly to carbonates [28].

It can be seen (Fig. 1) that most of the copper distribution is in carbonates followed by organic bound. In similar study by Alina [29], greatest amount of Cu has been found for Fe–Mn oxides fraction. On the other hand, exchangeable fraction of copper has the lowest concentration as this fraction does not hold much copper.

The speciation study concludes that KCF2 having higher organic matter (4.98%) shows relatively more species bonded to organic fraction. It is also noted that organic matter bound species of toxic metal Cr is only found in KCF2. This peculiar feature also recommends the selection of KCF2 soil as adsorbent.

Pearson's co-relation studies at significance level of 0.05 (two-tailed) revealed interesting self-paired metal

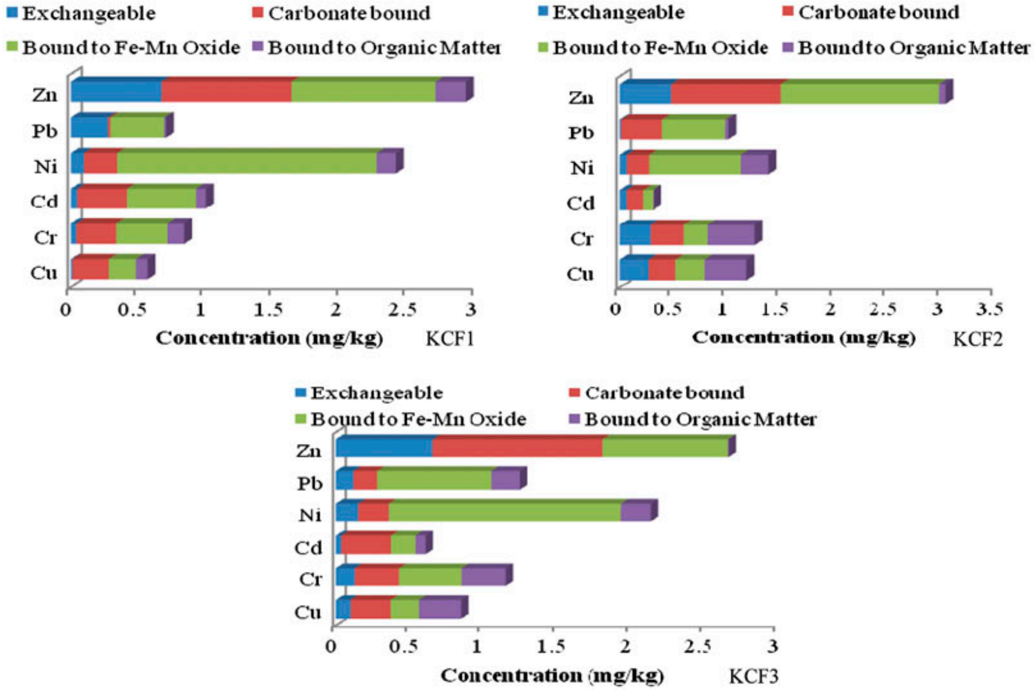

Fig. 1. Chemical fraction of metals in soils of cotton fields of Khanewal.

positive and negative correlation for Cd (carbonate vs. organic) and Cu (carbonate vs. Fe–Mn oxide), respectively. It was encouraging to note that organic bound species of chromium revealed no positive relation with any of the other metal fractions. It further strengthens and optimizes the use of soil as adsorbent.

3.4. Decontamination: batch adsorption

Batch experiments were conducted to determine the adsorption capacity of soil of selected cotton fields for imidacloprid. The batch experiments were designed to determine the adsorption capacity of the cotton field soil samples toward the selected pesticide. Composite soil sample of KCF2 was further applied as adsorbent due to relatively higher organic content and low K_{oc} in comparison with other two soil samples. The results are comparable to another study where adsorption of polycyclic aromatic hydrocarbons (PAH) was found high on garden soil due to higher organic matte [30].

Nine sets of batch experiments were administered to investigate the effect of varying pH on pesticide adsorption as function of time.

3.4.1. Effect of pH

The effect of change in pH on pesticide adsorption was investigated at acidic, neutral, and basic range represented by pH (4, 7, and 10).

pH has a significant role on adsorption, and pH 7 is observed as optimum for adsorption of imidacloprid. On close investigation, it also appears that in moving from acidic through neutral to basic range the equilibrium time increases as shown in Fig. 2(a). A noteworthy dimension of the effect of pH on the equilibrium time shows that both have a direct relation; time to attain equilibrium increases with increase in pH and this effect is manifested strongly at pH 10.

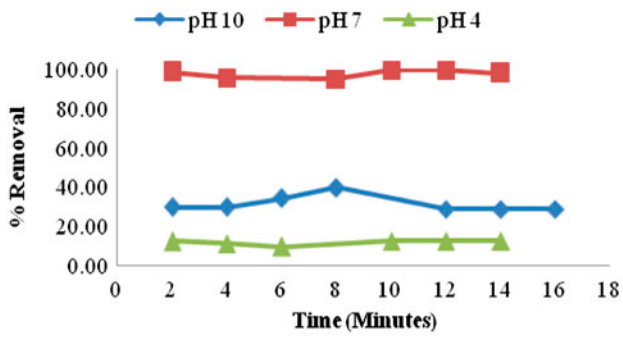

Fig. 2(a). Effect of pH on adsorption of imidacloprid.

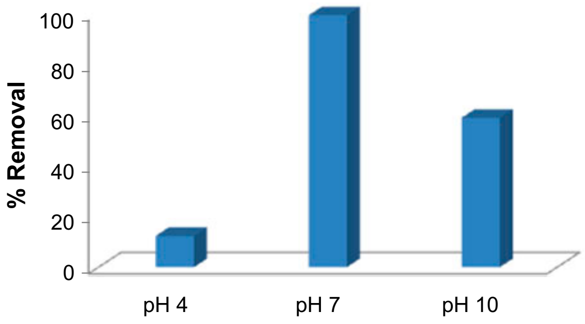

Fig. 2(b). % Adsorption of imidacloprid at different pH.

Time, pH, and percent adsorption also reveal interesting relationship. More adsorption is observed at relatively higher pH; however, lower pH adsorbs more quickly. pH 4 has lower adsorption than pH 7 and 10 for the entire duration of contact (see Fig. 2 (a)), depicting a non-competitive behavior.

This behavior may be attributed to the surface functional group of the pesticide and nature of the characteristics of surface soil making the adsorption complex. Increase in pesticide uptake through neutral toward basic pH is investigated in the realm of acidic nature of pesticide as pH of imidacloprid is reported in range of 4–9. So, the increase in adsorption depends on the pesticide structure and its nature.

The general trend of pH effect on percent adsorption follows the sequence as pH 7 > pH 10 > pH 4. It is also noted that a significant increase of 40 and 87 orders of magnitude in shift from neutral to basic and neutral to acidic, respectively (see Fig. 2(b)). Similar trend of increase in adsorption trend at low pH was also observed by Qian et al. [31].

3.4.2. Effect of time

The purpose of studying the effect of time on adsorption is to establish the equilibrium reaction time between adsorbent and adsorbate.

The adsorption batch experiments are investigated till the achievement of equilibrium. The present batch experiments follow dynamic equilibrium resulting in different sets of equilibrium interactions. Results show that time is a significant factor contributing largely to adsorption under different sets of conditions. Adsorption is a time dependent parameter as time is required for adsorbate to diffuse into the adsorbent [32]. A number of studies relate to the fact that reaction increase with an increase in time, thus affecting the equilibrium achievement.

It is interesting to relate equilibrium time in the realm of induced concentration, pH, and adsorbent mass. Each parameters affect in its own way toward attainment of equilibrium. It is observed that generally equilibrium time increases with increase in mass (see Fig. 3) depicting a linear relationship. This is related to the fact that increases in soil contents increase time to equilibrate adsorbate with adsorbent [33]. However, an inverse trend is reported by Gamal et al. [34]. On other hand, lower the pH, less time is required to approach first equilibrium (see Fig. 2(a)).

3.5. Adsorption trends

Adsorption capacity for imidacloprid is assessed in relation to its adsorbed concentration till equilibrium. A sorption–desorption pattern is very evident, and it signifies that adsorbent–adsorbate interaction in a solution either toward or away from the surface.

Adsorption models of Freundlich and Langmuir (Figs. 4 and 5) were applied to conduct the isotherm studies. On average, it can be seen that soil as adsorbent behaves ideally for the removal of imidacloprid.

Estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the materials was calculated using the Langmuir isotherm model since the saturated monolayer isotherm can be explained by the nonlinear equation of Langmuir Equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}$$

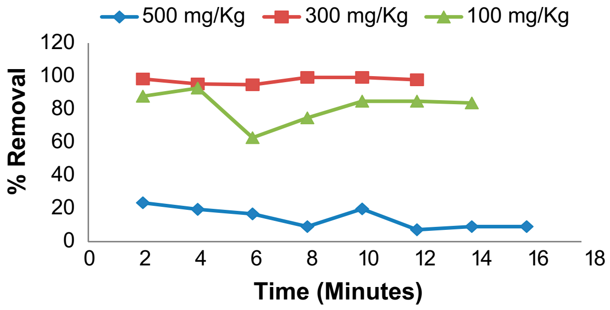

Fig. 3. Removal of imidacloprid as a function of time at varying adsorbent mass.

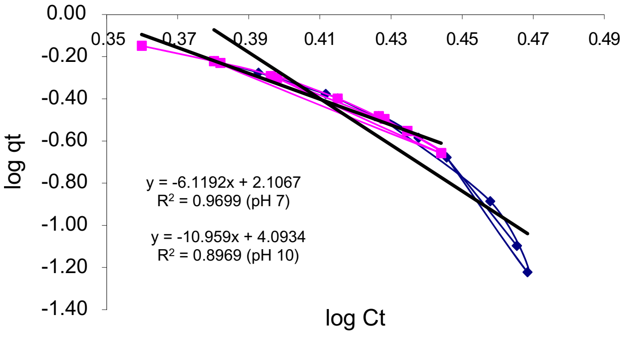

Fig. 4. Freundlich isotherm plot for adsorption of imidacloprid on soil.

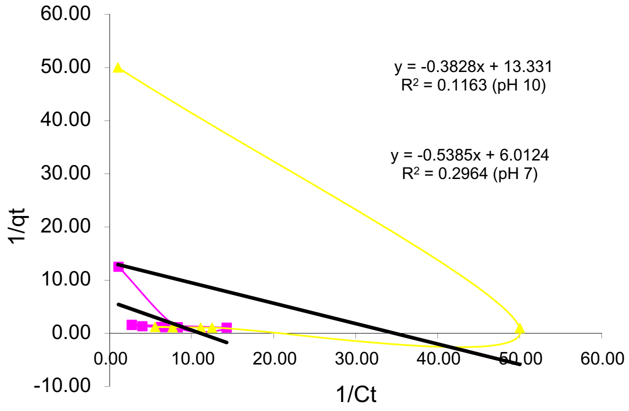

Fig. 5. Langmuir isotherm plot for adsorption of imidacloprid on soil.

Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents [17]. The Freundlich equation is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

It is generally observed that the rate of uptake of imidacloprid is rapid in the beginning followed by a zigzag pattern. This behavior is reasonably approximated by an instantaneous equilibrium. It can be explained on the basis that initially, there is a rapid reversible sorption of the solute adhering to accessible sites of the soil surface.

The present study investigation suggests a close system experiment having both adsorption and desorption as necessary for pesticide mobility characterization [35]. Due to the matter of fact that a variety of artifactual processes and effects take place when a batch equilibrium experiment is performed, followed by a subsequent desorption experiment.

Furthermore, Freundlich model is significant with correlation coefficient of 0.969 (Fig. 4). The Freundlich model is a case for heterogeneous surface energies, and it gives an exponential distribution of active sites.

4. Conclusions

The following conclusions can be drawn from the present study:

- Lower residual concentrations of imidacloprid in soil in comparison with water indicated that soil can serve as a better degradation agent.
- Chemical fractions identified the prevalence organic bound fractions due to low K_{oc} and higher organic matter content.
- The toxic species of Cr did not show any positive correlation indicating negligible effect of Cr on other chemical species and suggesting safe use of that soil as adsorbent.
- Adsorption experiments optimize pH 7 and 45 min of contact in decontaminating 99.5% of imidacloprid on soil.
- The good fit of Freundlich equation (0.969) approximates for heterogeneous surface energies and exponential distribution of active sites.
- The study recommends that soil as adsorbent can be effectively used for removal of imidacloprid and provides a good and environment friendly resource management.

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