Toxicol Res. (2023) 39:127–133
https://doi.org/10.1007/s43188-022-00152-2

Online ISSN 2234-2753
Print ISSN 1976-8257

Toxicological Research

ORIGINAL ARTICLE

Explanation of difenoconazole removal by chitosan with Langmuir adsorption isotherm and kinetic modeling

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Received: 7 January 2022 / Revised: 1 June 2022 / Accepted: 22 August 2022 / Published online: 31 October 2022

Abstract

In this study, the adsorption of toxic difenoconazole pesticide was investigated by using chitosan. In the first phase of the study, chitosan was extracted from deep-water pink shrimp (*Parapenaeus longirostris*) shells, by deacetylation of the chitin, which is separated and disposed of after meat extraction in processing facilities in Turkey. The deacetylation degree, molecular weight, viscosity, moisture, and crude-ash values of the extracted chitosan were determined. Chitosan, having a high deacetylation degree (90.21%), was used as the adsorbent. In the second phase of the study, the effects of pH, temperature, and pesticide concentration on the adsorption were investigated. The optimum pH level for pesticide adsorption was determined as 5. It was observed that the adsorption increases as the temperature increases. A rapid increase was observed within the first 5 min of the 60-minute adsorption process in difenoconazole concentrations of 5, 15, and 25 µg/L, and after 10 min, the adsorption rate was stable. The Langmuir isotherm parameters regarding the adsorption were determined as aL = 0.635, kL = 15.10, and the Q_{max} value was calculated as 23.77 mg/g. In the evaluation of overall study results, it was determined that the chitosan biopolymer is a suitable adsorbent for difenoconazole pesticide adsorption.

Keywords Fungicide · Pesticide · Shrimp shell · Chitosan extraction · Adsorption isotherm

Introduction

Pesticides are mixtures containing material(s) used for preventing, controlling, and reducing the damage caused by harmful organisms. Pesticides include insecticides, herbicides, fungicides, and rodenticides, and in the case of their intensive and uncontrolled use, they are likely to leave residues in food, soil, water, and air. As a result of the increased use of pesticides to enhance productivity in agriculture, such chemicals contaminate groundwater and drinking water supplies, in various ways, which leads to pollution and poses a threat to all living beings. The presence of pesticides in water is now a global concern, and the importance of removal studies increases day by day.

Various conventional methods are used in wastewater treatment process, and adsorption leads the way amongst them. Types of adsorptions are known to be physical, chemical, and ion exchange adsorption. The adsorption process is affected by temperature, pH, molecular size, surface area, as well as the properties of the adsorbent and the adsorbate [1]. Most commonly use method in wastewater treatment processes is solid-liquid adsorption. Accumulation of the dissolved matter on water surface depends on the affinity between the solvent and the adsorbent. Nonpolar molecules in the water move towards the interim surface between the adsorbent and the liquid. Consequently, adherence to the adsorbent surface begins, and the surface tension of the solvent decreases. The rate of adherence to the absorbent significantly impacts the efficacy of the water treatment process [2]. Lately, studies are being conducted on the use of chitosan as the adsorbent in adsorption process for wastewater treatments and other industrial applications. Chitosan is the most abundant biopolymer in nature after cellulose. Chitosan

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is obtained by the deacetylation of chitin (poly-β-(1–4)-*N*-acetyl-D-glucosamine), which is extracted from the shells of marine crustaceans such as shrimp, lobster, and crab, and the exoskeleton of arthropods, fungal cell walls, and certain bacteria. Chitosan is apt to be used as a bio adsorbent and to be modified with other chemicals to enhance its adsorption capacity due to its primary and secondary hydroxyl (–OH) and primary amine (–NH_2) groups [3, 4]. Moreover, the wide surface area of chitosan due to its fibrillar structure enables it to absorb organic-inorganic pollutants, dye, phenol, heavy metals, pharmaceutical residues, and other pollutants. Chitosan use in scientific researches increases day by day, due to its efficient adsorption properties for pesticides [5–15]. However, the adsorption studies on fungicide-type pesticides such as Difenoconazole are limited. Since they are likely to be adsorbed by biological materials and passed on to humans through the food chain, determining the adsorption and kinetics of such pesticides are of great importance. Therefore, in the present study, adsorbing difenoconazole, a pesticide that causes severe problems in wastewaters, by utilizing chitosan obtained from shrimp wastes was aimed as well as determining the effects of pesticide concentration, temperature, adsorption isotherm, and kinetic modeling on the adsorption.

Materials and methods

Materials

The chitosan biopolymer, which was used as the adsorbent in the study, was obtained from the shells of deep-water pink shrimp (*Parapenaeus longirostris*). The shells were transported to the laboratory in the cold chain, and the chitosan was obtained as described by Chang [16] According to this method, chitosan was obtained in 4 steps: deproteinization, demineralization, decolorization, and deacetylation, respectively. To put it briefly, the shell samples were washed after rough cleaning and soaked in 2.5 N NaOH for 6 h for deproteinization, in 1.7 N HCl, 6 h for demineralization, and in HCl: H_2O_2 (Merck 107,298 Hydrogen peroxide 30%) for decolorization, respectively, to obtain chitin. The chitosan was obtained by deacetylating the chitin in NaOH at a high deacetylation degree (HDD ≥ 90%) at 120 °C. For the characterization of the chitosan, deacetylation degree [17], molecular weight [18], viscosity, moisture, and crude ash analyses AOAC [19] were performed.

Difenoconazole, a broad-spectrum fungicide, was used as the adsorbate. Difenoconazole is a licensed agricultural pesticide that was first manufactured in 1993 by different companies in Turkey and used either solely or in combination with other fungicide pesticides in the treatments of pear scab (*Venturia pirina*), leaf spot disease (*Cercospora beticola*), apple scab (*Venturia inaequalis*), and sugar-beet powdery mildew (*Erysiphe betae*) [20, 21]. The chemical properties of difenoconazole are shown in Table 1.

Methods

Adsorption interactions

Adsorption-pH interaction

To determine the effect of pH on pesticide adsorption, six different difenoconazole solutions of 15 µg/L concentration were prepared, with pH levels of 3, 4, 5, 6, 7, and 8. Afterwards, 50 mg/L of chitosan included in the solutions. Solutions were left to mix in an orbital shaker for 60 min at 120 rpm. The samples were filtered and analyzed with LC-MS/MS.

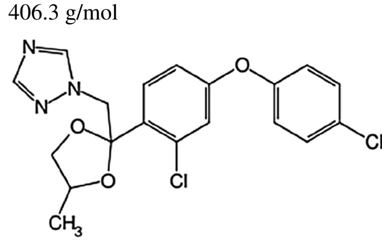
Adsorption-temperature interaction

Adsorption was performed at 20, 40, and 60 ℃ by mixing 50 mg/L of chitosan and 15 µg/L pesticide at 120 rpm. Afterward, the results were analyzed with LC-MS/MS.

Adsorption-concentration and duration interaction

Three different difenoconazole solutions were prepared: 5, 15, and 25 µg/L. The pH of the solution was adjusted to 5 and 50 mg/L of solid chitosan particles were added on top of it. The solution was then mixed at 120 rpm for 60 min at

Table 1 Difenoconazole identity [21]

ISO common name	Difenoconazole
Synonyms	CGA 169,374
IUPAC name	1-[2-[2-chloro-4-(4-chloro-phenoxy)-phenyl]-4-methyl [1,3] dioxolan-2-ylmethyl]-1 H-1,2,4-triazole
Chemical abstracts name	1-[[2-[2-chloro-4-(4-chlorophenoxy) phenyl]-4-methyl-1,3-dioxolan-2-yl] methyl]-1 H-1,2,4-triazole
CAS number	119446-68-3
CIPAC number	687
Molecular formula	$C_{19}H_{17}Cl_2N_3O_3$
Molecular mass	406.3 g/mol
Structural formula	

20°C. During the 60-min mixing period, samples were taken at certain intervals (at minutes 0, 5, 10, 15, 20, 25, 30, 40, 50, and 60), centrifuged, and analyzed by using LC-MS/MS.

LC-MS/MS analysis

The detection and quantification of difenoconazole were carried out as previously described by Daglioglu [22] by using Shimadzu 8040 liquid chromatography-tandem mass spectrometry (LC-MS/MS) equipped with Shimadzu (Kyoto, Japan) Simpack FC-ODS column (150 mm x 2 mm). Flow rate was set to 0.4 mL/min with the column temperature of 40ºC, and the injection volume of 20 µL. In the mobile phase, ultrapure water with 10 mM ammonium formate (solution A) and methanol (solution B) were used. The gradient program with the total run time of 20 min was ran as follows: 5% of solution B was maintained for 0.1 min, and it linearly increased to 95% in 10 min, isocratic for 5 min, followed by a decrease to the initial conditions in 0.05 min and equilibration time for 4.95 min. The analyte was analyzed in positive ionization mode (ESI+), while the quantitative analysis was performed in multiple reaction monitoring mode (MRM). The limit of detection (LOD) and the limit of the quantification (LOQ) were determined to be 0.31 ng/mL and 1.03 ng/mL, respectively.

Results and discussion

Characterization of chitosan

In the current study, chitosan, which has a high degree of deacetylation, was particularly preferred, and for this purpose, chitosan with this property, was obtained from the shells of deep-water pink shrimp. The properties of chitosan obtained from the shells of deep-water pink shrimp (*Parapenaeus longirostris*) are shown in Table 2.

Chitosan, commercially produced from mostly crab, shrimp, and lobster shells, is used in various fields such as food, chemistry, medicine, agriculture, and textile due to its properties. The 3 most important parameters for chitosan characterization are deacetylation degree, molecular weight, and viscosity [23–25]. It has been determined by many previous studies that the properties of the obtained chitosan vary [24, 26–29]. Moreover, the molecular weight of the chitosan is affected by various factors present in the production process. These are shear stress, dissolved oxygen concentration, chitin concentration, particle size, previous treatment of the chitin, reaction time, concentration of alkali, and high temperature [30–33]. It has been suggested that the term "chitosan" should be used when the deacetylation degree is above 70% [31, 34]. In the present study, the deacetylation degree of the extracted chitosan was determined to be 90.21%.

Table 2 Properties of the chitosan obtained from shrimp shells

Parameter	
Deacetylation degree (%)	90.21 ± 4.21
Molecular weight (kDa)	1039.93 ± 53.26
Viscosity (cP)	46.16 ± 1.14
Moisture (%)	1.26 ± 0.40
Ash (%)	0.72 ± 0.09

± Indicates standard deviation

Adsorption interactions

Adsorption-pH interaction

In the current study, 6 different pH levels (3, 4, 5, 6, 7, 8) were studied to investigate the effect of pH on pesticide adsorption. For this purpose, solutions containing 15 µg/L of pesticide, and 50 mg/L of chitosan were prepared. The effect of pH on difenoconazole adsorption in aqueous solutions is shown in Fig. 1.

pH is a significant factor in adsorption processes [35–38]. In the present study, the adsorption values were found to be 9 µg/mg at pH 3, 11 µg/mg at pH 4, 12.7 µg/mg at pH 5, 11 µg/mg at pH 6, 8 µg/mg at pH7, and 7 µg/mg at pH 8. It was observed that the pesticide adsorption begins at the pH level of 3. It was noted that the highest adsorption occurred at pH 5, and the adsorption value began to decline after this level (pH 6–8). The amine group in the structure of chitosan is $-NH_2$. Considering the fact that chitosan dissolves in acid, the amine groups in the structure of chitosan are protonated with the dissolving process, and thus, chitosan becomes cationic. Since the surface charge of the adsorbent is positive when the pH level is lower than the isoelectric point value of the absorbent, the adsorption of anionic pesticide will be

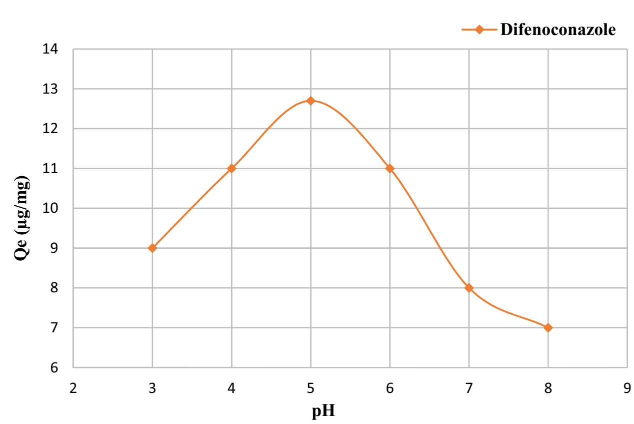


Fig. 1 The effect of pH on the adsorption

more efficient and lead to higher parameters at lower pH levels. In the contrary case, at higher pH levels, a decrease in the adsorption capacity was observed. One of the possible reasons for this could be the competition between the hydroxyl (–OH) ions in the solution and the methyl (CH3–) ions in the difenoconazole structure to interact with the cationic chitosan structure. Our results agree with another study, which reported that the acidic environment of the adsorbent surface enhances the adsorption of negative ions in comparison with alkaline environments, and alkaline environments enhance the capacity of the adsorption of positive ions [39]. Likewise, in their study, Ngah [40] reported that the adsorption mechanism of chitosan composites is quite spectacular and unique. It was determined by the researchers that the amino groups of chitosan composites provide the adsorption of positively charged molecules through various interaction mechanisms such as electrostatic attraction and chelation. In another study, it was reported that chitosan is superior to many other adsorbents due to its surface properties, which constitute a complex environment for ionic molecules during the adsorption process [41].

Adsorption- temperature interaction

The effect of temperature on adsorption was investigated by mixing 15 μg/mL of pesticide with 50 mg/L of chitosan in temperatures of 20, 40, and 60 ℃ at a pH level of 5. The results are shown in Fig. 2.

At the end of the experiments, difenoconazole adsorption was detected as 21.22 μg/mg at 20 ℃, 23.91 μg/mg at 40 ℃, and 24.16 μg/mg at 60 ℃. It was observed that the adsorption increased rapidly from 20 to 40 ℃, and when the temperature surpassed 40 ℃, difenoconazole adsorption remained stable without significant changes. Under normal circumstances, it is known fact that adsorption is inversely proportional to the temperature. However, as can be seen in the graph, an increase in adsorption was observed as the temperature increases. This shows that the reaction is endothermic. It is expected that, as the temperature increases, the metallic matrix and the surface charges decrease, and the cation hydrolysis increases. Thus, with increasing temperature, the electrostatic repulsion between the surface and the pesticide groups will also increase, and consequently, adherence will become less likely to happen and the dissolution will increase. In addition to the rise in temperature, the contemporary cations and rate of the reaction also affected the adherence condition. As a consequence, the chitosan biopolymer dissolves with the rise in temperature and the difenoconazole adsorption increases.

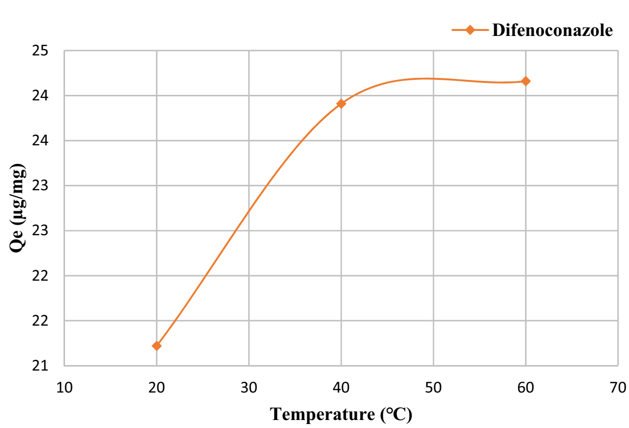


Fig. 2 The effect of temperature on the adsorption

Adsorption-concentration and duration interaction

The effects of various difenoconazole concentrations (5, 15, and 25 μg/L) and the durations on the adsorption capacity are shown in Fig. 3.

As seen in Fig. 3, it was observed that the adsorption increased rapidly with the increase in the pesticide concentration at the beginning, and afterward, it remained stable at a certain adsorption plateau depending on the increase in the concentration. It was noted that the adsorption exhibited a rapid increase within the first 5 min whereas, it remained generally stable at min 10 with slight increases. It was determined that the initial pesticide concentration did not make significant differences in the system's reaching equilibrium.

Adsorption isotherm

The Langmuir isotherm regarding difenoconazole adsorption of the chitosan is shown in Fig. 4.

Isotherms are theoretical calculations that are investigated for kinetic modeling of the adsorption in engineering studies. In the present study, the work was conducted according to the Langmuir adsorption isotherm model and it was observed that the results were suitable for this model. The Langmuir adsorption isotherm is used for determining the equilibrium distribution between solids and liquids. When

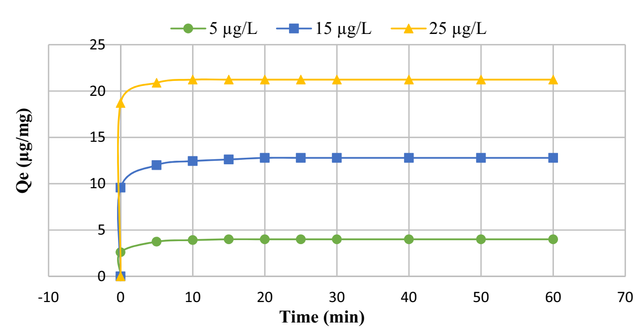


Fig. 3 The effects of the difenoconazole concentrations and the durations on the adsorption

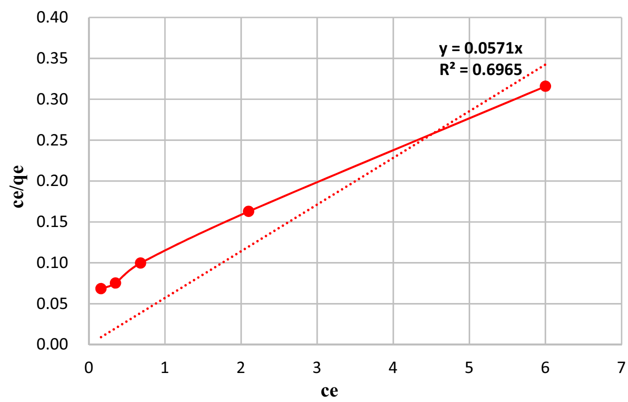


Fig. 4 The Langmuir isotherm regarding difenoconazole adsorption of the chitosan

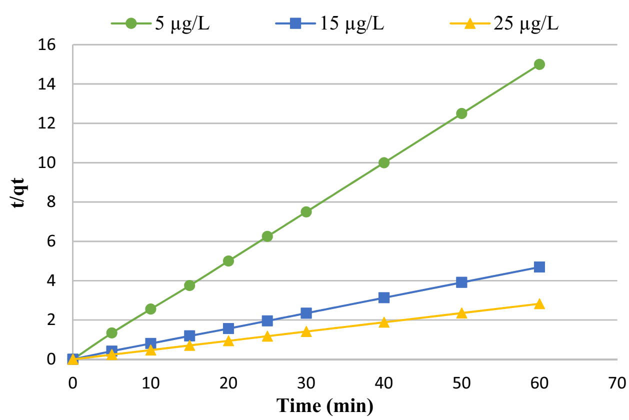


Fig. 5 Pseudo-second order kinetic modeling for difenoconazole adsorption values in varying chitosan concentrations

the correlation coefficients were analyzed according to the data obtained in this study, it is seen that the properties of the chitosan were coherent with the Langmuir adsorption isotherm, and the study yielded favorable results. The Langmuir isotherm parameters for chitosan were found to be $a_L = 0.635$, $k_L = 15.10$, and the Q_{max} value was calculated as 23.77 mg/g. Similarly, Rissouli [42] studied pesticide adsorption by utilizing chitin and chitosan and found that the Langmuir isotherm was the most favorable option to describe the adsorption behavior.

Kinetic modeling

Pseudo-second order kinetic modeling for difenoconazole adsorption values in varying chitosan concentrations is shown in Fig. 5.

In the study, it was observed that the kinetic modeling results for the adsorption of difenoconazole with chitosan, at 5, 15, and 25 µg/L difenoconazole concentrations, and at minutes 5, 10, 15, 20, 25, 30, 40, 50, and 60, complied with the pseudo-second order kinetic model. According to the kinetic modeling, it can be seen that as difenoconazole concentration increases the adsorption capacity decreases. Moreover, when the isotherm and the kinetic model are evaluated, it was determined that chitosan is a suitable bio-adsorbent for pesticide removal from wastewaters.

Today, many different types of pesticides are used and eventually mixed into surface waters in various ways. These substances in wastewaters and surface waters bring many problems and risks along. Recent scientific findings suggest that these chemicals bioaccumulate and this should be prevented. In this research, it was aimed to provide the removal of Difenoconazole, a fungicide used in agricultural activities, from water using chitosan obtained from waste shrimp shells and thus prevent the deterioration of the ecological balance.

It is known that chitosan can be utilized advantageously in industrial areas for the removal of drugs, pesticides, dyes, etc. since it can have a positive effect on adsorption in a flexible pH range. Supportively, the results of the present study showed that chitosan has a high adsorption capacity compared to other biological adsorbents and it is apt to be applied in the removal of pesticides as an adsorbent, not only experimentally but also in the industry. In this era, in which global climate change has become a universal problem, the use of a natural polymer and the removal of such chemicals from wastewaters to protect usable water sources are of great importance for both the environmental and public health.

Author contributions All authors contributed to the study's conception and design. Material preparation, experiments, analysis, and preparation of the manuscript were performed by AEK and ŞA. AK, OG, and MÇ contributed to the development of the protocol and reviewed the manuscript. All authors read and approved the final manuscript.

Funding This study was supported by Çukurova University, Unit of Research Projects with the grant number FYL-2019-11654.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper. The authors declare that there are no conflicts of interest

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