Süleyman Demirel Üniversitesi Fen Edebiyat Fakültesi Fen Dergisi https://dergipark.org.tr/sdufeffd
Süleyman Demirel University Faculty of Arts and Sciences Journal of Science e-ISSN: 1306-7575
Research Article, 2025, 20(1): 95-102, DOI: 10.29233/sdufeffd.1642167

Investigation of Adsorption Properties of Some Pesticide Species with Chitosan

Hüseyin Özkan[1], Tahir Tilki[2,*]

[1] Directorate of Personnel Department, Isparta University of Applied Sciences, 32200, Isparta, Türkiye
https://orcid.org/0009-0000-7683-2346
[2]Department of Chemistry, Engineering and Natural Sciences, Süleyman Demirel University, 32200, Isparta, Türkiye
https://orcid.org/0000-0002-1040-2375
*corresponding author: *tahirtilki@sdu.edu.tr*

(Received: 18.02.2025, Accepted: 17.04.2025, Published: 25.05.2025)

Abstract
In this study, the removal of certain insecticides and herbicides from aqueous solutions using the adsorption method was aimed. For this purpose, chitosan was used. Chitosan was treated with insecticide and herbicide solutions, and the effects of contact time and changes in insecticide and herbicide concentrations on adsorption were separately examined. The applicability of the Langmuir adsorption isotherm was tested at 25°C. Quantitative analyses were performed based on the initial amount of the substance added to the water and the remaining amount in the solution. The quantifications were carried out using a GC-MS device. Based on the plotted graphs, it was demonstrated that chitosan can be used as an adsorbent.

Keywords: Chitosan, Adsorption, Pesticide, Herbicide, GC-MS.

1. Introduction

Chemicals or biological agents known as pesticides prevent, manage, or eliminate pests that could endanger crops, plants, animals, or human life. Insects, weeds, fungus, rodents, germs, and other creatures that disrupt agriculture, public health, or the environment are examples of pests [1]. Pesticides are essential to modern farming because they defend crops from pests and illnesses, increase crop yields, and ensure food security [2]. Additional exposures may result from the widespread use of pesticides in several other contexts, such as residences, workplaces, schools, and hospitals. Pesticides can be categorized into many groups based on the species they target, including insecticides, herbicides, fungicides, nematicides, rodenticides, acaricides, molluscicides, and herbicides [3].

Although pesticides can be useful in keeping pests under control and safeguarding crops, there are possible hazards associated with using them. Pesticide resistance, environmental damage, and health hazards can result from excessive or improper use of pesticides [4]. Pesticide residues can be found in soil, water, air, fruits, vegetables, and processed foods. Particularly in developing nations, food exposure and the acute and long-term health impacts of agricultural pesticides pose major public health risks. Chemical pesticides have the potential to be mutagenic, cytotoxic, and carcinogenic to humans [5]. The United Nations Environment Programme (UNEP) and the World Health Organization (WHO) reported that exposure to pesticides causes 200.000 deaths and three million poisonings globally, primarily in developing nations [6]. Pesticides cause reactive oxygen species to be produced, which reduces antioxidant levels and weakens their capacity to shield cells from oxidative harm. Proteins, lipids, and nucleic acids also impact cellular signaling pathways as a result of the imbalance. Oxidative stress and reactive oxygen species are the causes of long-term health problems [7]. Inaccurate pesticide application often results in a variety of negative health effects, ranging from acute intoxication to chronic conditions such as Alzheimer's disease (AD), Parkinson's disease, neurotoxicity, infertility, leukemia, diabetes, and various cancers [8–12] (brain, breast, prostate, bladder, and colon cancer).

The natural polymer chitosan is derived from chitin. Its distinct physicochemical characteristics, biocompatibility, and biodegradability make it useful in a wide range of fields [13]. Additionally, chitosan has a broad range of pH stability, excellent surface adherence, and exhibited chelating capabilities. Chitosan's efficacy as a bio-adsorbent against certain harmful ions, dyes, and organic contaminants has been demonstrated [14–16]. Chitosan, due to its amino ($-NH_2$) and hydroxyl (-OH) functional groups, can adsorb pesticides through electrostatic interactions, hydrogen bonding, van der Waals forces, and hydrophobic interactions. Atrazine and desethylatrazine can establish π-π interactions via their triazine rings, while endosulfan and chlorthiamid may adsorb onto the chitosan surface through physical adsorption or weak chemical bonding [17].

In light of the aforementioned information, the indiscriminate and excessive use of pesticides and herbicides presents a substantial threat to both environmental and human health. Therefore, this study aims to remove certain pesticides and herbicides from aqueous solutions through the adsorption method. For this purpose, natural chitosan, known for its high water absorption capacity, was utilized. Initially, chitosan was treated with pesticide and herbicide solutions, and the effects of contact time on pesticide and herbicide adsorption as well as the influence of varying pesticide and herbicide concentrations on adsorption, were individually examined. The applicability of the Langmuir adsorption isotherm at 25 ºC was tested. Quantification was determined based on the initial amount of substance added to the water and the remaining amount in the solution. Quantitative analyses were conducted using a GC-MS.

2. Material and Method

2.1. General Information

Endosulfan (Fluka)(% 99,4), Atrazine (Fluka)(%98,8), chlorthiamide (Fluka)(%99,9), Atrazine-desethyl (Fluka)(%99,5), Ethanol (Sigma Aldrich) (%99,8), Methanol (Sigma Aldrich) (%99,8), Acetone (Sigma Aldrich) (%99,8), Chitosan (60-70 mesh 242-283 microne, Kayseri Erciyes University), ultra pure water (Millipore, 18,2 mΩcm) chemicals and Weighing balance: Metler Toledo AB204-s, GC MS; Shimadzu GCMS-QP5050A column: HP-5MS, 30 m, 0.25 mm ID, 0.25 mm film tickness; inlet: 300 °C (split modus); detector: 300 °C; carrier gas: He; flow rate: 1 mL/min. (constant flow modus); Split ratio: 1/10; oven program: 80 °C (1 min.), 5 °C/min. to 285 °C; total analyses time: 42 min. magnetic stirrer: Variomag poly 15, shaker: Heidolph Rotamax 120 devices were used in adsorption studies.

2.2. Adsorption studies

2.2.1. Structures of used chemicals

Chemical structures of the used pesticide and chitosan were given in figure 1.

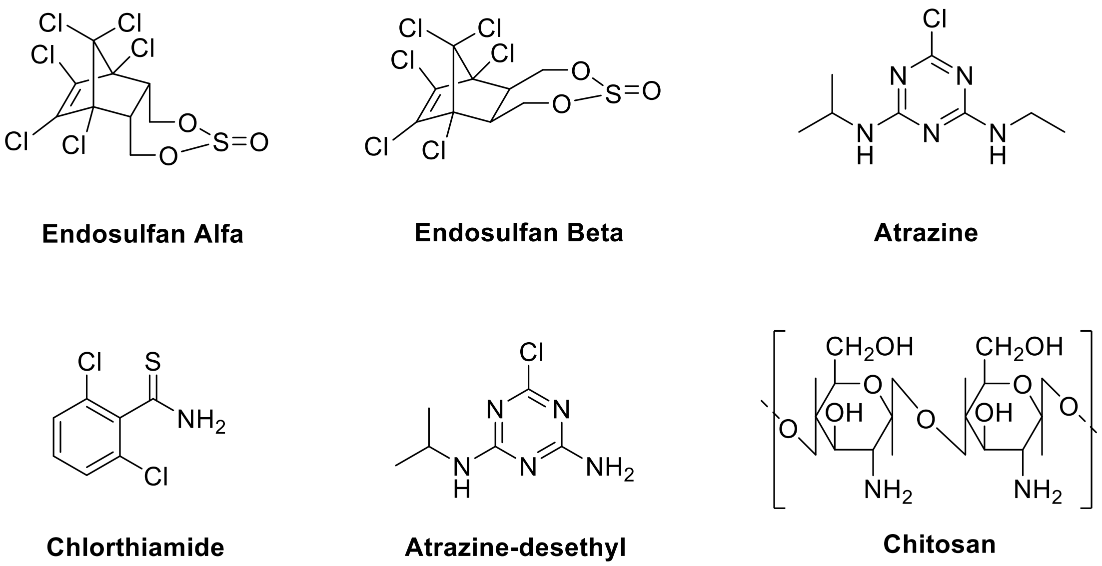

Figure 1. Structures of used chemicals

2.2.2. Time effect upon pesticide adsorption

1200 ppm stock solutions of pesticides (alfa/beta-endosulfan (in ethanol), atrazine (in methanol), chlorthiamide (in acetone), and atrazine-desethyl (in ethanol)) were prepared. The using these stocks, 10 ppm solutions (6 pieces of each solution) of endosulfan, atrazine, chlorthiamide, and Atrazine-desethyl were prepared using distilled water (833 µL to 100 mL). Then 0.1 g chitosan was added into the each 10 ppm solution. The 10 ppm solutions containing 0.1 g chitosan were shaken at room temperature for 30 min., 1 h, endosulfan 2 h, 3 h, 6 h, and 24 hours, respectively. The heterogeneous solutions were filtered by using whatman filter paper (20-25 microns). The remaining pesticides concentrations were determined using GC-MS device.

2.2.3. Concentration effect upon adsorption

Using 1200 ppm endosulfan, atrazine, chlorthiamide, atrazine-desethyl stock solutions 6, 10, 15, 30 and 45 ppm 100 mL pesticide solutions in distilled water were prepared to use adsorption studies. Then 0.1 g chitosan was added into these solutions, and the solutions were shaken at 450 rpm for 2 h at ambient temperature.

3. Results

3.1. Time effect upon pesticide adsorption

Figure 2 illustrates the adsorption kinetics of five different pesticides-Alpha Endosulfan, Beta Endosulfan, Atrazine, Chlorthiamide, and Atrazine Desethyl—onto chitosan as a function of time. Each subfigure (a–e) corresponds to a specific pesticide and depicts the percentage adsorption over time.

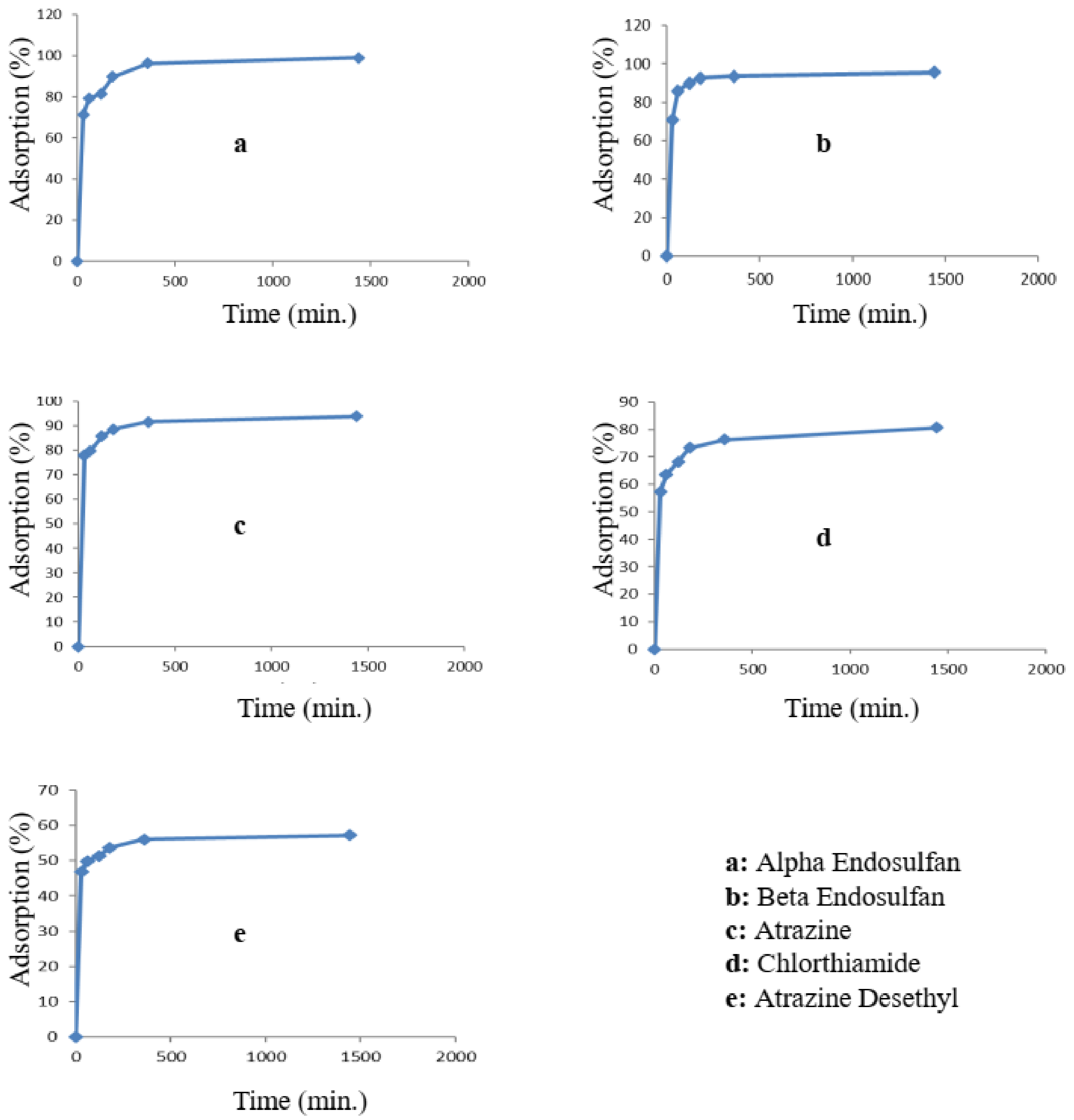

Figure 2. Time effect upon pesticide adsorption with chitosan

In all five cases, a sharp increase in adsorption is observed within the first few minutes. This behavior suggests that chitosan provides abundant active sites at the beginning, facilitating rapid pesticide uptake. After the initial phase, adsorption gradually reaches a plateau, indicating that the system is approaching equilibrium. The time required for equilibrium varies slightly among the pesticides. The maximum adsorption percentages differ for each pesticide, suggesting variations in the affinity of chitosan toward different compounds. Alpha Endosulfan (a) and Beta Endosulfan (b) achieve nearly 100% adsorption. Atrazine (c) also exhibits high adsorption efficiency. Chlorthiamide (d) and Atrazine Desethyl (e) show relatively lower adsorption efficiencies, indicating weaker interactions with chitosan. The rapid adsorption phase followed by equilibrium suggests that the process might be governed by a pseudo-second-order kinetic model, implying chemisorption as the dominant mechanism. The differences in adsorption capacity could be attributed to variations in molecular structure, polarity, and solubility of the pesticides.

3.2. Concentration effect upon adsorption

Figure 3 illustrates the adsorption isotherms of five different pesticides-Alpha Endosulfan, Beta Endosulfan, Atrazine, Chlorthiamide, and Atrazine Desethyl-onto chitosan as a function of initial pesticide concentration (ppm). Each subfigure (a–e) represents a different pesticide, with adsorption capacity (q, mg/g) plotted against concentration.

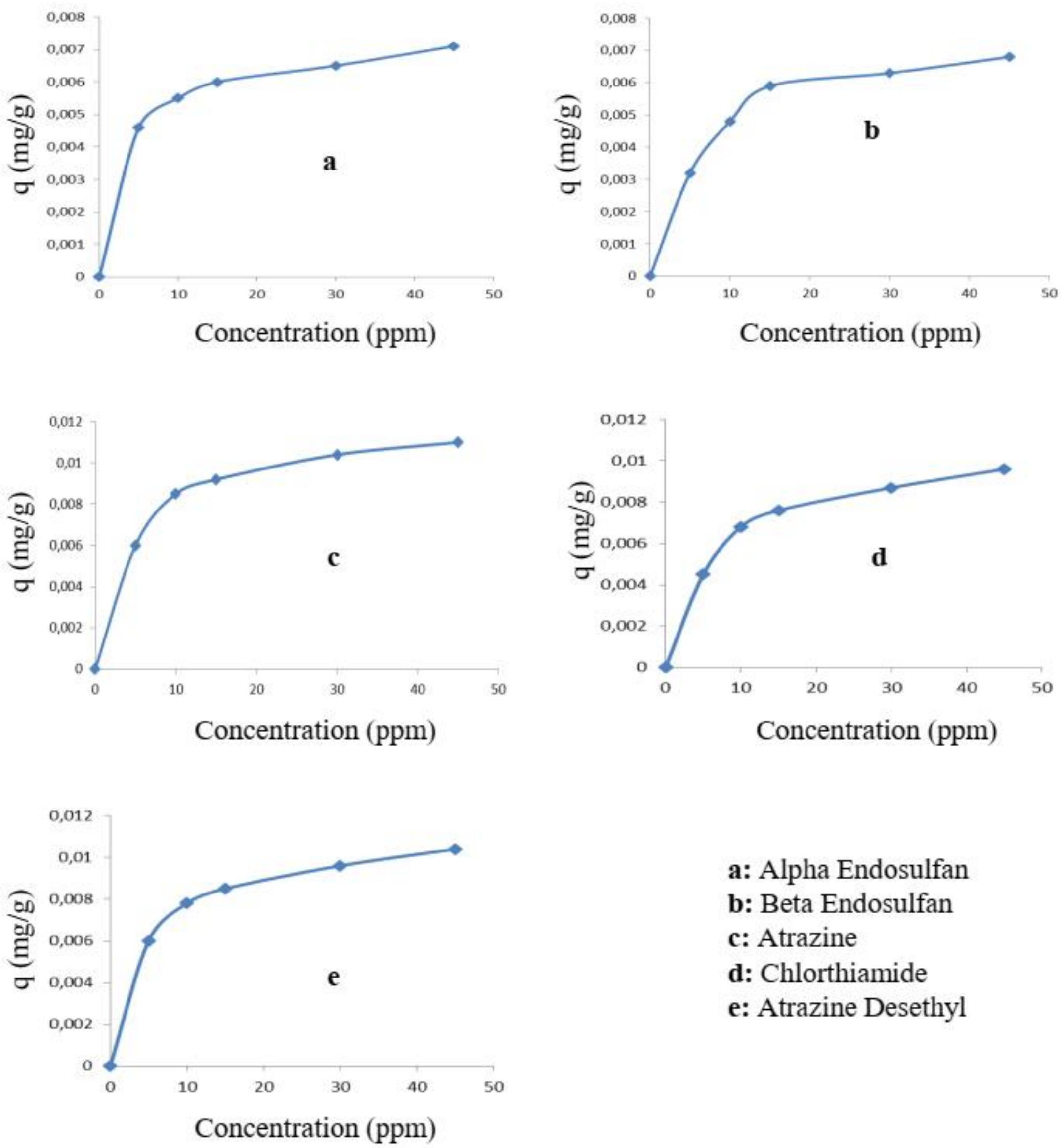

Figure 3. Concentration effect upon pesticide adsorption with chitosan

In all cases, adsorption capacity (q) increases sharply at lower concentrations, indicating that chitosan provides abundant active sites for pesticide binding. As the concentration increases, adsorption slows down, forming a plateau-like region. This suggests that available adsorption sites become occupied, and further increases in concentration result in only marginal increases in adsorption capacity. Atrazine (c) and Atrazine Desethyl (e) exhibit relatively higher adsorption capacities, implying strong interactions between these compounds and chitosan. Alpha Endosulfan (a) and Beta Endosulfan (b) show moderate adsorption trends, reaching near saturation at higher concentrations. Chlorthiamide (d) displays the lowest adsorption capacity, suggesting weaker affinity for chitosan.

The observed trends suggest that the adsorption process follows Langmuir isotherm, where adsorption increases with concentration but eventually reaches a limit. The plateau region implies monolayer adsorption, where chitosan's binding sites become fully occupied at higher concentrations.

DOI: 10.29233/sdufeffd.1642167 2025, 20(1): 95-102

3.3. Langmuir Adsorption Isotherm

The Langmuir isotherm was selected for the analysis as it assumes homogeneous and monolayer adsorption on the adsorbent surface. This model considers that adsorption occurs at specific active sites without interactions between adsorbed molecules. Given that chitosan adsorbs pesticides through its functional groups, the Langmuir isotherm provides valuable insights into the maximum adsorption capacity and equilibrium characteristics of the adsorption process [18].

Figure 4 presents the Langmuir adsorption isotherms for Alpha Endosulfan, Beta Endosulfan, Atrazine, Chlorthiamide, Atrazine Desethyl adsorbed onto chitosan, an adsorbent known for its high affinity towards organic pollutants. The adsorption isotherm is an essential tool to describe the interaction between the adsorbate (pesticide/insecticide) and the adsorbent (chitosan), providing insights into the adsorption capacity and efficiency. The high R^2 values (ranging from 0.9967 to 0.9996) indicate an excellent fit of the Langmuir model, confirming monolayer adsorption on a homogeneous surface. When the figure 4 was examined, It was observed that Alpha Endosulfan (132.02) has the highest adsorption capacity, whereas Atrazine Desethyl (87.80) has the lowest.

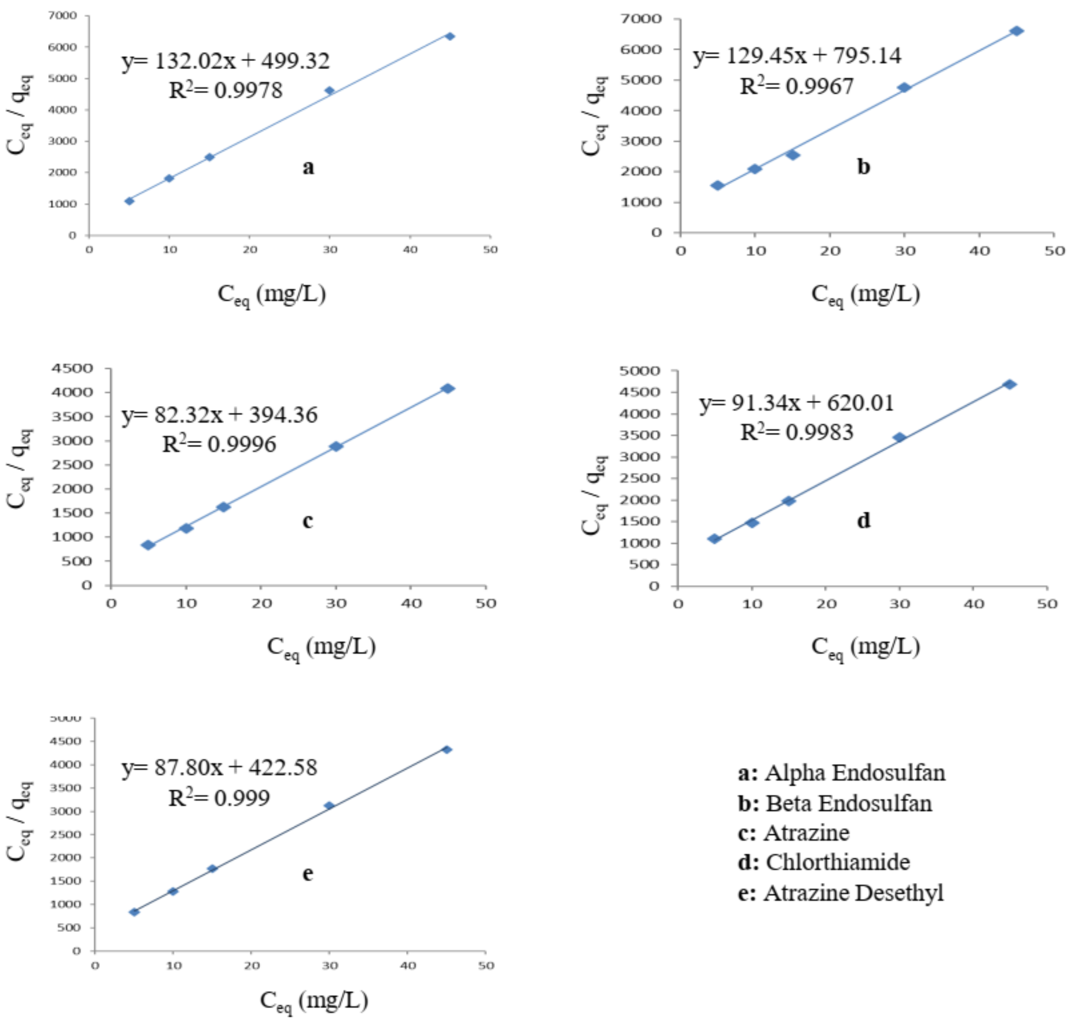

Figure 4. Langmuir Adsorption Isotherms of pesticide/insecticide with chitosan

Alpha Endosulfan (a) and Beta Endosulfan (b) exhibit higher adsorption capacities, likely due to their higher hydrophobicity and affinity for chitosan. Chlorothiamide (d) and

Atrazine Desethyl (e) show relatively lower adsorption capacities, possibly due to differences in their functional groups, solubility, or steric hindrance effects. This study confirms that chitosan efficiently adsorbs the tested Alpha Endosulfan, Beta Endosulfan, Atrazine, Chlorthiamide, Atrazine Desethyl following the Langmuir adsorption model with high accuracy. The results suggest that adsorption is monolayer, and chitosan presents a high binding affinity for these compounds, making it a promising material for environmental remediation and pesticide removal applications.

4. Conclusion

In this study, experiments were conducted to remove certain insecticides and herbicides from aqueous solutions using chitosan. In the experiments examining the effect of contact time on adsorption, a rapid increase in adsorption was observed within the first two hours. However, over time, the adsorption reached a plateau and gradually stabilized at an approximately constant value. In experiments conducted with different insecticide/herbicide concentrations, an initial increase in adsorption was observed with rising concentration, but after a certain point, further increases in concentration led to adsorption reaching a steady state. Based on the adsorption isotherms plotted for chitosan, it was found that the data fit the Langmuir isotherm more accurately. As a result, it was determined that atrazine, atrazine desethyl, chlorthiamide, and endosulfan components could be adsorbed using natural chitosan from aqueous solutions. Given the current concerns about water pollution, wastewater treatment, and the efficient use of water resources, this study demonstrates that chitosan can be used for the removal of these pesticides. When compared with literature studies, the correlation coefficients (R^2) obtained were at least 0.99, indicating strong agreement with the Langmuir isotherm and confirming the study's objectives. Additionally, these findings suggest that adsorption studies using chitosan could be extended to other chemical groups in future research.

Authorship contribution statement

H. Özkan: Investigation, Conceptualization, Methodology, Review and Editing, Original Draft Writing, **T. Tilki**: Conceptualization, Data Curation, Original Draft Writing, Resource/Material/Instrument Supply, Project Administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This study was funded by [SDU-BAP] under Grant/Project No [4073-YL1-14].

Ethics Committee Approval and/or Informed Consent Information

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

References

[1] Y. Rodriguez-Santiago, K.E. Nava-Castro, J. Morales-Montor, “Environmental pollution as a risk factor to develop colorectal cancer: The role of endocrine-disrupting chemicals in the inflammatory process as a risk factor to develop colorectal cancer, in: Immunotherapy in Resistant Cancer: From the Lab Bench Work to Its Clinical Perspectives”, *Elsevier*, 131–148, 2021.

[2] K. Ramadhan Makame, M. Sherif, L. Östlundh, J. Sándor, B. Ádám, K. Nagy, “Are encapsulated pesticides less harmful to human health than their conventional alternatives? Protocol for a systematic review of in vitro and in vivo animal model studies”, *Environment International*, 174, 107924, 2023.

[3] I. Sierra, S. Morante-Zarcero, "New Advances in Food Sample Preparation With Nanomaterials for Organic Contaminants Analysis by Liquid Chromatography, in: Nanomaterials in Chromatography", *Elsevier*, 118–154, 2018.
[4] R. Cech, J.G. Zaller, A. Lyssimachou, P. Clausing, K. Hertoge, C. Linhart, "Pesticide drift mitigation measures appear to reduce contamination of non-agricultural areas, but hazards to humans and the environment remain", *Science of The Total Environment*, 854, 158814, 2023.
[5] L. Fang, X. Liao, B. Jia, L. Shi, L. Kang, L. Zhou, W. Kong, "Recent progress in immunosensors for pesticides", *Biosensors and Bioelectronics* 164, 112255, 2020.
[6] W. Boedeker, M. Watts, P. Clausing, E. Marquez, "The global distribution of acute unintentional pesticide poisoning: estimations based on a systematic review", *BMC Public Health* 20, 1875, 2020.
[7] R. Kaur, G.K. Mavi, S. Raghav, I. Khan, "Pesticides Classification and its Impact on Environment", *International Journal of Current Microbiology and Applied Sciences*, 8, 1889–1897, 2019.
[8] L. Rani, K. Thapa, N. Kanojia, N. Sharma, S. Singh, A.S. Grewal, A.L. Srivastav, J. Kaushal, "An extensive review on the consequences of chemical pesticides on human health and environment", *Journal of Cleaner Production*, 283, 124657, 2021.
[9] G.B. Frisoni, D. Altomare, D.R. Thal, F. Ribaldi, R. van der Kant, R. Ossenkoppele, K. Blennow, J. Cummings, C. van Duijn, P.M. Nilsson, P.-Y. Dietrich, P. Scheltens, B. Dubois, "The probabilistic model of Alzheimer disease: the amyloid hypothesis revised", *Nature Reviews Neuroscience*, 23, 53–66, 2022.
[10] L. Perrin, J. Spinosi, L. Chaperon, S. Kab, F. Moisan, A. Ebaz, "Pesticides expenditures by farming type and incidence of Parkinson disease in farmers: A French nationwide study" *Environmental Research*, 197, 111161, 2021.
[11] A. Rafeeinia, G. Asadikaram, V. Moazed, M.K. Darabi, "Organochlorine pesticides may induce leukemia by methylation of CDKN2B and MGMT promoters and histone modifications" *Gene*, 851, 146976, 2023.
[12] J.Á. Hernández-Mariano, M.C. Baltazar-Reyes, E. Salazar-Martínez, L.A. Cupul-Uicab, "Exposure to the pesticide DDT and risk of diabetes and hypertension: Systematic review and meta-analysis of prospective studies", *International Journal of Hygiene and Environmental Health*, 239, 113865, 2022.
[13] M. Rafiq, J. Ahmed, H.A. Alturaifi, N.S. Awwad, H.A. Ibrahium, S. Mir, A. Maalik, S. Sabahat, S. Hassan, Z.U.H. Khan, "Recent developments in the biomedical and anticancer applications of chitosan derivatives", *International Journal of Biological Macromolecules*, 283, 137601, 2024.
[14] P. Chassary, T. Vincent, E. Guibal, "Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use", *Reactive and Functional Polymers*, 60, 137–149, 2024.
[15] E. Guibal, C. Milot, J.M. Tobin, "Metal-Anion Sorption by Chitosan Beads: Equilibrium and Kinetic Studies", *Industrial & Engineering Chemistry Research*, 37, 1454–1463, 1998.
[16] F. Ma, R. Qu, C. Sun, C. Wang, C. Ji, Y. Zhang, P. Yin, "Adsorption behaviors of Hg(II) on chitosan functionalized by amino-terminated hyperbranched polyamidoamine polymers", *Journal of Hazardous Materials*, 172, 792–801, 2009.
[17] E.Atangana, T. O.Ajiboye, A. A. Mafolasire, S. Ghosh, B. Hakeem, "Adsorption of Organic Pollutants from Wastewater Using Chitosan-Based Adsorbents", *Polymers*, 17(4), 502, 2025.
[18] R.A. Latour, "The Langmuir isotherm: a commonly applied but misleading approach for the analysis of protein adsorption behavior", *Journal of Biomedical Materials Research Part A*, 103(3), 949-958, 2015.