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Glyphosate removal from aqueous solution by an adsorption process on natural zeolite-bearing rock

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ABSTRACT

Pollution of groundwater and surface water compartments is one of the major concerns related to the use of glyphosate in plant-protection products, and is attributed to the postulated endocrine-disrupting activity of the compound. There is a consensus that glyphosate cannot be inactivated in water by the addition of other substances that may also be foreign to that compartment. Therefore, a good, environment-friendly solution would involve use of natural zeolite-bearing rock to remove glyphosate from water. The main purpose of this study was to demonstrate that the content of glyphosate in water can be reduced by 50% through its adsorption on natural zeolites. An additional purpose was to identify the mechanism underlying the process – demonstrated to be adequately characterized by Freundlich and Langmuir isotherms. In natural zeolite-bearing rock with grain diameter <0.02 mm, the maximum monolayer adsorption capacity was 3.66 mg glyphosate/g sorbent. Glyphosate was shown to be adsorbed inside medium-sized heulandite channels with internal diameters of 0.4–0.6 nm; moreover, the adsorption of glyphosate onto heulandite crystal was shown to be a physisorption, unaccompanied by the formation of chemical bonds.

Keywords: Glyphosate; Heulandite; Clinoptilolite; Adsorption process; Material studio

1. Introduction

Glyphosate is a commonly used herbicide with a broad spectrum of applications. Its mode of action is through inhibition of 5-enolpyruvylshikimate-3-phosphate synthase – an enzyme important for plants, because it is involved in the metabolic transformation pathway of shikimic acid [1,2]. The global consumption of glyphosate was estimated to be 650,000 tons in 2011 [3]. Extensively used, glyphosate is a considerable pollutant of the water compartment – it is detected in groundwater and surface water, both of which are often used as sources of drinking water [4–6]. The pollution of surface waters by glyphosate in France exceeded 86 μg/L [7], whereas the recorded concentration of glyphosate in storm water was 430 μg/L [8]. In addition, glyphosate poses a considerable threat to the groundwater compartment – the average level detected in north-eastern Spain – Catalonia was 0.2 μg/L, with a recorded maximum of 2.5 μg/L [9]. The sources of glyphosate pollution of water are activities and phenomena related to its production and use, including:

- migration from the treated field areas;
- inadequate handling of wastewater from washing of sprayers;
- industrial wastewater from plants manufacturing glyphosate;
- outflows from inadequately protected landfills on which the waste-containing glyphosate residues were stored during the non-statutory period; and
- accidents during transportations.

When present in the aquatic environment, glyphosate not only has an adverse effect on aquatic organisms

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[10,11], but also may pose a serious threat to human health because of its bioaccumulation potential and entry into the food chain [12,13]. In humans, this compound can induce health problems such as gastrointestinal disorders, obesity, diabetes, cardiac diseases, depression, autism, infertility, and Alzheimer's disease [14]. Furthermore, it has a toxic effect on the liver and kidneys [15–17]. At present, its postulated endocrine-disrupting activity is widely discussed [18–22]. Being a substance of high concern, glyphosate should be efficiently removed from water or inactivated therein. This, however, cannot be performed by introducing other compounds that are foreign to the aquatic environment. The removal of glyphosate from water by its adsorption onto natural zeolite-bearing rock materials seems to be a good, environment-friendly solution. Natural zeolites may be used because of their specific physicochemical properties arising from their highly organized structure of channels and chambers that vary in diameter, with high external and internal surface and porosity. Zeolites are capable of selective sorption related to these abovementioned properties, not only through behaving as molecular sieves but also due to the intrinsic properties of the adsorbate such as polarity, shape, dimension of the molecule, dipole moment, and so on [23,24]. The chemical properties, such as ion-exchange capacity, selectivity, sorptive, and catalytic activities, of zeolites are related to their specific structure [25,26].

The aims of the study were to:

- assess the utility of natural zeolite-bearing rock with varied granulation for removing glyphosate from aqueous solutions and
- identify and characterize the probable mechanism of adsorption of glyphosate on heulandite – the mineral which dominates in natural zeolite-bearing rock.

2. Materials and methods

2.1. Research material

This research used a natural zeolite-bearing rock with varied granulation (grain diameter <0.02 mm and from 0.50 to 1.00 mm) and the plant protection agent ROUNDUP 360-SL, which includes glyphosate as an active substance. The criterion for the selection of the active substance for this research was its general application, seen practically worldwide, and its toxicity to humans and animals.

The natural zeolite-bearing rock used for the research consisted of heulandite (60%), clinoptilolite (20%), and amorphous components (20%), which was confirmed by microscopic examination using both scanning and transmission electron microscopy and indicated the presence of both a crystalline and an amorphous structure (Figs. 1 and 2).

The main minerals in a natural zeolite-bearing rock were identified by X-ray diffraction (XRD) analysis (using an X'Pert Pro diffractometer from the Company PANalytical). As confirmed by XRD investigations, the dominant component of a natural zeolite-bearing rock is heulandite and, to a lesser extent, clinoptilolite. A natural zeolite-bearing rock with a grain diameter <0.02 mm is characterized by a 30% larger outer surface area, as measured by nitrogen isotherms, and a 190% greater total volume of all pores, which can indicate its higher activity against the pesticide investigated.

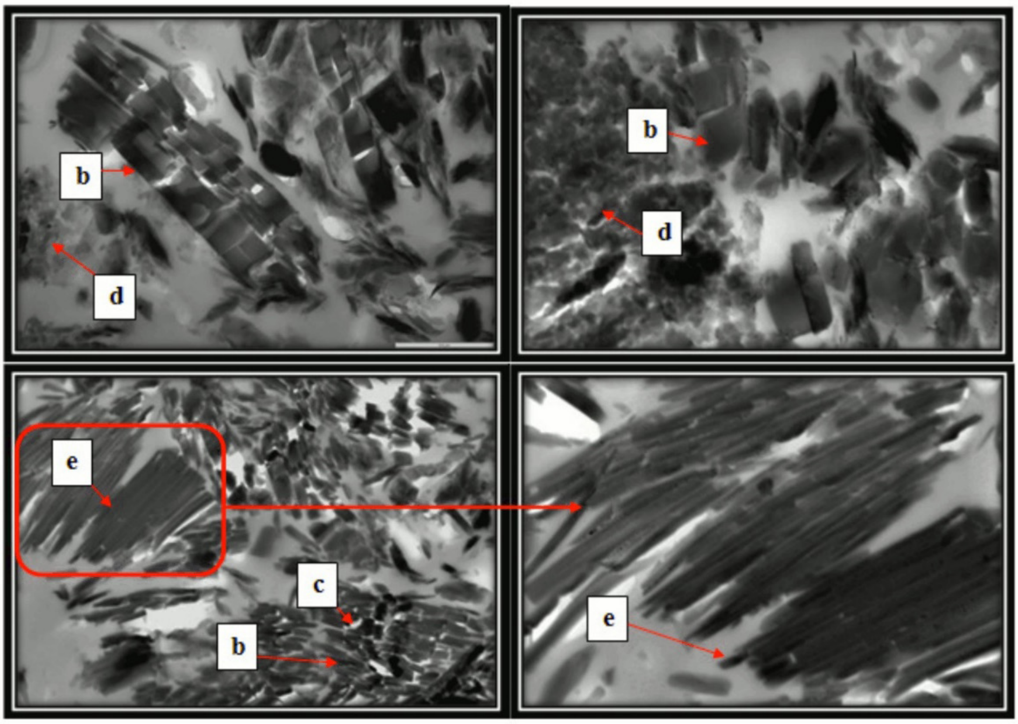


Fig. 1. Cross-sections of heulandite crystals in a natural zeolite-bearing rock with a grain diameter of <0.02 mm imaged by a transmission electron microscope (TEM). (a) Longitudinal cross-section of a heulandite crystal, (b) transversal section of a heulandite crystal, (c) space between heulandite crystals, (d) amorphous structure, and (e) cross-section across heulandite crystals stuck together.

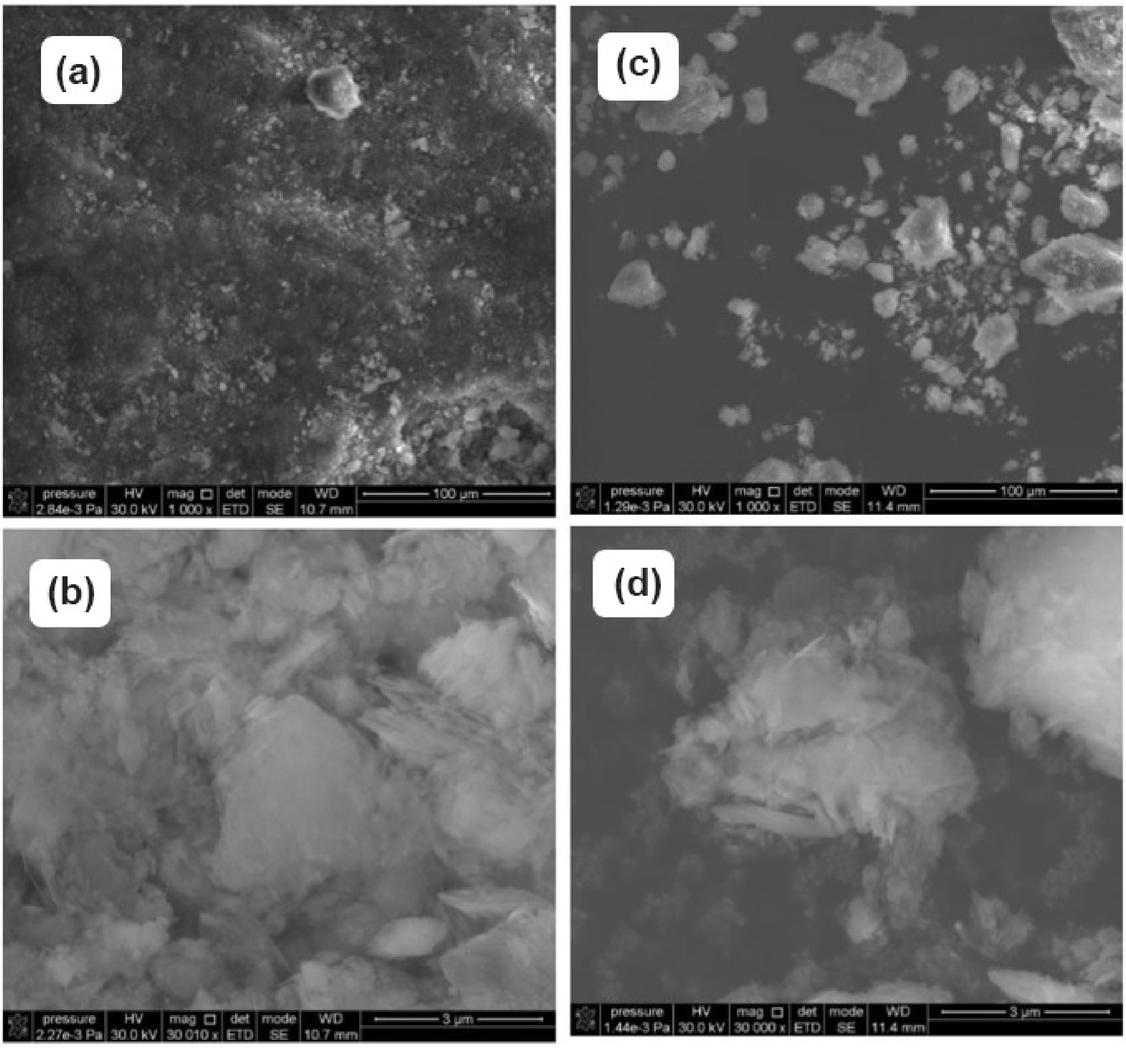


Fig. 2. Scanning electron microscopic images of the outer surface of a natural zeolite-bearing rock used in this research. ((a) and (b)) A natural zeolite-bearing rock with a grain diameter of 0.5–1.0 mm; ((c) and (d)) a natural zeolite-bearing rock with a grain diameter <0.02 mm.

The main physicochemical properties of zeolite-bearing rock that were investigated are shown in Table 1. The Si/Al ratio for natural zeolite-bearing rock in both cases is 3.8.

2.2. Experimental procedure

In conical flasks, 400 mL aqueous solutions of glyphosate (concentration: 90; 540; 720; 900; 1,080 mg of active ingredient [a.s.] per L) were shaken for 12 h with 50 g natural zeolite-bearing rock of varied granulation (grain diameter <0.02 mm and 0.50–1.00 mm). The conical flasks were wrapped in aluminum foil to prevent photodegradation. After 12 h, the sample mixtures were centrifuged 10 min at 5,100 rpm. The experiment was repeated six times ($n = 6$) at room temperature ($t = 24$°C). In the supernatants thus produced, glyphosate concentrations were determined both before and after the zeolite was added. Additionally, the glyphosate content in a natural zeolite-bearing rock was determined after this experiment was completed.

2.3. Methods

2.3.1. Extraction and purification

We introduced 0.1 M NaOH into a 500 mL water sample to obtain a pH of 9. A solid-phase extraction column was filled with 500 mg quaternary amine, conditioned three times with 2 mL portions of methanol, then rinsed three times with 2 mL portions of deionized water, and this was poured through the 500 mL water sample column. Elution was conducted with two 1 mL portions of HCl with pH of 1. The elutant thus collected was transferred to an autosampler flask.

2.3.2. Instrumental analysis

The glyphosate content in the research material was determined by high-performance liquid chromatography (HPLC) with fluorescence detection (water and zeolites). The chromatographic conditions of the HPLC analysis are presented in Table 2.

Table 1
Basic properties of the zeolite-bearing rock investigated in this study

Zeolite type	Inner surface area (S_{BET}) and outer surface area (S_{ext}) of pores N adsorption isotherms	Chemical composition SEM–EDX investigations Si/Al ratio	Dominating mineral XRD investigations	Total pore volume (cm^3/g)	Micropore volume calculated from alpha-s plot (cm^3/g)	Volume of the other pores without micropores (cm^3/g)
ZN	S_{BET} = 30 m^2/g S_{ext} = 27 m^2/g Bimodal material (micro–mesoporous) with a relatively small inner surface area	C (0.2%), O (64%), Mg (0.5%), Al (6%), Si (23%), K (2%), Ca (1.5%), Fe (0.6%) Si/Al ratio: 3.8	Chemical formula: $CaAl_2Si_7O_{18}{\cdot}6H_2O$ Zeolite name: heulandite	0.516	0.005	0.511
ZNg	S_{BET} = 30 m^2/g S_{ext} = 20 m^2/g Bimodal material (micro–mesoporous) with a relatively small inner surface area	C (4%), O (63%), Mg (0.3%), Al (6%), Si (23%), K (2%), Ca (1.5%), Fe (0.6%) Si/Al ratio: 3.8	Chemical formula: $Ca(Al_2Si_7O_{18}){\cdot}6H_2O$ Zeolite name: heulandite	0.178	0.001	0.177

ZN – a natural zeolite-bearing rock with a grain diameter of <0.02 mm and ZNg – a natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm.

Table 2
Chromatographic conditions of HPLC analysis

Instrument	Waters Alliance 2695 HPLC system with the Waters 2475 fluorescence detector and a two-stage post-column derivatization instrument		
HPLC column	HPLC Pickering Laboratories Potassium Cation Exchange column, 4.0 × 150 mm × 8 µm		
Column temperature	55°C		
Mobile phase	Phase A (4 g H_3PO_4 + 1 g KH_2PO_4 in 1 L water) Phase B (3 g KOH in 1 L water)		
Elution	Time (min)	Phase A (%)	Phase B (%)
	0	100	0
	20.0	100	0
	20.1	0	100
	22.0	0	100
	22.1	100	0
	32.0	100	0
Flow rate	0.4 mL/min		
Detection	$\lambda_{excitation}$ = 330 nm; $\lambda_{emission}$ = 465 nm		
Volume injection	1 µL		
Retention time	5.75 min		

2.3.3. Validation of the method

The method was validated. The calibration curve of the peak areas as a function of the glyphosate concentration showed linear behavior with a regression coefficient of 0.999. Calibration was conducted at four levels: 0.05, 1.0, 10.0, and 100.0 µg/L. When the glyphosate content in a natural zeolite-bearing rock was determined, the average recovery rate was 74%, reproducibility 9.8%, and uncertainty 23%. In turn, when the glyphosate content was determined in aqueous solutions, the average recovery rate was 86%, reproducibility 8.9%, and uncertainty 21%. The uncertainty of the method was estimated with a *k* factor of 2 and credibility level of 95%.

2.4. Modeling of glyphosate sorption on a natural zeolite-bearing rock using the Material Studio software from Accelrys (adsorption locator module)

A probable mechanism of glyphosate adsorption on heulandite (the main mineral of the rock) was proposed.

Glyphosate adsorption sites on heulandite were visualized and, at the same time, the energy of glyphosate adsorption sites on the sorbent was calculated. The modeling process was performed using the molecular modeling program Material Studio from Accelrys, version 7.0 (adsorption locator module; 100,000 loading steps, three heating cycles, and optimization of energy). The universal force field was used in the calculations (charges – use current; summation method: group based; cutoff distance: 12.5 Å). The geometrical optimization of a glyphosate molecule was obtained using the FORCITE PLUS module built into the Material Studio program. We determined the energetically favorable sites for adsorption of the adsorbate on a heulandite crystal that were characterized by the lowest energy of the system and their adsorption energy. This is a modern tool of computational chemistry using Monte Carlo simulation that is designed to determine the most probable spatial configurations of an adsorbate which is adsorbed on an adsorbent with the lowest energy of the system. Adsorption energy can be defined according to the following formula [27–30]:

$$\Delta E_{\text{Adsorption energy}} = E_{\text{surface(a)}} - E_{\text{surface (b)}} - nE_{\text{glyphosate}} \tag{1}$$

where $E_{\text{surface(a)}}$ is the total energy of system when a glyphosate molecule adsorbed on the heulandite crystal, $E_{\text{surface (b)}}$ is the energy of the heulandite crystal, and $nE_{\text{glyphosate}}$ is the glyphosate molecular energy. The greater the adsorption energy ($E_{\text{Adsorption energy}}$) to the absolute value, the more stable is the system. If $E_{\text{Adsorption energy}} > 0$, the glyphosate molecule cannot be adsorbed on the heulandite crystal.

3. Results and discussion

The results of our research are presented in tabular form (Tables 1–4) as the arithmetic mean from six repetitions ($n = 6$). A natural zeolite-bearing rock significantly reduced the glyphosate concentration in its aqueous solution as compared with the control – that is, by 20%–48%, depending on the initial glyphosate concentration in the solution and the granulation of the rock. The highest percentage reduction in the glyphosate concentration in its water solution as compared with the control (i.e., by 50%) was found for a natural zeolite-bearing rock with a grain diameter <0.02 mm (Table 3).

The experiment showed that the granulation of a natural zeolite-bearing rock significantly contributed to the efficiency of glyphosate removal from the aqueous environment as a result of the enhanced adsorption capacity of the minerals investigated. The introduction of a natural zeolite-bearing rock with a grain diameter <0.02 mm into the aquatic environment caused a significant reduction in the glyphosate concentration of >40%, regardless of the initial concentration investigated. In contrast, in the case of a natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm, the glyphosate concentration was found to reduce by 20% only. After zeolites had been introduced into contaminated water, their glyphosate content increased as the initial

Table 3
Glyphosate concentrations in its aqueous solution before and after the addition of a natural zeolite-bearing rock ($n = 6$)

Initial glyphosate concentration in an aqueous solution (mg/L)	$\bar{X}$ glyphosate concentration in an aqueous solution in mg/L (±SD)			LSD	MR_1	MR_2
	V_1	V_2	V_3			
1,080	1,046.35 (±9.23)	589.33 (±17.83)	824.96 (±11.95)	20.32	43	21
900	884.11 (±14.25)	515.66 (±12.85)	703.93 (±10.54)	19.04	42	20
720	715.48 (±10.89)	406.18 (±5.61)	562.76 (±9.85)	13.67	43	21
540	531.51 (±8.58)	288.45 (±6.94)	405.23 (±13.09)	14.89	45	24
90	81.33 (±4.11)	42.02 (±3.46)	58.38 (±9.74)	9.67	48	28

V_1 – without the addition of a natural zeolite-bearing rock; V_2 – with the addition of a natural zeolite-bearing rock with grain diameter <0.02 mm; V_3 – with the addition of a natural zeolite-bearing rock with grain diameter of 0.50–1.00 mm; LSD – the lowest statistically significant difference, the Tukey test for $p = 0.05$; MR_1 – the percentage removal of glyphosate from the aqueous solution after the addition of V_2 [%]; MR_2 – the percentage removal of glyphosate from the aqueous solution after the addition of V_3 [%].

Table 4
Average glyphosate content in a natural zeolite-bearing rock after adsorption

Initial glyphosate concentration in an aqueous solution (mg/L)	$\bar{X}$ glyphosate concentration in a natural zeolite-bearing rock in mg/L (±SD)		LSD
	V_1	V_2	
1,080	3,661.93 (±22.67)	2,020.42 (±13.01)	26.67
900	3,065.88 (±12.22)	1,428.26 (±12.62)	15.98
720	2,438.25 (±19.41)	1,140.48 (±19.85)	25.26
540	1,877.61 (±22.07)	985.22 (±12.07)	22.89
90	320.92 (±11.99)	183.96 (±8.21)	13.22

V_1 – a natural zeolite-bearing rock with a grain diameter <0.02 mm; V_2 – a natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm; LSD – the lowest statistically significant difference, the Tukey test for $p = 0.05$.

concentration grew. This research demonstrated that, after the experiment had been completed, the glyphosate content in a natural zeolite-bearing rock with a grain diameter <0.02 mm was higher by approximately 50% than in a natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm. This was clearly related to a larger active surface area in the former case (Table 3). The best effect was achieved for the highest investigated concentration of 1,080 mg a.s./L, wherein a natural zeolite-bearing rock with a grain diameter <0.02 mm adsorbed >3,600 mg a.s./kg (Fig. 3).

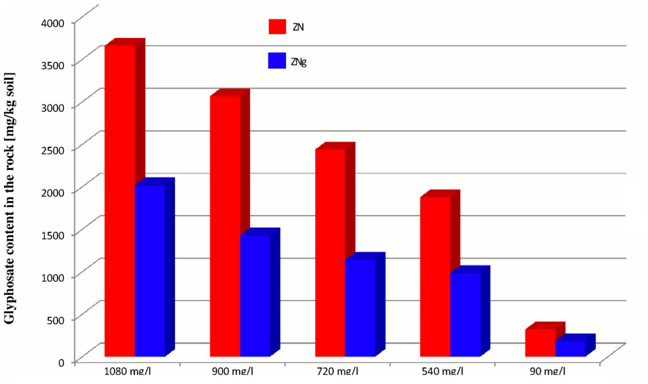


Fig. 3. Average glyphosate content (mg/kg) in a natural zeolite-bearing rock after adsorption. ZN – a zeolite-bearing rock with a grain diameter of less than 0.02 mm. ZNg – a zeolite-bearing rock with a grain diameter of 0.50–1.00 mm.

The sorption process was described by the Freundlich and Langmuir equation (Fig. 4). The isotherm constants (*a*, *k*) were determined using the IZO v.1.2(C) JP program. The values of the isotherm parameters (*a*, *k*), the correlation coefficient *R*, and the SD (S) of the isotherm equations derived are shown in Table 5. The quantity of glyphosate adsorbed was determined by the following equation [31]:

$$Q_e = (C_o - C_e) * V/m \tag{2}$$

where Q_e is the amount of glyphosate adsorbed at equilibrium (mg/g), C_o is the initial glyphosate concentration (mg/L), V is the volume of the glyphosate solution (L), and m is the mass of adsorbent used (g).

Table 5
Coefficients of the adsorption isotherms

Isotherm	*a*	*k*	*R*	*S*
A natural zeolite-bearing rock with a grain diameter <0.02 mm				
Freundlich $A = ac^k$	0.00995	0.92000	0.99	0.05000
Langmuir $A = ac/1 + kc$	0.00728	0.00044	0.97	0.01440
A natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm				
Freundlich $A = ac^k$	0.00579	0.84600	0.96	0.07440
Langmuir $A = ac/1 + kc$	0.00308	0.00065	0.98	0.03890

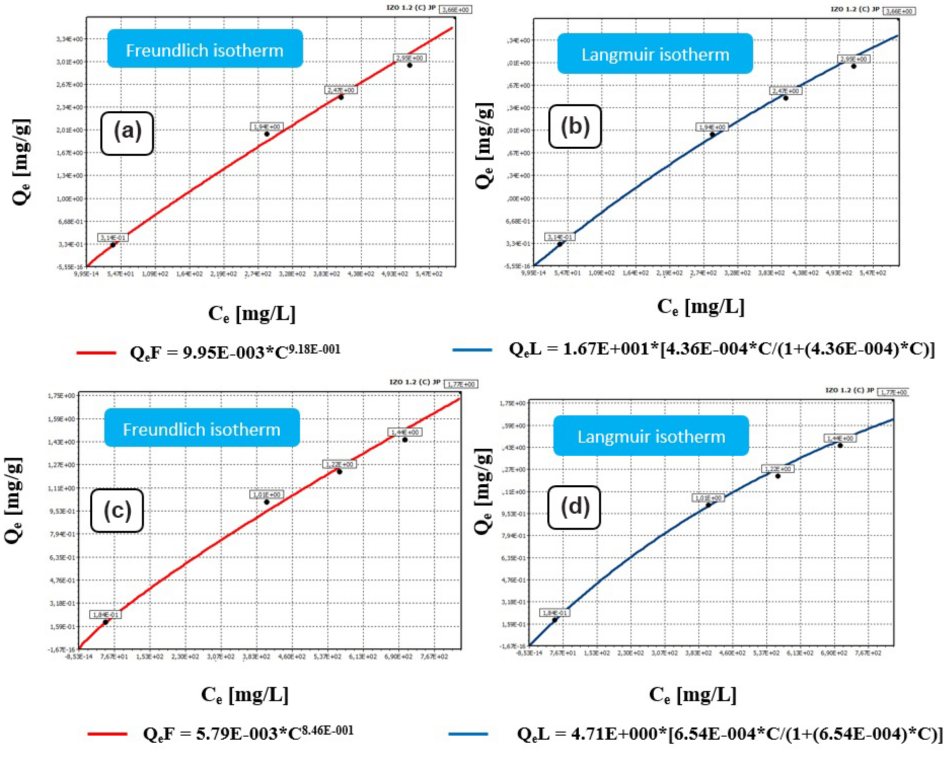


Fig. 4. Isotherms of glyphosate adsorption on a natural zeolite-bearing rock: (a) and (b) – with a grain diameter <0.02 mm – Freundlich and Langmuir isotherms, and (c) and (d) – with a grain diameter of 0.50–1.00 mm – Freundlich and Langmuir isotherms, where Q_e is the amount of glyphosate adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L).

The correlation coefficients calculated for the fit of the model of Freundlich and Langmuir isotherms describing the process of glyphosate sorption from the aqueous phase on a natural zeolite-bearing rock are high – that is, equal to 0.96–0.99. This demonstrates that the models used very accurately fit the sorption process considered.

The estimated values of $k < 1$ in the Freundlich equation for all the zeolites investigated indicate physical adsorption. The knowledge of the value of the parameter k ($1/n$) in the Freundlich equation makes it possible to assess the intensity of glyphosate adsorption from the aqueous phase on the sorbent, whereas the value of the constant a then defines the sorption capacity of the sorbent for the equilibrium concentration in the solution. A higher value of the coefficient a also corresponds to a larger sorption capacity. In the present research, the highest values of the coefficients a and k were found for a natural zeolite-bearing rock with a grain diameter <0.02, confirming its usefulness for removing glyphosate from the aquatic environment. Moreover, it was found that glyphosate sorption on a natural zeolite-bearing rock could be described using the Langmuir model (Fig. 4), which suggested the formation of a monolayer on the surface of an adsorbate. The maximum capacity of the adsorption monolayer was 3.66 mg glyphosate/g of a natural zeolite-bearing rock with a grain diameter <0.02 mm. For all of the sorption models, the same group of isotherms according to the GILES classification was found – that is, L-type isotherms [32]. It consists of the isotherms of the systems where the solvent is not strongly adsorbed and does not compete with the dissolved substance being adsorbed. Furthermore, the shape of the isotherm indicates a flat alignment of the adsorbate at the active centers of the sorbent. The obtained isotherms did not reach the plateau value.

The affinity coefficient k is calculated from the ratio between the equilibrium glyphosate concentration in the aqueous solution of the pesticide (mg/L) and the glyphosate content in zeolites after the equilibrium has ceased to exist (mg/kg of dry soil). This indicates the degree of affinity between the mineral and the glyphosate. The lower the value of k, the higher is the affinity between the mineral and a given active substance. In the experiment, the lowest value of the coefficient k was found for a natural zeolite-bearing rock with a grain diameter <0.02 mm; therefore, it is a sorbent which is characterized by the highest affinity to glyphosate among all the zeolites investigated, irrespective of the concentration considered (Table 6).

Irrespective of the degree of rock granulation, the lowest value of the coefficient k was found for the lowest initial concentration investigated – that is, 90 mg a.s./L. The degree of rock granulation did not affect the value of the reaction of the aqueous solutions of glyphosate after the sorbent had been added. For a natural zeolite-bearing rock with a grain diameter <0.02 mm, the pH of equilibrium solutions fell within the range from 6.5 to 6.9, whereas for a natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm, they varied, respectively, between 5.4 and 6.1. In the literature that glyphosate adsorption on montmorillonite grows as the reaction of the solution decreases. However, in solutions with a very acid reaction ($pH < 3$), both montmorillonite and glyphosate have a positive charge, which causes repulsion and a reduction in the amount of glyphosate adsorbed on the mineral [33].

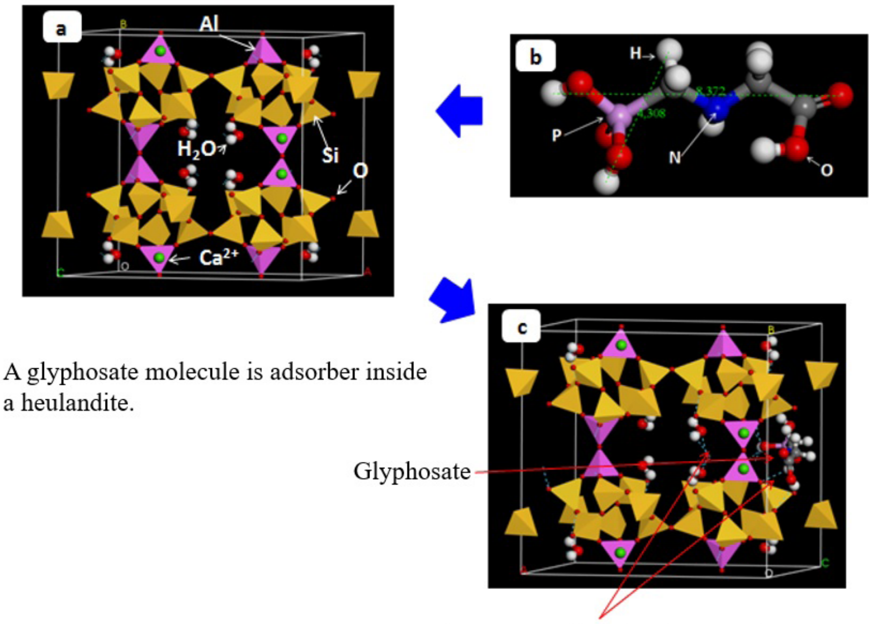
Moreover, this study proposed a probable mechanism of glyphosate adsorption on a heulandite crystal (Fig. 5). Heulandite is characterized by a complicated system of channels and chambers. These channels can be divided into smaller (diameter <0.4 nm) and medium-sized (0.4–0.6 nm). In turn, these chambers can be divided into those with a diameter of 0.6–0.8 nm (medium-sized) and a diameter <0.6 nm (small). Glyphosate is a small molecule. The size of glyphosate in space (its diameter), as estimated using the Material Studio program, is 0.83 × 0.43 nm. This means that glyphosate can diffuse into heulandite channels (Fig. 6).

Glyphosate sorption on montmorillonite, illite, and kaolinite decreases in the order in which the following cations occur in their structures: $Al^{3+} > Fe^{3+} > Cu^{2+} > Mg^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Na^{+}$ [35]. The increased glyphosate sorption on minerals that contain, in their structure, a larger number of bivalent and trivalent cations can be explained by the

Table 6
Reaction of an aqueous glyphosate solution before and after the addition of a natural zeolite-bearing rock

Initial glyphosate concentration in an aqueous solution (mg/L)	pH of the pesticide solution before the addition of the rock (±SD)	pH of the pesticide solution after the addition of the rock (±SD)	Coefficient k
A natural zeolite-bearing rock with a grain diameter <0.02 mm			
1,080	5.33 (±1.1)	6.50 (±2.1)	0.16
900	5.36 (±3.8)	6.70 (±4.7)	0.16
720	5.51 (±2.9)	6.90 (±0.8)	0.16
540	5.30 (±4.3)	6.90 (±3.5)	0.15
90	5.68 (±0.9)	6.90 (±0.4)	0.13
A natural zeolite-bearing rock with a grain diameter of 0.50–1.00 mm			
1,080	5.33 (±1.1)	5.40 (±11.3)	0.41
900	5.36 (±3.8)	5.40 (±2.8)	0.49
720	5.51 (±2.9)	5.30 (±3.9)	0.49
540	5.30 (±4.3)	5.60 (±0.7)	0.41
90	5.68 (±0.9)	6.10 (±5.6)	0.32

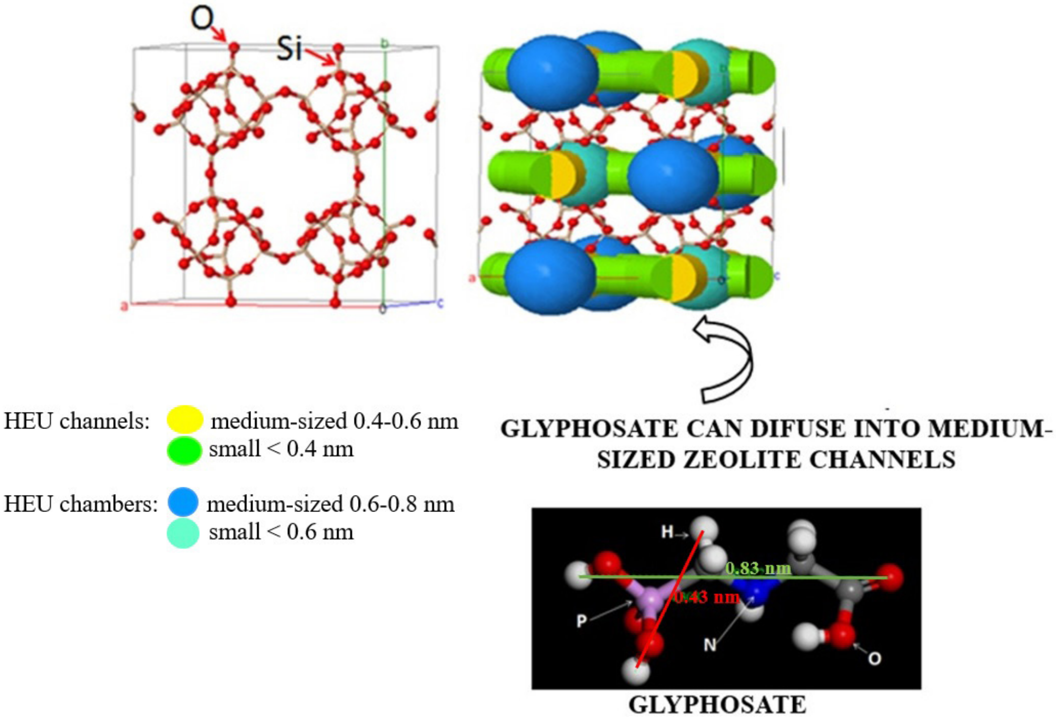
Coefficient k – calculated from the ratio between the equilibrium glyphosate concentration in the aqueous solution of the pesticide (mg/L) and the glyphosate content in zeolites after the equilibrium has ceased (mg/kg of dry soil).



A glyphosate molecule is adsorber inside a heulandite.

Hydrogen bonds form between the glyphosate molecule (the hydrogen atoms of the amine, phosphonate and carboxyl groups) and the oxygen atoms in the heulandite structure.

Fig. 5. Mechanism of glyphosate adsorption on heulandite ((a) – heulandite crystal with water molecules and calcium cations; (b) – a glyphosate molecule, along marked distances between atoms; (c) – the most favorable site of glyphosate adsorption on a heulandite crystal characterized by the lowest energy of the system.



GLYPHOSATE CAN DIFUSE INTO MEDIUM-SIZED ZEOLITE CHANNELS

Fig. 6. A system of channels and chambers in a heulandite crystal (HEU) visualized by the ZEOMICS application [34].

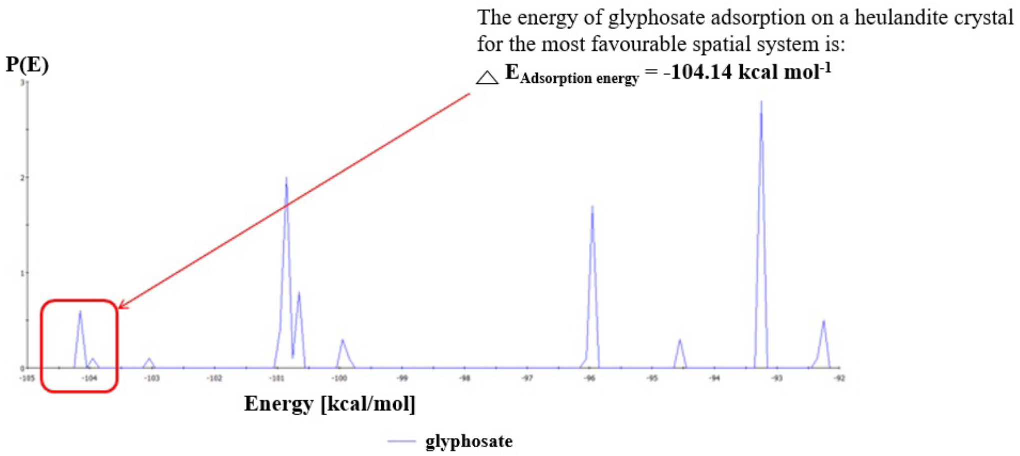


Fig. 7. Distribution of the energy of glyphosate adsorption on heulandite crystal, along with water molecules and calcium cations present in the zeolite channels, calculated using the adsorption locator module (Material Studio from Accelrys).

formation of complexes between cations located between mineral packages and glyphosate. Aluminum and iron oxides (gibbsite, goethite, hematite, and ferrihydrite) adsorb glyphosate better than the silicates (kaolinite, illite, montmorillonite) can. The number and situation of the sorption sites cause this. The glyphosate sorption sites on silicates are mostly the edges of octahedral layers where cations are located. The complex of the herbicide and a cation which is probably a part of the mineral is the main path of glyphosate adsorption on montmorillonite [36,37].

In the case of glyphosate adsorption on a natural zeolite-bearing rock, glyphosate was found to be adsorbed inside medium-sized heulandite channels with a diameter of 0.4–0.6 nm. Glyphosate adsorption on a heulandite crystal is unaccompanied by the formation of chemical bonds; therefore, it can be expected that, in this case, the effect of physical adsorption unfolds as a result of intermolecular forces – Van der Waals, ion-dipole, or dipole–dipole electrostatic interactions. The energy of glyphosate adsorption on a heulandite crystal is –104.14 kcal mol^{-1} for the most favorable spatial system (Fig. 7).

Hydrogen bonds form between the hydrogen atoms of the amine, phosphonate, and carboxyl groups in a glyphosate molecule and the oxygen atoms in the heulandite structure (Fig. 5(c)). In their structures, heulandite and clinoptilolite contain calcium cations, which probably also play a major role in the inactivation of glyphosate from the aqueous solution. Glyphosate can be adsorbed by clay minerals, thereby forming complexes with cations situated between mineral layers. In soils, glyphosate is strongly adsorbed, mainly due to the phosphonic acid group, which takes part in its adsorption. The most important glyphosate adsorption sites in soil are aluminum and iron oxides, sites of defects in aluminum silicates, and the edges of layered silicates [38].

Research on the use of natural zeolites to inactivate pesticides in the aquatic environment has been presented in several studies; however, that did not concern the active substance – glyphosate – considered in the present study [39,40]. The present study has demonstrated the possibility of using a natural zeolite-bearing rock containing heulandite and clinoptilolite to remove glyphosate from the aquatic environment.

4. Conclusions

- The introduction of a natural zeolite-bearing rock into the aquatic environment significantly reduced the glyphosate concentration in its aqueous solution – that is, by approximately 50% as compared with the control. The maximum reduction in the glyphosate concentration occurred after the introduction of a natural zeolite-bearing rock with a grain diameter <0.02 mm.
- The granulation of a natural zeolite-bearing rock significantly affected its binding efficiency with the glyphosate. A natural zeolite-bearing rock with a grain diameter <0.02 mm had twice the glyphosate sorption capacity as a rock with a grain diameter of 0.50–1.00 mm; this was related to a larger active surface area in the first case. Moreover, this is indicated by the value of coefficient k.
- The process of glyphosate sorption on the sorbent investigated is best described by the Freundlich and Langmuir model. The maximum capacity of the adsorption monolayer was 3.66 mg glyphosate/g of a natural zeolite-bearing rock with a grain diameter <0.02 mm. For all of the sorption models, the same group of isotherms according to the GILES classification was found – L-type isotherms.
- Glyphosate is adsorbed inside medium-sized heulandite channels with a diameter of 0.4–0.6 nm. Glyphosate adsorption on a heulandite crystal is unaccompanied by the formation of chemical bonds; therefore, it can be expected that, in this case, the effect of physical adsorption takes place. Hydrogen bonds form between the hydrogen atoms of the amine, phosphonate, and carboxyl groups in a glyphosate molecule and between the oxygen atoms in the heulandite structure.

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