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Contribution to the elimination of Linuron by the adsorption process using Chitin and Chitosan biopolymers

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Abstract

Fishing industries generate each year, millions of tons of marine shells rich in chitin. These residues are discharged into the sea or buried in the ground. However chitins have a high economic value due to their physicochemical properties and their industrial and biomedical applications. Modern agriculture relies on extensive use of pesticides, which generate a number of risks, specially the contamination of groundwater. Studies carried out in scope of Loukkos perimeter by INRA of Tangier showed the presence of residues in groundwater because the uncontrolled and excessive use of pesticides. The aim of this work was to decontaminate waters using chitin and chitosan as adsorbents of Linuron, a toxic pesticide widely used as herbicide. Chitin is a biopolymer obtained from the shells of shrimp and Chitosan was prepared by deacetylation process in alkali media (NaOH). Characterization of chitin and chitosan was achieved by infrared spectroscopy. Linuron adsorption was carried out using the Batch method under different experimental conditions such as contact time, pH and pesticide concentration. The adsorption process was followed by *in situ* UV-spectrophotometric technique in a specially designed adsorption cell. Linuron adsorption was characterized by studying the adsorption and desorption kinetics and isotherm. The results show that Chitin and Chitosan are good adsorbents for the removal of pesticides from aqueous solutions. The quantity eliminated was depended on the initial concentration of Linuron, herbicide-adsorbent, contact time and pH of solution. The pesticide adsorption on chitin and chitosan is at its maximum at pH [5, 7].The adsorption was described by Freundlich and Langmuir models and the corresponding isotherms were well fitted both to the two models.

Keywords: Chitin, Chitosan, Adsorption, Linuron, Isotherm.

1. Introduction

Water pollution by organic and inorganic chemical pollutants has become a primary public concern in the last few years [1]. Pesticides are organic compounds detected frequently in drinking water and wastewater effluents of pesticide industry and domestic activities [2, 3]. Their presence in surface and ground water is due to their extensive and intensive application in agricultural activities [4]. However, their mobility causes environmental problems particularly those related to drinking water quality. Only a part of the applied pesticides is actually bioactive, while the rest is distributed in the environment and submitted to different processes which can lead to its transport to aquatic ecosystems [5]. In Morocco, as well as in other countries, there is a growing concern about contamination of groundwater by pesticides, generated from intensive agricultural systems [6,7]. Loukkos perimeter (northwest Morocco) is among the most important Moroccan irrigated agricultural area. The major agricultural activity in this zone is intensive horticulture, mainly the production of vegetables such as strawberry, potato, peanut, etc [8, 9]. Several rural and urban communities at Loukkos zone rely heavily on groundwater for drinking water. For example, the shallow unconfined groundwater aquifer under this zone, including R'mel groundwater, provides the drinking water for Larache city and rural communities.

Pesticides are toxic and cancerous even at low concentrations. They have many undesirable side effects to human health [1], include birth defects, toxicology to a fetus, production benign or malignant tumors, nerve

disorders, blood disorders, genetic changes, endocrine disruption and reproductive effect [10]. As a result, many treatment processes have been applied for the removal of pesticides from drinking water and industrial wastewater such as photocatalytic degradation, biological oxidation, advanced oxidation processes, nanofiltration membranes, ozonation and adsorption [11]. The adsorption method is one of the most efficient methods for removing pollutants from wastewater. Also, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available [11]. It has been reported that many different types of adsorbents are effective in removing pesticides such clay mineral [12-14],clay modified [15], clay calcined [16], hydrotalcite [17,18], shale ash [19] and activated carbon [20,21],however very few studies are reported in the literature for the removal of pesticides from water by sea materials such chitin and chitosan [11,22-24]. It has been shown that chitin and chitosan are promising and efficient adsorbents for pesticides [25,26]. Chitin is the second most abundant polysaccharide worldwide after cellulose [27] (Fig.1). It is usually found as a component of crustacean shells [28]. Chitin and chitosan have been used in photography [29], water engineering, metal capture from wastewater [30,31] and solid-state batteries [32]. Recently it has been considered as biomaterial in various fields such as cosmetic, dressings [33], pharmacology [34,35] and biotechnology [36] due to its biocompatibility, biodegradability, and biological activities[37].Chitin (Figure.1) is substantially composed of 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine) units [38]. The most common derivative component is chitosan, obtained from partial deacetylation of chitin [37]. The degree of acetylation (DA) is one of the most important parameter of the two polymers. Various properties of the polymers are closely related to the DA [39]. The solubility of chitosan is depending on DA. When the degree of acetylation is lower than 0.5, chitosan becomes soluble in acidic aqueous solutions and it behaves as a cationic polyelectrolyte [28]. Many techniques are available to determine the DA, such as conductometric titration [40,41], chromatography [42,43], spectrometric methods such as nuclear magnetic resonance (^{1}H NMR) [9, 28] infrared spectroscopy [38,43, 44] and ultra-violet spectroscopy [45,46].

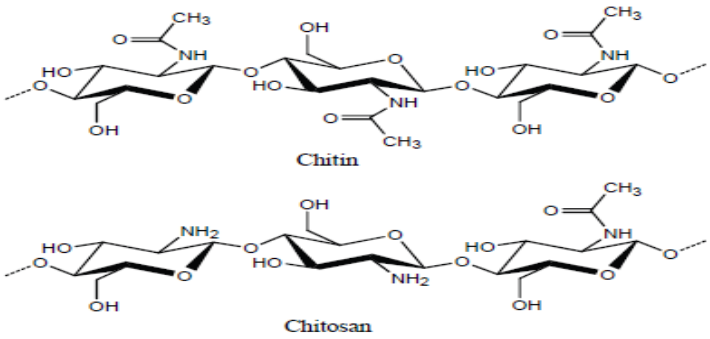

Figure1. Structures of chitin and chitosan [47].

Thus, the main objective of this work is to study the adsorption capacity characteristics of the herbicide Linuron bychitin and chitosan.

Linuronis a substituted urea herbicide (phenyl-urea) used to control many annual and perennial broadleaf and grassy weeds on various crop and non-crop sites (Figure.2). It acts as photosynthesis inhibitors in target weed plants [48]. It is used in soybean, cotton, pea, potato, winter wheat, carrot, corn and sunflower and fruit crops [48]. In Loukkos perimeter, it is used as pre-emergence herbicide mainly on potato, strawberry, peanut crops [8,9,49]. Linuron is suspected of being endocrine disruptors [50]. It is classified as an unquantifiable group C carcinogen and shows some evidence of developmental and reproductive toxicity [51]. Linuron is herbicide with a water solubility of 81 mg. L^{-1}, pKa=12.13, and persistence in soils DT50=47.5 days [52].

2. Materials and methods

2.1. Preparation of chitin and chitosan

The shrimp shells were obtained in solid form from North Moroccan seaside. They were washed, desiccated at room temperature, cut and dried at atmospheric air as long as wanted [28].

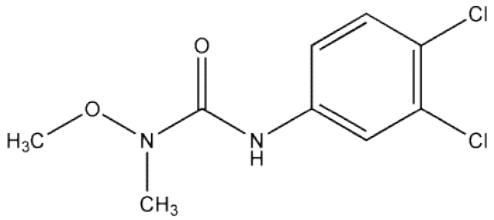

Figure 2: Chemical structure of Linuron

2.1.1. Demineralization

Demineralization step was carried out at room temperature using 0.55M hydrochloric acid baths. Each bath was performed with 100 ml of acid solution and 10g of raw material. The number of baths and their duration (between 15 and 60 min) were dependent upon the source. Demineralization step was followed by pH evolution toward neutrality due to acid consumption. The end of the repeated series of baths was indicated by stability of medium acidity [28].

2.1.2. Deproteinization

The demineralized shell was deproteinized by alkaline treatments with 0,3M sodium hydroxide solutions at 80–90 °C. This treatment was repeated twice during 1h.The absence of protein was indicated by the absence of color of the medium at the end of the last treatment. Washing with distilled water, was then carried out up to neutrality after which the samples were dried. After demineralization and deproteinization steps, chitin was dried in an oven at 50°C during 24 h. At this stage, chitin was lightly pink. The Pigment traces responsible for this color, were removed by H_2O_2 33% [28].

2.1.3. Deacetylation of chitin

The conversion of chitin to chitosan involved deacetylation using the process suggested by Kurita[53]. A suspension of 500 mg of chitin in 30 ml of aqueous sodium hydroxide solution (50% w/v) was heated up to (85-100 °C) under constant stirring. After 9-10h, the solid was filtered off, washed with distilled water to neutral pH, then with methanol, and finally with acetone. Drying was then performed in an oven at 50°C during 12h.

2.2. Characterization of chitin and chitosan

The samples of chitin and chitosan produced were characterized in KBr pellets by infrared spectrophotometer JASCO FT/IR- 410 in the range of 400 to 4000 cm^{-1}.

The Degree of deacetylation (DDA) was calculated using Baxter's equation [54]:

$$\mathbf{DDA\ \% = 100 - (A_{1650}/A_{3450} \times 115)}$$

Where:

DDA: The Degree of deacetylation.

A_{1650} and A_{3450}: The absorbance of bands at1650 and 3450 cm^{-1} respectively.

2.3. Adsorption experiments

Adsorption experiments were carried out by the batch equilibrium technique at room temperature. After adsorption, the supernatants were recovered and the residual pesticide concentration was determined by UV-VIS spectroscopy. The absorbance was performed at 245 nm on a JANWAY 6305 spectrophotometer [55].

Batch tests of Linuron removal were carried out with contact between Linuron solutions and adsorbents under various conditions. For all experiments, adsorbent was added firstto the flasks followed by Linuron solution. The shaking speed was maintained at 380 rpm.

Kinetic studies were performed in a centrifuge tube containing 20 mL of Linuron solution (at a concentration of 10 mg/L with an initial pH of 5.75) and 25 mg of adsorbent at room temperature. Sampling (about 2−3 mL) was undertaken at set periods (0−120 min) to determine the variability in Linuron concentration with time contact.

The effect of Linuron concentration was studied in a series of centrifuge tubes containing 20 ml of Linuron solution at a various concentrations ranging from 1mg/l to 20 mg/l with 25 mg of adsorbent.
The effect of pH was evaluated using a series of centrifuge tubes containing 20 mL of Linuron solution at concentration of 10 mg/L at different initial pH values (5.5−7.5 adjusted by addition of 0.05 M NaOH or 0.05 M HCl) and 25 mg of adsorbent.
The quantity of Linuron adsorbed was determined by the following equation:

$$\boldsymbol{Qe} = \frac{(\mathbf{Co} - \mathbf{Ce}) \times \mathbf{V}}{\mathbf{m}}$$

where *Qe* is the amount of Linuron adsorbed at equilibrium (mg/g), $\boldsymbol{Co}$ is the initial Linuron concentration in liquid phase (mg/L), *Ce* is liquid-phase Linuron concentration at equilibrium (mg/L),*V* is the volume of Linuron solution (L) and *m* is the mass of adsorbent (chitin, chitosan) used in g.

2.4. Desorption experiments
Desorption experiments were carried out with the original chitin and chitosan.The sampling was undertaken to trace variability of water concentration at the same periods of adsorption (0−120 min).

3. Results and discussion

3.1. FTIR analysis
The FTIR spectra of chitin and chitosan are presented in Figure3. Chitin and chitosan showed peaks at 3490 cm^{-1} and 3449 cm^{-1} which are assigned to the intermolecular hydrogen bonds O-H(6)•••O C and O-H(3)•••O-5, respectively [27].The peak at 3490 cm−1 is disappearing in chitosan.
The bands due to NH of the amide group at 3264 and 3109 cm^{-1} in chitin, are assigned to the vibrational modes involved intermolecular hydrogen bonding CO•••HN and the intramolecular bonds NH groups, respectively [27]. These bands are disappearing in chitosan [56]. Two separate peaks were observed at 1656 cm^{-1} and 1626 cm^{-1}which were attributed to the occurrence of the intermolecular hydrogen bond CO•••HN and the intramolecular hydrogen bond CO•••$HOCH_2$, respectively [27], while the peaks due to CH stretching vibrations are observed at 2889 cm^{-1} in chitin and 2878 cm^{-1} in chitosan [57].The absorbance bands at 1414 cm^{-1}in chitin and 1418 cm^{-1}in chitosan indicated the CH2 bending and CH3 deformation [58]. Chitin and chitosan showed peaks at 3490 cm^{-1} and 3449 cm^{-1} which are assigned to the intermolecular hydrogen bonds O-H(6)•••O C and O-H(3)•••O-5, respectively[27] .

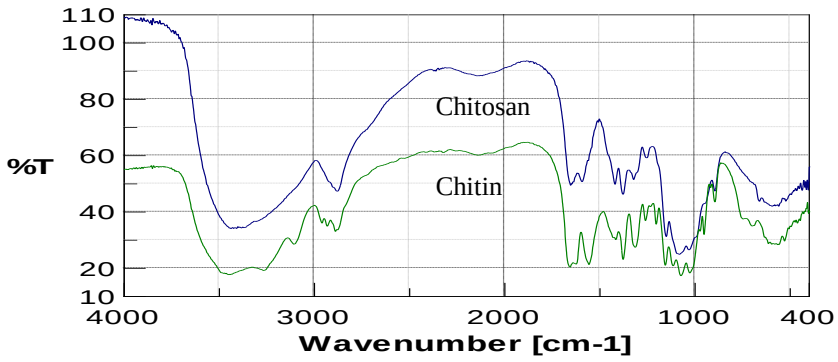

Figure 3: FTIR Spectra for chitin and chitosan.

3.2. Measurements of degree of Deacetylation
The DDA of shrimp chitosan was calculated by Baxter's equation [54]:
DDA=70.26 %
The degree of deacetylation is greater than 50%, so that chitin is deacetylated.

3.3. Effect of contact time

The nature of the adsorption of Linuron on chitin and chitosan is illustrated in Figure 4.It show that % sorption increases slowly with increasing contact time, the adsorption equilibrium state is reached after a contact time of 96 h and 60 h for chitin and chitosan, respectively, since no change in the adsorbed amount is detected afterwards. The rate of adsorption is respectively 56.2% and 63% for chitin and chitosan. The same study was carried out by Harmoudi [11] on the herbicide 2, 4-D.For this author, the adsorption equilibrium state is reached during less than an hour; this is due to the anionic form of 2, 4-D and the protonation of theamino and hydroxyl groups of chitin and the chitosan in acidic medium. Contrary, Linuron exists in three forms due to the mesomeric effect of the carbonyl function (Figure. 5); in such situation, less electrostatics bonds exist between biopolymers and Linuron.

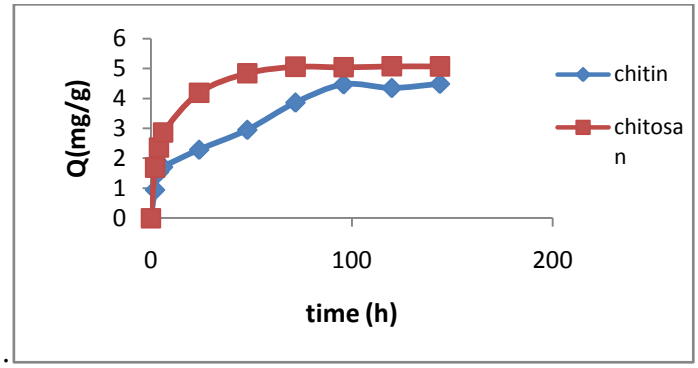

Figure 4: Effect of contact time on Linuron adsorption

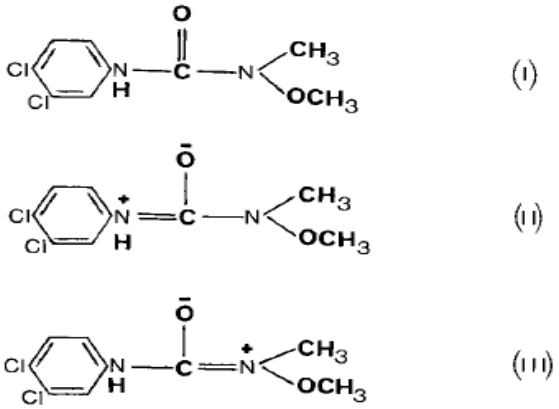

Figure 5: mesomeric structure of Linuron.

3.4. Effect of pH

The pH experiments indicated that the herbicide adsorption on chitin and chitosan is at its maximum at pH=5.75. It appears that adsorption of linuron on chitin involves coordination of the herbicide by nitrogen cations on the nitrogen fonction in chitosan. Chitosan present much higher capacity in adsorbing Linuron than chitin polymer(Figure.6). This could be explained by the fact that chitosan has more amine groups dispersed on the surface than chitin. This group has a great ability to adsorb contaminants due to its Lewis base character [59] (Figure.7).At pH acid, the amino (±NH2) and hydroxyl (±OH) groups of chitin and chitosan are protonated, then to maintain neutrality in an aqueous environment, negative counter ions are adsorbed, which are movable but they are not exchanged by Linuron ions from (II, III) as shown in figure 5.These biopolymers groups are protected.

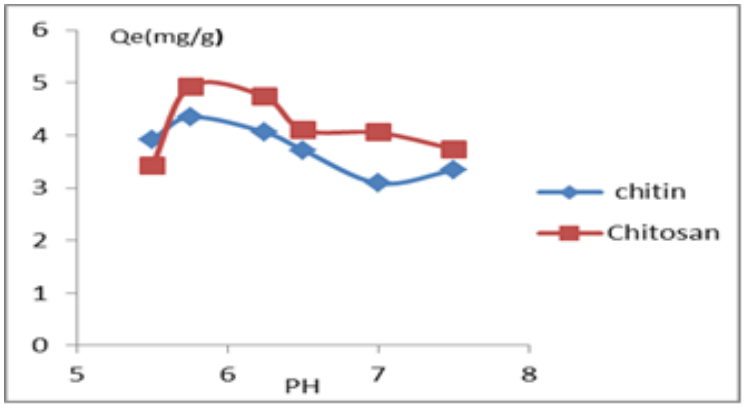

Figure6: Effect of pH on adsorption of Linuron

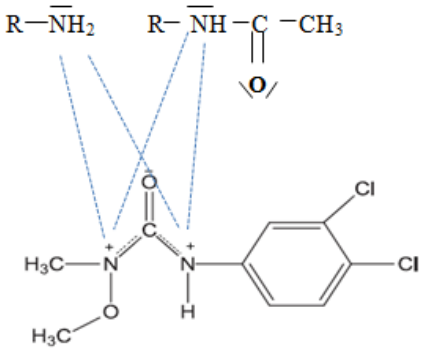

Figure7: Attraction between biopolymers functionand Linuron.

3.5. Adsorptions isotherms

The adsorption isotherms for Linuron by chitin and chitosan are shown in Figure.8. The adsorption isotherms show that the Linuron retention by chitin and chitosan was a L-type curve according to the classification of Giles; it indicates that as the adsorption proceeded, the surface of adsorbent became crowded with adsorbed molecules of Linuron attached to its active spots and as a result it became increasingly difficult for the free Linuron molecule in solution to find a vacant site.

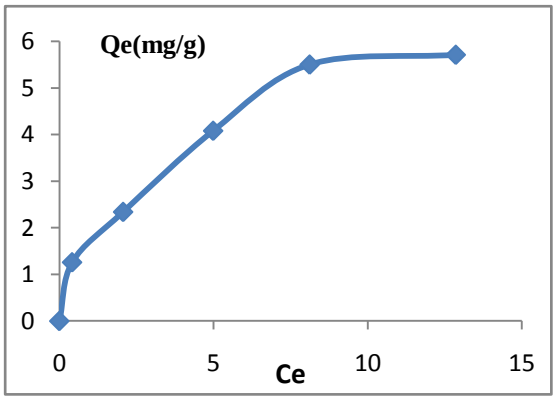

Figure 8.a: The chitin adsorption isotherm.

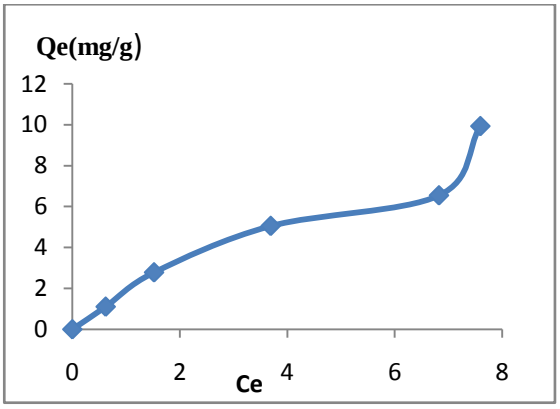

Figure 8.b: The chitosan adsorption Isotherm

Langmuir and Freundlich models were tested to fit the isotherm data for the adsorption of Linuron on chitin and chitosan. The linearized form of Langmuir isotherm is:

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{b\,Qm}$$

Where:

Qe : Linuron sorbed per gram of biopolymer.
Ce: equilibrium solution concentration.
$\mathbf{Q_m}$**:** maximum amount of Linuron that can be adsorbed in a monolayer (sorption capacity).
b: constant related to the energy of sorption.

The linearized form of Freundlich isotherm is:

$$LogQ = Log\ k + \frac{1}{n} LogCe$$

Where :
Q: is the amount of pesticide per unit mass of adsorbent.
Ce: the equilibrium concentration of the adsorbate.
K and **n**: constants that estimate the adsorption capacity and intensity respectively.

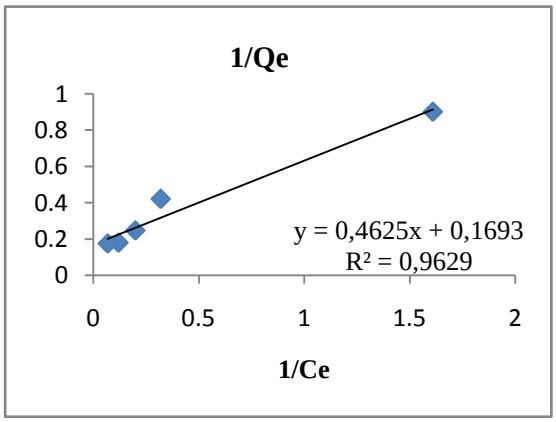

Figure 9.a: Langmuir isotherm for Linuron adsorption by Chitin.

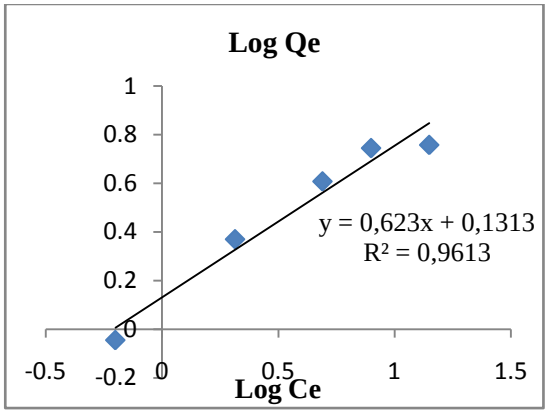

Figure 9.b: Freundlich isotherm for Linuron adsorption by Chitin

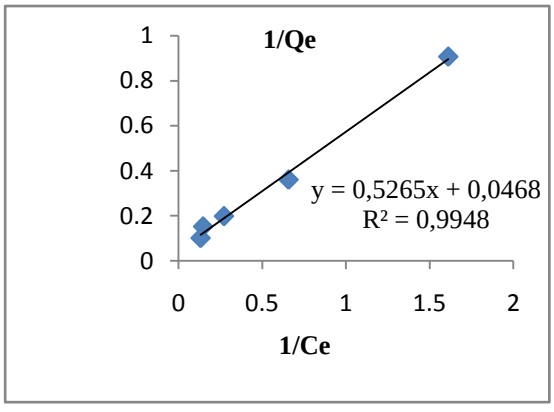

Figure 9.c: Langmuir isotherm for Linuron adsorption by chitosan.

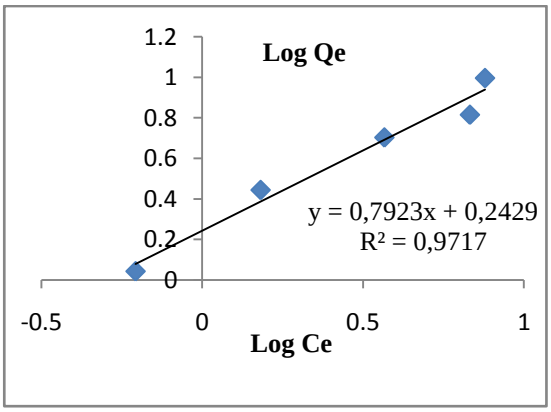

Figure 9.d: Freundlich isotherm for Linuron adsorption by chitosan.

Langmuir and Freundlich parameters of Linuron adsorption are summarized in Table 1.

Table 1: Isotherm parameters for Linuron adsorption by chitin and chitosan.

Polymers	Langmuir			Freundlich		
	Q_{max}	b	R^2	1/n	K	R^2
Chitin	5,91	0,361	0,962	0,623	1,353	0,961
Chitosan	21,73	11,43	0,994	0,792	1,749	0,971

The data of sorption of Linuron by chitin and chitosan were fairly fitted to the Langmuir and Freundlich isotherm models with the regression coefficient (R^2) between 0.961 and 0.994 (Figures: 9.a, 9.b, 9.c, 9.d).It is interesting to note that Langmuir model is more applicable than Freundlich model. These results indicated that Linuron is absorbed by monolayer adsorption with uniform energies and no transmigration of Linuron occurred in the plane of the surface. 1/n is an indicator of the sorption intensity [60]. It has been stated by Anndurai [61] that the magnitude of the exponent 1/n gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values n > 1 represent favorable adsorption conditions according to Treybal [62]. In most cases, the exponent between 1 <*n* < 10 shows beneficial adsorption.

3.5. Desorption kinetic

After the adsorption step, desorption kinetics were determined. The results show that the amounts of liberated Linuron in solution increased as a function of desorption time till 72h, the desorption of Linuron from a chitin and chitosan was 40% and 43% respectively, however, the desorption is slow and incomplete by batch process. These results, compared with adsorption kinetics, showed that an incomplete reversibility of the adsorption occurs corresponding to the Hysteresis phenomenon. The hysteresis of desorption du strong interactions between Linuron and biopolymers because the creation of chemical bonds.

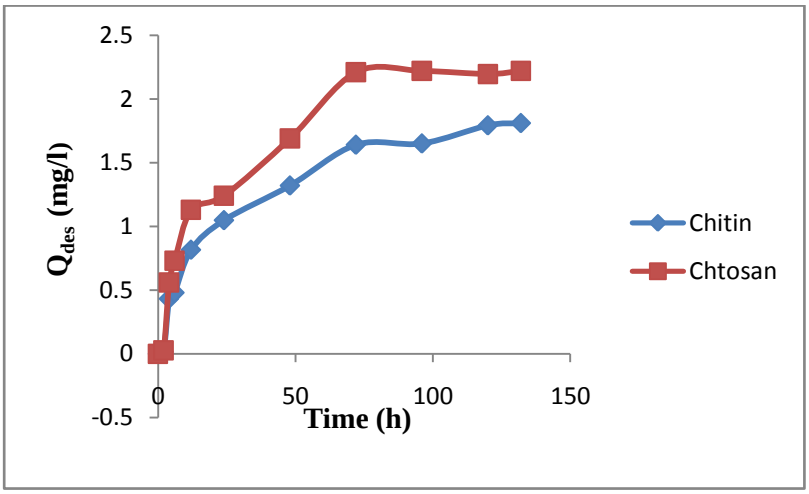

Figure10: Kinetic desorption of Linuron.

Conclusion

The use of chitin and chitosan for removing pesticides from water presents many attractive features such as the outstanding adsorption capacity, especially for the fact, that these materials are low cost, non-toxic and biocompatible. The aim of this work wasto study adsorption capacity of Linuron at chitin and chitosan, The study has shown thatchitin and chitosan can both be used to remove Linuron pesticides in water samples, but the adsorption kinetics of chitin and chitosan is relatively slow, However this leads us to undertake other pesticides and begin to test other chitosan-based adsorbents to improve the quality of adsorption.

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