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DOI: 10.2478/eces-2022-0016 ECOL CHEM ENG S. 2022;29(2):217-226

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THIABENDAZOLE FUNGICIDE ADSORPTION ONTO FOUR AGRICULTURAL SOILS COLLECTED FROM THE LOUKKOS AREA OF NORTHWESTERN MOROCCO

Abstract: A serious environmental problem can arise from the presence of pesticides in soils and waters. Hence, in this study we have carried out the adsorption of the Thiabendazole fungicide onto four soils collected from several areas in Morocco as Larache, Laouamra, Ksar kebir and Tlata drissana. Physicochemical properties, elemental analysis, X-ray diffraction (XRD) were investigated to characterise the four selected soils. The experimental equilibrium data were analysed using Langmuir, Freundlich models. The equilibrium data were best described by a Langmuir model for all adsorbents. The maximum estimated adsorption capacity was 0.747 $mg{\cdot}g^{-1}$, 0.751 $mg{\cdot}g^{-1}$, 0.473 $mg{\cdot}g^{-1}$ and 1.083 $mg{\cdot}g^{-1}$, for Larache, Laouamra, Ksar kebir and Tlata drissana soils, respectively.

Keywords: adsorption mechanism, pesticide, Thiabendazole, soil, isotherm

Introduction

The growth of human activities requires a continuous enhancement of the quality and stability of products, which in a certain manner results in using new substances that cause pollution of the environment. Chemical pesticide application in fruit crops is necessary to control pests that reduce production, and also to provide better quality fruit for consumers [1, 2].

However, over the years, it has become apparent that these chemical pesticides also have drawbacks, such as risks to the environment [3], contamination of soils [4-6], water [7, 8], food [9, 10] and agricultural products [5], health hazards to farm workers and consumers, through the presence of residues in foodstuffs, impacts on populations of species useful to cultures, as well as the development of pesticide resistance by crop pests [11].

Thiabendazole is a compound derived from benzimidazole, primarily used in agriculture to control mould, blight and other fungi responsible for diseases in fruits and vegetables [12]. High amount of Thiabendazole used as a post-harvest fungicide results in water contamination as it has toxicity to animals causing liver and intestinal disorders [13].

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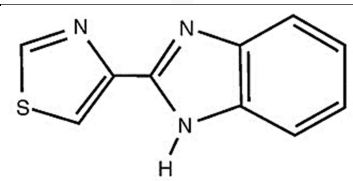
Finally, there is a need to find valuable solutions to avoid their accumulation in natural resources.

Adsorption process is considered a successful, and an attractive approach as well as now being considered to be better than other techniques for water treatment in terms of initial cost, the wide availability of adsorbents, high efficiency, ease of use, simplicity of design and reusability [14, 15].

In this work, we studied the adsorption capacity of Thiabendazole fungicide herbicide (Table 1) from an aqueous solution by four soils from different sites in Morocco such as: Larache, Laouamra, Ksar kebir and Tlata drissana. The adsorbents were characterised by elemental analysis and XRD. In addition, the adsorption isotherm models of Thiabendazole fungicide were also evaluated by Langmuir and Freundlich models to explore the adsorption mechanism.

Table 1

The chemical structure and characteristics of Thiabendazole

Pesticide	**Thiabendazole**
Molecular formula	$C_{10}H_7N_3S$
Molecular weight [g·mol^{-1}]	201.248
Solubility in water	55 mg·L^{-1}
pK_a	4.64
Half-life in soil DT_{50} [day]	29
Structure	

Materials and methods

Soil samples

Four surface soil samples were collected from a depth (0-20 cm) of the Loukkos Valley region (Fig. 1). The study area is located in the north region of Morocco, namely: Larache, Laouamra, Ksar kebir and Tlata drissana. Each individual soil sample (1 g) was collected randomly from an area of five square meters to obtain a homogeneous and representative sample. Then it was placed separately in a glass flask and labelled. The samples were stored in a refrigerated container and transferred directly to the laboratory. The collected samples were sieved to < 2 mm and stored at –20 °C until analysis.

Characterisation of adsorbents

The structure of samples was characterised by X-ray diffraction (XRD, LABXXRD-6100 SHIMADZU) using K_α radiation (λ = 1.5418 Å) in the 2θ range of 5° - 70°. The X-ray tube was operated at 40 kV with a Cu target. Diffraction measurements were then analysed using Rietveld refinement, which is a method employing the MAUD calculation code that allows the identification and quantification of crystalline mineral phases [16].



Fig. 1. Satellite photo of sample area

Adsorption isotherms

Different volumes of Thiabendazole stock solution (41.2 mg · L^{-1}) were added to 1 g of the different soil samples previously hydrated in distilled water for 24 hours. The overall volume was adjusted to 25 mL by adding distilled water, to obtain pesticide concentrations between 0.20 mg · L^{-1} and 16.5 mg · L^{-1}. The resulting suspensions were stirred at 20 °C at natural soil pH for a fixed period of time equal to 24 h. After shaking, the soil suspensions were filtered through nylon membranes (0.22 μm) and the filtrates analysed by HPLC to determine the residual amount of pesticide in the solution. The adsorption amount Q_e [mg · g^{-1}] of the sample was calculated by using the following formula [17]:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium Thiabendazole fungicide concentration [mg · L^{-1}], respectively, V is the volume of solution [mL] and m is the mass of absorbent [mg].

Thiabendazole analysis

The used chromatographic chain (VARIAN ProStar) of Thiabendazole is equipped with a diode array UV-visible detector and a silica-based apolar C18 Kromasil column (length = 100 mm, particle size = 5 μm). The detection wavelengths of Thiabendazole is 242 nm, the flow rate is 0.7 mL · min^{-1} and the injection volume is 20 μL. The chosen

mobile phase is an acetonitrile/water mixture at 70/30 (% v/v), the retention time is 2 minutes.

Results and discussion

Physicochemical characteristics

Table 2 presents some physicochemical characteristics of the four soils studied. The granulometric analysis reveals that most of the soils have a rough texture (mostly sandy). All four soils have a basic pH in solution between 7.4 and 8.3 characteristic of calcareous soils. Organic matter (OM) and limestone show great variability between samples. Indeed, OM contents vary from 3.2 % to 22.2 % depending on the soil. Generally speaking, the soils studied can be considered rich in organic matter: only one soil in four has less than 4 % OM. In Morocco, out of more than 270,000 soils analysed, 75 % of the samples have an OM content lower than 4 %, and 50 % have OM levels lower than 2.6 % [18].

Table 2

Physicochemical characteristics of the studied soils

Soils	Clay [%]	Sand [%]	OM [%]	Limestone [%]	*CEC* [meq/100 g]	pH [-]
Larache	21.3	54.7	22.2	7.6	49.4	7.4
Laouamra	26.1	55.1	9.8	6.2	33.0	7.6
Tlata drissana	31.9	25.5	4.2	70.4	9.9	8.3
Ksar kbir	22.7	36.1	3.2	49.6	8.8	8.3

The Larache and Laouamra soils are distinguished by their particular high OM content (% OM of 22.2 % and 9.8 %, respectively). For these two soils, these high OM contents are logically translated into high cation exchange capacities (*CEC*) (49.4 meq/100 g for Larache and 33.0 meq/100 g for Laouamra).

Elemental analysis

The elemental analysis provides detailed proportions of the various constituents of the studied soils. The findings of this analysis are reported in Table 3.

Table 3

Elemental composition of soil samples [% d.m. soil]

	Ca	Si	Al	Fe	Ti	Na	K	Mg	C	H	N	O
Larache	5.3	21.1	2.9	1.7	0.2	< 0.1	0.5	0.4	14.2	2.0	0.8	50.9
Tlata drissana	27.5	7.3	1.7	0.8	0.1	0.1	0.5	0.2	10.8	0.5	0.3	50.2
Laouamra	4.2	24.4	3.3	2.2	0.4	< 0.1	1.1	0.3	8.6	1.4	0.4	53.7
Ksar kebir	18.7	14.3	2.5	1.4	0.1	0.3	0.9	0.2	7.7	0.5	0.2	53.2

d.m. = dry mass

The element calcium can be correlated to the presence of limestone in the soils. Indeed, the comparison of its content in the different samples allows to find globally the different groups of soils previously defined according to their richness in limestone. Thus, the Larache and Laouamra soils, weakly calcareous, have the lowest levels of calcium

(3.8 ≤ % Ca ≤ 5.3), while the Ksar kebir and Tlata drissana soils, strongly calcareous, have much higher levels of Ca (18.7 % and 27.5 %, respectively).

The main elements present in the soil are silicon, carbon, calcium, aluminum and iron. Silicon, aluminum and iron contents can be correlated to the quantities of quartz, clays and iron oxides present in the soils. Silicon and iron come respectively from quartz and iron oxides, but also enter (to a lesser extent for iron) in the composition of clay minerals. Aluminum, for its part, comes exclusively from clays. Thus, as an example, the presence of these elements (Si, Al and Fe) in the lowest proportions in the Tlata drissana soil is in agreement with the low quantities of quartz, clays and iron oxides phases determined by XRD in this soil.

X-ray diffraction (XRD)

Mineralogical analysis of the four soil samples was performed by X-ray diffraction (XRD) in order to identify the major constituent phases of the soil mineral fraction. The diffractograms obtained are shown in Figure 2.

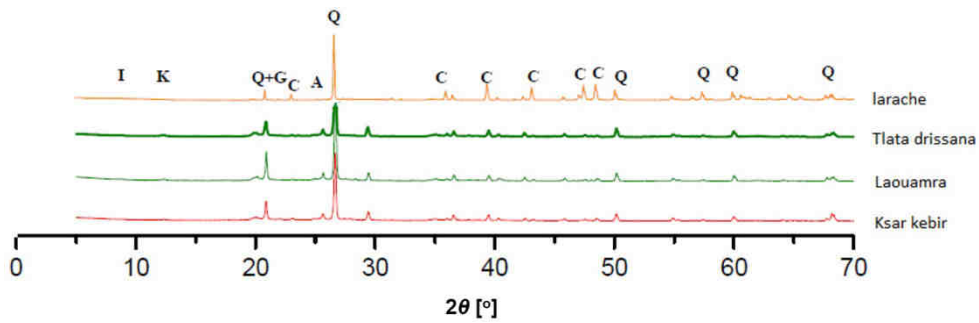


Fig. 2. X-ray patterns of the studied soils: C: calcite, Q: quartz, K: kaolinite, I: illite, G: goethite, R: rutile, A: anatase

Analysis of these diffractograms shows that the main peaks correspond to quartz (2θ = 20.8°, 26.7°, 50.3°, 60.1°) and calcite (2θ = 36.5°, 39.5°, 43.1°, 46.3°, 48.4°). Other less intense peaks show the presence of goethite (2θ = 21.2°) and mineralogical clays, more precisely kaolinite (2θ = 12.4°) and illite (2θ = 8.9°). Titanium oxides TiO_2 in the rutile form (2θ = 27.5°) and anatase (2θ = 25.3°) are also present in negligible quantities.

In a second step, an analysis of these diffractograms by Rietveld refinement led to a quantitative determination of the different constituents of the soil mineral fraction. These quantitative data are reported in Table 4.

Table 4

Quantitative analyses of the mineral fraction of soils obtained by Rietveld refinement (results are expressed in % by mass of the mineral fraction)

Soil	Calcite	Quartz	Clay + Goethite	Titanium oxides
Larache	10.9	52.0	36.3	0.8
Tlata drissana	8.2	55.5	55.2	1.1
Laouamra	51.7	31.0	15.8	1.5
Ksar kebir	74.8	11.9	11.5	1.9

Note that during this quantitative analysis of the mineral fraction, clay minerals (kaolinite and illite) and goethite were grouped together because they are often less well crystallised than calcite and quartz. It is therefore difficult to quantify them precisely, even if they are identified by the DRX analysis.

The analysis of the data in Table 4 shows that the mineral fraction of the soils consists mainly of three phases: quartz, calcite and clay minerals associated with goethite. The classification of the soils according to their total limestone content is confirmed by the XRD analysis. Indeed, we find the same three groups of soils, classified this time according to the richness of their mineral fraction in calcite. In the low calcareous soils (Larache and Laouamra), calcite constitutes less than 11 % of the mineral fraction. In these soils, quartz is the most abundant mineral (> 48 %), followed by the clay fraction (32.5 % on average). On the other hand, in the soils Ksar kebir and Tlata drissana, calcite is dominant, it can represent up to 75 % of the fraction. Lastly, titanium oxides, negligible, represent only a minor part of the mineral fraction (< 2 %).

Adsorption isotherms of Thiabendazole

Analysis of adsorption isotherms is of fundamental importance to describe how adsorbent molecules can interact with the adsorbent surface. The equilibrium investigations identify the capacity of the adsorbent as well as describe the adsorption isotherm through constants providing information on the surface properties and affinity of the adsorbents [19]. Figures 3-6 shows the adsorption isotherms of Thiabendazole fungicide on Larache, Laouamra, Ksar kebir and Tlata drissana soils over a concentration range of 0.20 $mg{\cdot}L^{-1}$ - 16.5 $mg{\cdot}L^{-1}$. Nonlinear forms of the Langmuir and Freundlich isotherms were used to analyse the elimination equilibrium data of Thiabendazole fungicide. Comparisons between linear and nonlinear regressions have commonly shown that the best parameter values are achieved by nonlinear optimisations [20, 21].

The Langmuir model can be described as follows:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where Q_e [$mg{\cdot}g^{-1}$] is the adsorption capacity of the adsorbent at equilibrium. Q_m [$mg{\cdot}g^{-1}$] is the maximum adsorption capacity. C_e [$mg{\cdot}L^{-1}$] is the concentration of the Thiabendazole fungicide solution at equilibrium and K_L [$L{\cdot}mg^{-1}$] is the Langmuir equilibrium adsorption constant related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate.

This formalism assumes that the adsorption takes place in a homogeneous way at the level of the adsorbent surface and that all the adsorption sites have the same affinity for the adsorbate molecules, i.e. the same adsorption energy [22].

The Freundlich equation is written as follows:

$$Q_e = K_F \, C_e^{\frac{1}{n}} \tag{3}$$

where K_F [$L{\cdot}g^{-1}$] is the Freundlich constant related to adsorption capacity and $1/n$ is the intensity of the adsorption or surface heterogeneity indicating the relative distribution of the energy and the heterogeneity of the adsorbate sites.

The Freundlich formalism suggests that adsorption of organic molecules occurs at heterogeneous sites with different adsorption energies [23].

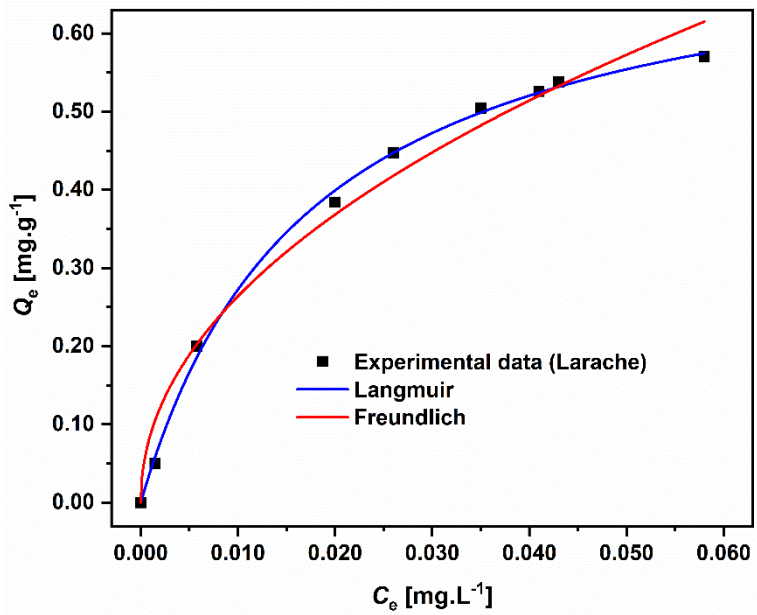


Fig. 3. Adsorption isotherms fitting at different initial concentration for Thiabendazole adsorption on Larache soil (conditions: natural pH; T = 20 °C; V = 25 mL; time = 24 h; adsorbent dose = 40 g · L^{-1})

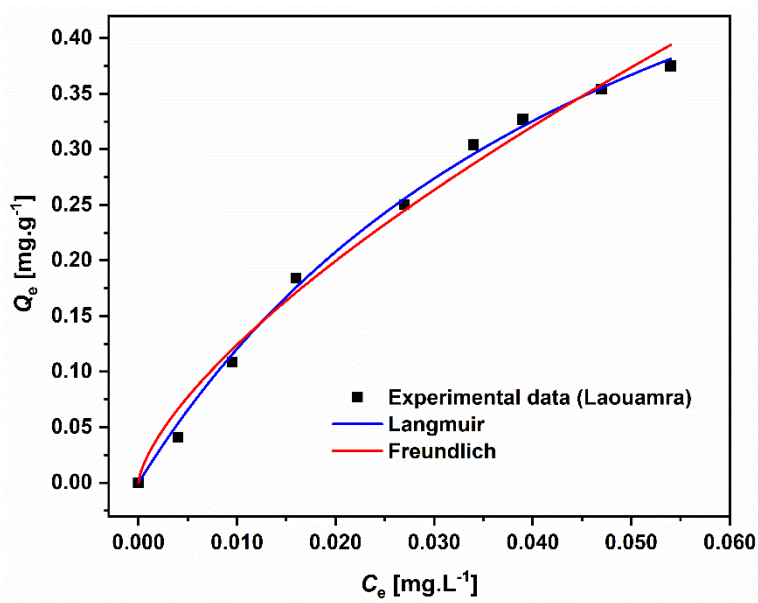


Fig. 4. Adsorption isotherms fitting at different initial concentration for Thiabendazole adsorption on Laouamra soil (conditions: natural pH; T = 20 °C; V = 25 mL; time = 24 h; adsorbent dose = 40 g · L^{-1})

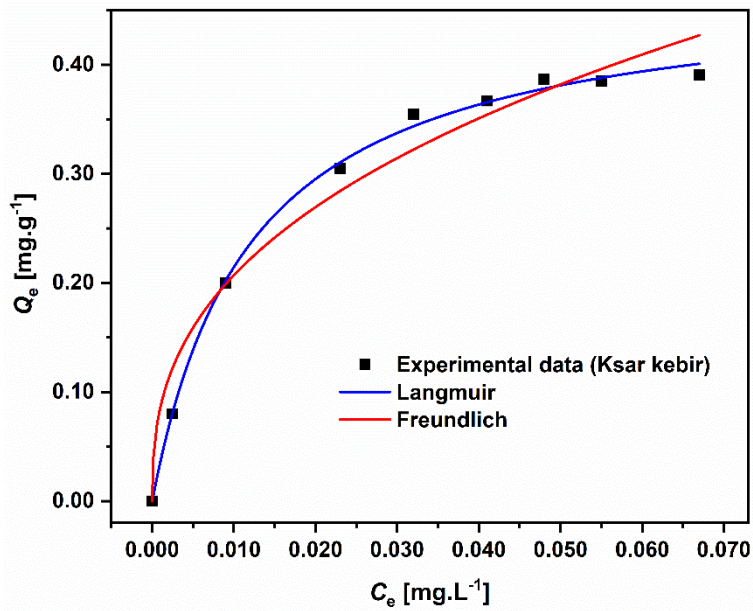


Fig. 5. Adsorption isotherms fitting at different initial concentration for Thiabendazole adsorption on Ksar kebir soil (conditions: natural pH; T = 20 °C; V = 25 mL; time = 24 h; adsorbent dose = 40 g · L^{-1})

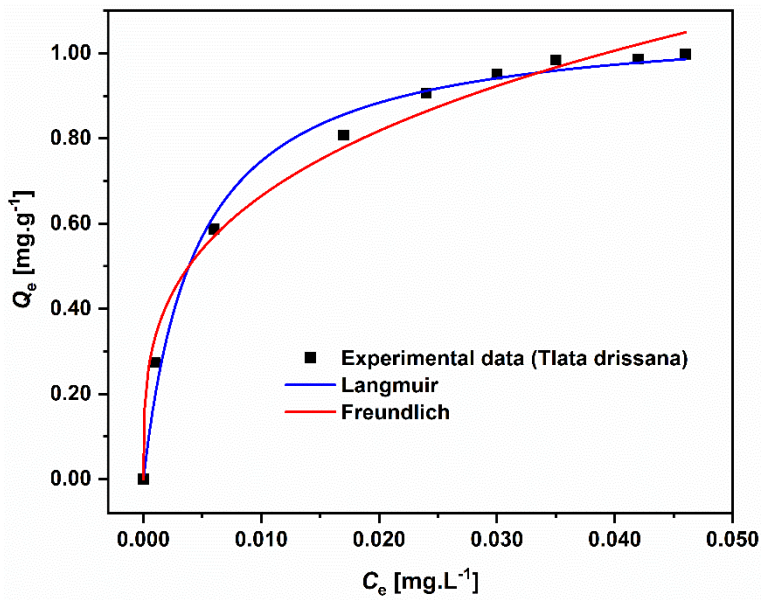


Fig. 6. Adsorption isotherms fitting at different initial concentration for Thiabendazole adsorption on Tlata drissana soil (conditions: natural pH; T = 20 °C; V = 25 mL; time = 24 h; adsorbent dose = 40 g · L^{-1})

Results of the parameters obtained from the nonlinear equations of each model are listed in Table 5. The comparison of the regression coefficients (R^2) shows that for the four soils, the adsorption isotherms of Thiabendazole are better described by the Langmuir model than by the Freundlich model, suggesting a monolayer adsorption. The maximum adsorption capacity achieved by the Langmuir isotherm model of Larache, Laouamra, Ksar kebir and Tlata drissana soils for the Thiabendazole fungicide is 0.747 mg · g^{-1}, 0.751 mg · g^{-1}, 0.473 mg · g^{-1} and 1.083 mg · g^{-1}, respectively. Similar results have also been reported by other researchers [24].

Table 5

The fitting parameters of adsorption isotherms for Thiabendazole fungicide adsorption

Isotherm models	Parameter	Larache	Laouamra	Ksar kebir	Tlata drissana
Langmuir	Q_m [mg·g^{-1}]	0.747	0.751	0.473	1.083
	K_L [L·mg^{-1}]	57.345	19.128	83.093	222.412
	R^2 [-]	0.99	0.99	0.99	0.99
Freundlich	K_F [mg·g^{-1}]	2.422	2.904	1.194	2.635
	$1/n$	0.481	0.684	0.380	0.289
	R^2 [-]	0.97	0.98	0.96	0.97

Conclusion

The present study provides elements for understanding the adsorption process of the Thiabendazole fungicide by four types of agricultural soils from different regions of Morocco. We found that all adsorbents have alkaline pH in solution characteristic of calcareous soils. The Larache and Laouamra soils are distinguished by their high OM content. The high OM content of these two soils results logically in high cation exchange capacities. Also, the major elements present in the soil are silicon, carbon, calcium, aluminum and iron. Therefore, the analysis of X-ray diffractograms shows that the main peaks correspond to the quartz and calcite for all four soils examined. The adsorption data are in good agreement with the Langmuir isotherm. with a maximum monolayer adsorption capacity of 0.747 mg·g^{-1}, 0.751 mg·g^{-1}, 0.473 mg·g^{-1} and 1.083 mg·g^{-1}, for Larache, Laouamra, Ksar kebir and Tlata drissana soils, respectively. The adsorption capacity of the studied soils makes them promising adsorbents for industrial applications and environmental protection.

References

[1] Roca Jalil ME, Vieira RS, Azevedo D, Baschini M, Sapag K. Improvement in the adsorption of thiabendazole by using aluminum pillared clays. Appl Clay Sci. 2013;71:55-63. DOI: 10.1016/J.CLAY.2012.11.005.

[2] Bertomeu-Sánchez JR. Introduction. Pesticides: past and present. HoST - J Hist Sci Technol. 2019;13(1):1-27. DOI: 10.2478/HOST-2019-0001.

[3] Zhao L, Li Y, Ren W, Huang Y, Wang X, Fu Z, et al. Pesticide residues in soils planted with Panax notoginseng in South China, and their relationships in Panax notoginseng and soil. Ecotoxicol Environ Safety. 2020;201:110783. DOI: 10.1016/J.ECOENV.2020.110783.

[4] Bhandari G, Atreya K, Scheepers PTJ, Geissen V. Concentration and distribution of pesticide residues in soil: Non-dietary human health risk assessment. Chemosphere. 2020;253:26594. DOI: 10.1016/J.CHEMOSPHERE.2020.126594.

[5] Kafaei R, Arfaeinia H, Savari A, Mahmoodi M, Rezaei M, Rayani M, et al. Organochlorine pesticides contamination in agricultural soils of southern Iran. Chemosphere. 2020;240:124983. DOI: 10.1016/J.CHEMOSPHERE.2019.124983.

[6] Murtala Y, Nwanguma BC, Ezeanyika LU. Staphylococcus Sp. Strain MY 83295F: A potential P,P'-DDT-degrading bacterium isolated from pesticide contaminated soil. Acta Biol Marisiensis. 2020;3(2):22-35. DOI: 10.2478/ABMJ-2020-0008.
[7] Mondal S, Subramaniam C. Xenobiotic contamination of water by plastics and pesticides revealed through real-time, ultrasensitive, and reliable surface-enhanced raman scattering. ACS Sustain Chem Eng. 2020;8(20):7639-48. DOI: 10.1021/ACSSUSCHEMENG.0C00902.
[8] Alencar BTB, Ribeiro VHV, Cabral CM, dos Santos NMC, Ferreira EA, Francino DMT, et al. Use of macrophytes to reduce the contamination of water resources by pesticides. Ecol Indic. 2020;109:105785. DOI: 10.1016/J.ECOLIND.2019.105785.
[9] Barron MG, Ashurova ZJ, Kukaniev MA, Avloev HK, Khaidarov KK, Jamshedov JN, et al. Residues of organochlorine pesticides in surface soil and raw foods from rural areas of the Republic of Tajikistan. Environ Pollut. 2017;224:494-502. DOI: 10.1016/J.ENVPOL.2017.02.031.
[10] Carvalho FP. Pesticides, environment, and food safety. Food Energy Secur. 2017;6(2):48-60. DOI: 10.1002/FES3.108.
[11] Abbou M, Chabbi M, Benicha M. Assessment of the pressure of pesticide use on the environment: Case of strawberry of Loukkos northwestern Morocco. African Mediterr Agric Res J Al-Awamia. 2021;(130):54-72. DOI: 10.34874/IMIST.PRSM/afrimed-i130.31379.
[12] Huang X, Ren J, Li P, Feng S, Dong P, Ren M. Potential of microbial endophytes to enhance the resistance to postharvest diseases of fruit and vegetables. J Sci Food Agric. 2021;101(5):1744-57. DOI: 10.1002/JSFA.10829.
[13] Perruchon C, Pantoleon A, Veroutis D, Gallego-Blanco S, Martin-Laurent F, Liadaki K, et al. Characterization of the biodegradation, bioremediation and detoxification capacity of a bacterial consortium able to degrade the fungicide thiabendazole. Biodegradation. 2017;28(5):383-94. DOI: 10.1007/S10532-017-9803-Z.
[14] El Aggadi S, El Hourch A. Removal of Reactive Blue 21 (RB21) Phthalocyanine Dye from aqueous solution by adsorption process: A review. Polish J Environ Stud. 2021;30(4):3425-32. DOI: 10.15244/PJOES/127384.
[15] Fan L, Luo C, Li X, Lu F, Qiu H, Sun M. Fabrication of novel magnetic chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue. J Hazard Mater. 2012;215-216:272-9. DOI: 10.1016/j.jhazmat.2012.02.068.
[16] Lutterotti L, Matthies S, Wenk HR. MAUD: a friendly Java program for material analysis using diffraction. IUCr Newsl CPD. 1999;21(14-15). Available from: http://hdl.handle.net/11572/57067.
[17] Feng C, Ren P, Li Z, Tan W, Zhang H, Jin Y, et al. Graphene/waste-newspaper cellulose composite aerogels with selective adsorption of organic dyes: Preparation, characterization, and adsorption mechanism. New J Chem. 2020;44(6):2256-67. DOI: 10.1039/c9nj05346h.
[18] Schvartz C, Walter C, B. Claudot, Bouedo T, Aurousseau P. Synthèse nationale des analyses de terre réalisées entre 1990 et 1994. I. Constitution d'une banque de données cantonales. Etude Gest des Sols. 1997;4(3):191-204. Available from: https://hal.archives-ouvertes.fr/hal-02068893
[19] Sen TK, Afroze S, Ang HM. Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of Pinus radiata. Water Air Soil Pollut. 2011;218(1-4):499-515. DOI: 10.1007/s11270-010-0663-y.
[20] Boulinguiez B, Le Cloirec P, Wolbert D. Revisiting the determination of langmuir parameters-application to tetrahydrothiophene adsorption onto activated carbon. Langmuir. 2008;24(13):6420-4. DOI: 10.1021/la800725s.
[21] Ho YS. Selection of optimum sorption isotherm. Carbon. 2004;42(10):2115-6. DOI: 10.1016/j.carbon.2004.03.019.
[22] Langmuir I. The constitution and fundamental properties of solids and liquids. Part I. Solids. J Am Chem Soc. 1916;38(11):2221-95. DOI: 10.1021/ja02268a002.
[23] Freundlich HM. Over the adsorption in solution. J Phys Chem. 1906;57(1):385-470. Available from: https://pubs.acs.org/loi/jpchax/group/d1900.y1906.
[24] Schimmel D, Fagnani KC, Dos Santos JBO, Barros MASD, Da Silva EA. Adsorption of turquoise blue qg reactive dye on commercial activated carbon in batch reactor: Kinetic and equilibrium studies. Brazilian J Chem Eng. 2010;27(2):289-98. DOI: 10.1590/S0104-66322010000200007.