Clinoptilolite in study of lindane and aldrin sorption processes from water solution

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Abstract

The scope of this study was adsorption of lindane and aldrin from water solution onto clinoptilolite rock with the following desorption using *n*-hexane. Both kinetic and equilibrium tests were conducted. During kinetic experiment the most part of aldrin and a half part of lindane were sorbed during the first hours. The sorption equilibria with removal of 95% of aldrin amount and about 68% of lindane amount have been set in for 48 h. The pseudo-second-order kinetics model gives somewhat better fit to the both pesticides' sorption data that may testify to the complicated and heterogeneous nature of interaction between active zeolite surface and the pesticides polar-dipole centers. OH^--groups and the coordinated exchangeable cations are probably the main active positions for the pesticide sorption on the clinoptilolite surface. Equilibrium experiment results show that adsorption isotherms for the low concentrations of lindane and aldrin (10–200 and 3–100 µg/L, respectively) fit well to the Freundlich and the Liner models. Only 10% of lindane sorbed and about 60% of aldrin sorbed were desorbed from the clinoptilolite using *n*-hexane under static conditions.
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Keywords: Lindane; Aldrin; Adsorption; Clinoptilolite; Sorption positions

1. Introduction

Although most organochlorine pesticides (OCPs) are now banned or severely restricted in industrialized countries, nevertheless they are commonly detected in air and precipitation of rural, urban or remote areas [1–3]. In some developing countries OCPs (including lindane and aldrin) are still used for agricultural purposes because of their low cost and versatility in controlling various insects. These OCPs have often been found in polluted ground and surface water near agricultural sites, and have therefore been detected from time to time in the food chain, drinking water and air. For example, aldrin and lindane have been found in the Gulf of Gdansk from 1996 to 2002 [4].

Aldrin has also detected by Turgut [5] in study conducted in 2000–2002 years in the most part of the surface water samples from Küçük Menderes (Turkey). Hexachlorocyclohexane and aldrine have been also discovered in the surface waters of Northern Greece [6]. The analysis of some OPCs in an urban atmosphere of the East France in 2001–2003 years showed presence of hexachlorocyclohexane and aldrine in all samples [7]. The hexachlorocyclohexane residues have been detected in human serum from an urban and two rural populations in Portugal [8] and in blood plasma of children and adolescents in an urban area in Germany [9]. Hence, elaboration of effective methods of treatment of water and other solutions for OPCs removal is still of great importance all over the world in spite of present prohibitions and restrictions of their use. Adsorption of some OPCs onto solid substances, such as clay minerals or activated carbon, has been rather wide-studied [10–13]. But only a few studies are devoted to OCPs (including lindane) sorption by zeolites [14,15].

The aim of this contribution is to study kinetics and equilibrium adsorption of lindane and aldrin from water solution onto the natural zeolite (clinoptilolite rock).
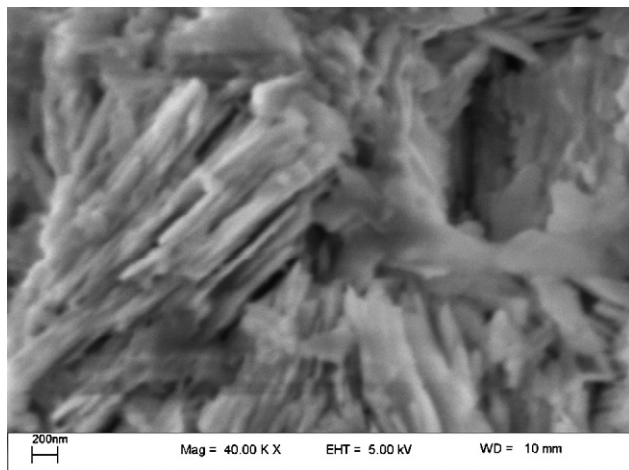
Fig. 1. The crystalline structure of the Sokyrnytsya clinoptilolite analyzed by the SEM (at 40,000× magnification).

2. Experimental

2.1. Reagents and chemicals

Clinoptilolite rock from Sokyrnytsya deposit (the Transcarpathian region, Ukraine) containing near 75% of clinoptilolite proper was used. Quartz, calcite, biotite, muscovite, chlorite, montmorillonite are the main associated minerals. The exchangeable cations are presented by Ca^{2+}, Mg^{2+}, Na^+ and K^+ with prevalence of the last one. Thermostability of the sorbent is from 923 to 973 K, static water-storage capacity and relative moisture are 9.03 and 10.19%, respectively [16]. Our preliminary investigation of the clinoptilolite by low-temperature nitrogen adsorption (obtained via ASAP 2010, version 2.00 instrument (Micrometrics, Norcross GA, USA) testifies that the Transcarpathian clinoptilolite may be resolutely referred to natural micro-mesoporous materials with the polymodal pore size distribution. The specific surface area (S_{BET}) is estimated as 13 m^2/g for the raw zeolite. Mesopores with diameters of 37 and 120–230 Å dominate [17]. According to our study, the specific surface area of the clinoptilolite microcrystals (Fig. 1) is more than 30 m^2/g [18].

Lindane (HCH—gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane) and aldrin (HHDN—1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene) were purchased from Institute of Organic Industrial Chemistry (Warsaw, Poland). Purities of lindane and aldrin were reported as 99.6% of HCH and 99.7% of HHDN, respectively. Aldrin (molecular formula $C_{12}H_8Cl_6$) and lindane ($C_6H_6Cl_6$) are characterized by the following physical properties: water solubilities—0.18 and 10.0 mg/L, boiling points—145.0 and 323.4 °C, molecular weights—364.9 and 290.8 g/mol, respectively.

2.2. Analytical procedure

The stock solution was made by solving of 405 μg HCH and 250 μg HHDN in 50 mL of methanol. Based on this stock solution the standard mixed solutions were prepared with lindane concentrations from 8.0 to 0.05 μg/mL and aldrin concentrations from 4.9 to 0.03 μg/mL. The pesticides sorption procedure was conducted as described bellow. The clinoptilolite was dried for 2 h at 105 °C. The corresponding amount of the stock solution was put in 50 mL glass flask and the volume was adjusted to 50 mL with double-distilled water. Then 0.5 g of the clinoptilolite was added to the flask. The flasks were shaken in a shaker with 200 vibrations per minute for the appointed time. Then solutions were separated with the following double extraction of lindane and aldrin from aqueous solutions using *n*-hexane. Anhydrous sodium sulfate was used to remove water from the pesticides. The extracts were concentrated to nearly 0.5 mL using an evaporator at the room temperature. After addition of 2 mL of *n*-hexane to extracts the lasts were concentrated to 1 mL. The pesticides were desorbed from the zeolite by 10 mL of hexane for 16 h under static conditions. Thereupon, the hexane extracts were used for determination of lindane and aldrin by gas chromatography (GC) analysis.

2.3. Gas chromatography analysis

Analysis of final extracts was conducted using Perkin–Elmer GC/ECD XL (Norwelk CT, USA), equipped with an electron capture detector and an automatic liquid sampler. We used the RTX 35 capillary column with cross-linked methylsiloxane: length—30 m; internal diameter—0.25 mm; film thickness—1.5 μm. The chromatographic conditions were as below: initial oven temperature −80 °C (1 min) increasing by 10 °C/min to 265 °C (8 min); injector temperature −200 °C and detector temperature −285 °C. The carrier helium was at a flow of 2 mL/min and nitrogen make up gas at a flow of 35 mL/min. Calibration was based on area given using external standards. Injection volume was 1 μL. The reported results were the mean of three injections. The retention periods of lindane and aldrin was 12.27 and 15.18 min, respectively. A calibration curve of peak areas as a function of concentration pesticides showed good determination. Determination coefficients were found to be 0.995 and 0.998 from lindane and aldrine, respectively. These calibration curves were used to convert peak areas into concentrations in kinetic and equilibrium studies. The standard deviation evaluated by repeatability was less than 1% for the standard pesticide solutions, while less than 3% for the investigated solutions.

2.4. Fourier transform infrared (FTIR) study of the clinoptilolite rock

The infrared spectra of the clinoptilolite rock were obtained using a Fourier transform IR spectrophotometer Spectrum 2000 (Perkin–Elmer) in order to determine the structure groups of the clinoptilolite in question. The FTIR spectra in the wave number range from 400 to 4000 cm^{-1} were obtained by using KBr pellet technique.

2.5. Sorption and desorption studies

The clinoptilolite mechanical fraction of 0.71–0.50 mm was used in the kinetic sorption study with lindane initial concen-

trations of 0.0405 and 0.0203 mg/L and aldrin ones—0.025 and 0.0125 mg/L. The samples were taken periodically from 0.5 to 48 h for analyses. The amount of the pesticide adsorbed (q) was calculated by formula:

$$q = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where V is the volume of the pesticide solution expressed (L), C_0 and C_e the initial and equilibrium concentrations of the pesticide in solutions (mg/L), and m is the mass of the zeolite (g).

The pesticide adsorption isotherms were determined on the basis of the batch experiments with initial lindane and aldrin concentrations of 0.010–0.200 and 0.003–0.100 mg/L, respectively. The clinoptilolite–pesticide contact lasted 48 h at 22 °C.

The sorption effectiveness (E) was evaluated by the following formula:

$$E = \frac{100m_a}{m_s} = 100m_a(VC_0) \tag{2}$$

where m_a is the mass of the pesticide adsorbed and m_s is the mass of the pesticide in the solution, both expressed in mg.

Results of the equilibrium tests were used to evaluate the distribution coefficients (K_d, L/g) using the following equation:

$$K_d = \frac{q_e}{C_e} \tag{3}$$

where q_e and C_e are the solid and liquid cation concentrations in mg/g and mg/L, respectively.

The specific surface area (S, m^2/g) of the clinoptilolite occupied by sorbed molecules of the pesticides was calculated by the formula:

$$S = qN\Omega \tag{4}$$

where q is the sorption capacity of the clinoptilolite towards the pesticide expressed (μmol/g), N Avogadro's number and Ω is the area occupied by one pesticide molecule (m^2).

2.6. Modeling of sorption kinetic and equilibrium data

Some probable kinetic models were applied in the present work to make a detailed analysis of the adsorption data. The models used included the intraparticle diffusion model [19] which can be formulated as:

$$q = kt^{1/2} \tag{5}$$

where q is the amount of pesticide sorbed, expressed (μg/g), k the rate constant (μg/g(h$^{1/2}$)), and t is the time of sorption duration (min).

The kinetics of metal ions adsorption was also modeled applying the pseudo-first- and pseudo-second-order kinetics models [20] expressed via Eqs. (6) and (7):

$$q = q_e(1 - \exp(-k_1 t) \tag{6}$$

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{7}$$

where k_1 and k_2 are the corresponding rate constants (1/h) and ((μg/g)h), respectively, q_e the equilibrium adsorption capacity (μg/g), and t is the time of sorption duration (h).

The experimental results were fitted to the isotherm equations of the Freundlich and the Linear models using Eqs. (8) and (9), respectively:

$$q_e = KfC_e^n \tag{8}$$

$$q_e = K_d C_e \tag{9}$$

where K_f is the surface adsorption equilibrium constant and n is the heterogeneity factor which is related to the affinity of surface measure of the non-linearity of the isotherm. All other symbols having been explained already.

The goodness-of-fit of the model to the experimental data was controlled by comparison of the correlation coefficients R and standard errors S. The CurveExpert 1.37 free ware program was used in all calculations with the confidence level set at 95%.

3. Results and discussion

3.1. FTIR study of the clinoptilolite rock

Our results on the FTIR spectra of Sokyrnytsya clinoptilolite rock show the most intensive vibrations in the band of 1200–1000 cm^{-1} corresponding to vibrations of the internal tetrahedron ties Si–O–Si and Si–O–Al [21,22]. The strongest vibrations of this band are observed at 1065 cm^{-1}. Perraki and Orfanoudaki [22] stated that a wave number of this peak depends on the Al/Si ratio decreasing with substitution of Al^{3+} for Si^{4+} due to the weaker character and increased length of the Al–O bond. These researches observed this peak at 1059 cm^{-1} for clinoptilolite, while at 1022 cm^{-1} for heulandite. Besides that the detected strong vibrations with peaks at 797, 608 and 460 cm^{-1} are assigned to T–O asymmetric stretching vibrations of the internal tetrahedra. The weak vibrations at 715 and 529 cm^{-1} are ascribed to T–O external symmetric stretching vibrations [22,23].

The vibration bands with peaks of 1634, 2354, 2925 and 3443 cm^{-1} may be connected with presence of the zeolite water. The strong wide band in 3400–3800 cm^{-1} can be characteristic of hydrogen bond of OH-groups of the water molecule to zeolites surface oxygen and attributed to interaction of the water hydroxyl with the cations too [22]. The band with peak of 1634 cm^{-1} is assigned to the usual bending vibration of water molecule.

3.2. Adsorption kinetics of pesticides

Adsorption of pesticides onto clinoptilolite was monitored chromatographically by the procedure described above. Adsorption results were converted into concentration data using the corresponding calibration curves. Then, the concentrations plotted as a function of time are demonstrated in Fig. 2.

The results show that about 40% of aldrin amount was adsorbed for 0.5 h of the run. About 80% of the initial pesticide amount in the solution were sorbed by the clinoptilolite
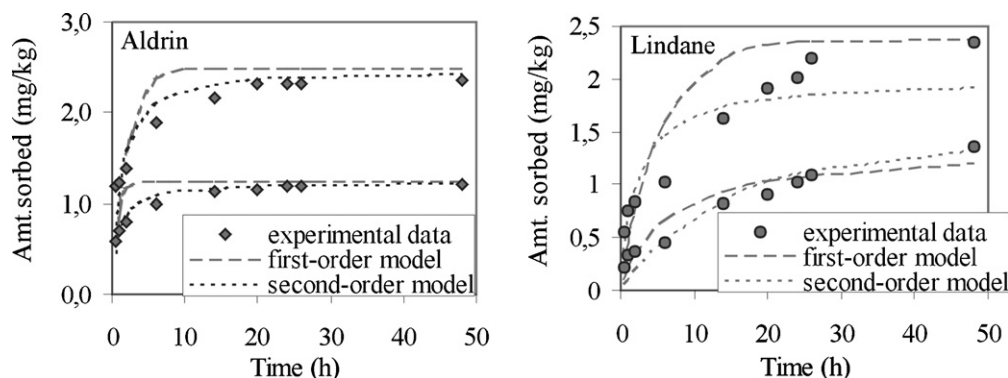
Fig. 2. Kinetics of aldrin and lindane sorption onto clinoptilolite from the mixed aqueous solution (C_0 of aldrin 0.0250 and 0.0125 μg/mL; C_0 of lindane 0.0405 and 0.02025 μg/mL).
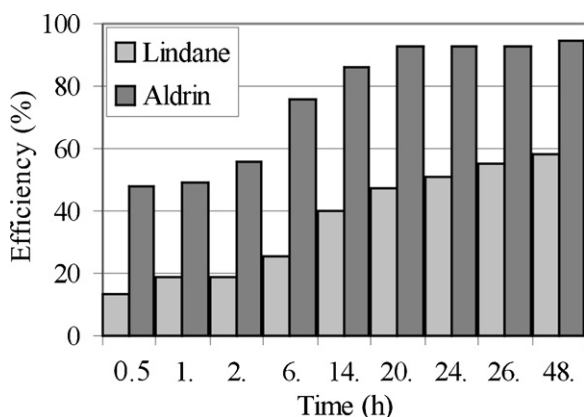

Fig. 3. Efficiency of lindane and aldrin sorption onto clinoptilolite during kinetic studies (C_0 of lindane 0.0405 μg/mL; C_0 of aldrin 0.0250 μg/mL).

for the next 6 h. Then the adsorption rate decreased slowly and the final aldrin adsorption reached about 95%. According to the form of the kinetic curve obtained the equilibrium time of the pesticides' adsorption was accepted as 48 h. This time period was used therefore in the batch study of adsorption isotherms.

As shown in Fig. 2, the kinetic curve of lindane adsorption differs somewhat from the corresponding aldrin curve. Only 25% of lindane amount were sorbed for 2 h with the final adsorption of 68%. Efficiency of lindane and aldrin sorption onto clinoptilolite during the kinetic studies is demonstrated in Fig. 3.

Values of the relative rate constants of the pesticides' adsorption calculated by formula (5) show that intraparticle diffusion of the pesticides changes significantly during the adsorption process. The values of this coefficient for aldrin ($C_0 = 0.0250$ μg/ml) estimated for time period from 0.5 to 48 h have been changed from 1.682 to 0.341 μg/g($h^{1/2}$) with the entire average mean 0.470 μg/g($h^{1/2}$) (Table 1). The corresponding coefficients for lindane ($C_0 = 0.0405$ μg/ml) are lower (0.772–0.34 μg/g($h^{1/2}$)) with the entire average mean 0.397 μg/g($h^{1/2}$). Two stages of the different sorption rate may be marked out in the sorption kinetics of the pesticides in question onto the clinoptilolite. The first one corresponds to the period of the "fast" adsorption occurring during the first hours when the main part of the pesticide is being sorbed. The second stage includes the slow adsorption period with the low sorption rate.

Plotting the experimental data of adsorption kinetics of the both pesticides using Eqs. (6) and (7) indicates that the pseudo-second-order kinetics model gives somewhat better fit to the data (Fig. 2). It may testify to the complicated and heterogeneous nature of interaction between the active zeolite surface and the pesticides. Values of the kinetic coefficients as well as the statistic parameters of the applied kinetic models are presented in Table 1.

3.3. Adsorption isotherms of the pesticides

In order to assess the potential adsorption capacity of the clinoptilolite toward the pesticides investigated, their adsorption isotherms were derived from the batch experiments. The experimentally observed adsorption isotherms are almost linear in shape (Fig. 4). The experimental adsorption data are well fitted to the Linear and the Freundlich models that is described by the high values of the correlation coefficients making up 0.999 for both lindane and aldrin (Table 2). The obtained adsorption equilibrium constants are also presented in Table 2. It may be noticed that the corresponding equilibrium constants K_d of the

Table 1
Rate constants and regression coefficients obtained from fitting the experimental data to the kinetic models

Pesticide	q (μg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model		
		K_1	S	R	K_2	S	R	K	S	R
Lindane	1.35	0.07	0.128	0.955	0.10	0.116	0.962	0.206	0.710	0.983
	2.37	0.183	0.275	0.939	0.187	0.265	0.943	0.397	0.243	0.933
Aldrin	1.23	1.321	0.146	0.926	0.959	0.065	0.985	0.249	0.371	0.890
	2.5	0.561	0.326	0.905	0.358	0.187	0.969	0.470	0.649	0.818

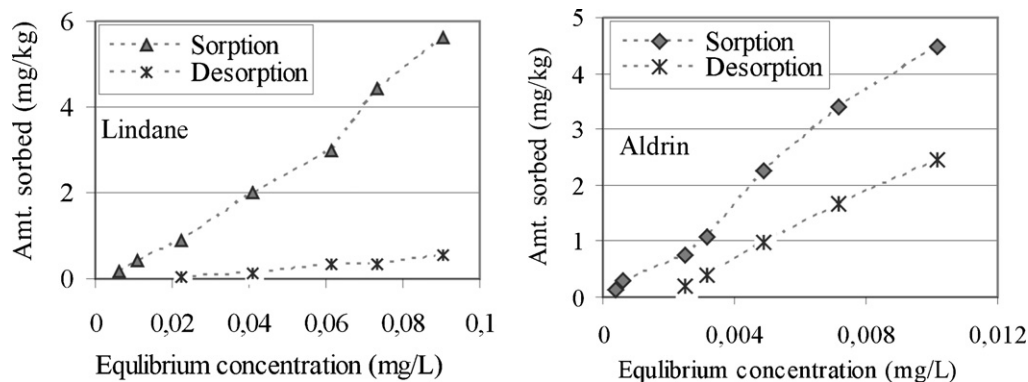R—the correlation coefficients; S—the standard errors.

Fig. 4. Adsorption and desorption isotherms of lindane and aldrin.

Linear model and K_f of the Freundlich one are very close to one another.

The adsorption capacities evaluated by the batch experiments are 5.60 and 4.99 µg/g for lindane and aldrin, respectively. Accordingly to the low initial concentrations of the pesticides (10–200 µg/L of lindane and 3–100 µg/L of aldrin) the equilibria have not be reached and the isotherms are linear in shape testifying to the higher ultimate sorption capacity of the clinoptilolite towards the studied pesticides. But the investigated pesticides concentrations were chosen taking into account their real environmental contents.

Only 10% of the lindane sorbed amount and about 60% of the aldrin one were desorbed from the clinoptilolite by *n*-hexane. The observed difference in aldrin and lindane desorption are probably caused by their physical–chemical properties and by the difference in chemical structure of their molecules in particular. We also suppose that the part of the pesticides molecules sorbed has been changed by catalysis as a result of an interaction with the clinoptilolite active surface. The additional close non-identified peaks found at the analyses of the desorption extracts may testify to the last assumption. Perhaps, the other desorption methods could be more effective for the studied pesticides.

Lemic et al. [15] reported that the maximum adsorption capacity of the clinoptilolite samples modified by stearyldimethylbenzylammoniumchloride towards lindane was 988.7 µg/g according to the Langmuir model. The initial lindane concentrations studied were from 116 to 11,283 µg/L. The maximum adsorption capacity of the various types of powdered activated carbon (PAC) towards lindane from aqueous solutions was estimated as 450–1000 µg/g at the pesticide initial concentration 20 mg/L [10]. During lindane sorption onto pine bark from 20 µg/L lindane solution adsorption reached values round-

ing 80% (65% in the average) of the initial concentration with the sorption capacity of 2.8 µg/g [24].

The surface area occupied by the sorbed pesticides calculated using formula (4) is only insignificant part of the clinoptilolite specific surface area. The maximum amounts of the lindane and the aldrin molecules sorbed under the studied condition are evaluated as 1.925×10^{-2} and 1.372×10^{-2} µmol/g with the occupied areas only 0.54×10^{-2} and 0.58×10^{-2} m^2, respectively. These area values are significantly lower than both the specific surface area ($S_{BET} = 13$ m^2/g) and the total surface area of the clinoptilolite microcrystals estimated over 30 m^2/g by Kowalczyk et al. [18]. The reasons outlined above as well as the linear shape of the obtained isotherms allow to assume that the ultimate sorption capacity of the clinoptilolite towards the pesticides may be considerably higher comparing with the determined in this study on the low concentration range.

3.4. The mechanisms of the pesticides sorption

The following task of our investigation was to clear the possible mechanisms of the pesticides sorption by the clinoptilolite. We have taken into consideration the physical–chemical properties with the chemical structure of the adsorbate molecule as well as the nature of the porous structure and the specification of the active surface of the sorbent. Since we have found no published data on sizes of lindane and aldrin, their diameters are evaluated in accordance with the known diameters of cyclohexane and naphthaldehyde, respectively. The lindane molecule sizes were modelled after cyclohexane molecule sizes taking into account the angle and the length values of Cl–C connection. The aldrin molecule sizes were modeled on naphthaldehyde molecule sizes in view of the chlorine connections. Diameter and thickness of cyclohexane were evaluated as 6.1 and 0.43 Å and α-naphthaldehyde molecule were sized as 9.2 Å × 6.1 Å × 3.7 Å [25]. The critical diameter of cyclohexan molecule was evaluated as 6.9 Å [26]. The primary porous structure of the clinoptilolite is studied well. Primary pores of three types were sized as 7.5 Å × 4.3 Å, 4.7 Å × 3.4 Å and 4.2 Å × 2.7 Å [27]. Hence, lindane and aldrin molecules diffusion into the primary porous structure of the clinoptilolite seems to be impossible (Fig. 5). Only active surface of the secondary porosity may be accessible for the pesticides diffusion

Table 2
Isotherm constants of lindane and aldrin

Pesticide	Linear model			Freundlich model			
	K_d	S	R	K_f	n	S	R
Lindane	50.32	0.148	0.999	56.98	1.067	0.076	0.999
Aldrin	89.33	0.147	0.999	78.02	1.243	0.157	0.999

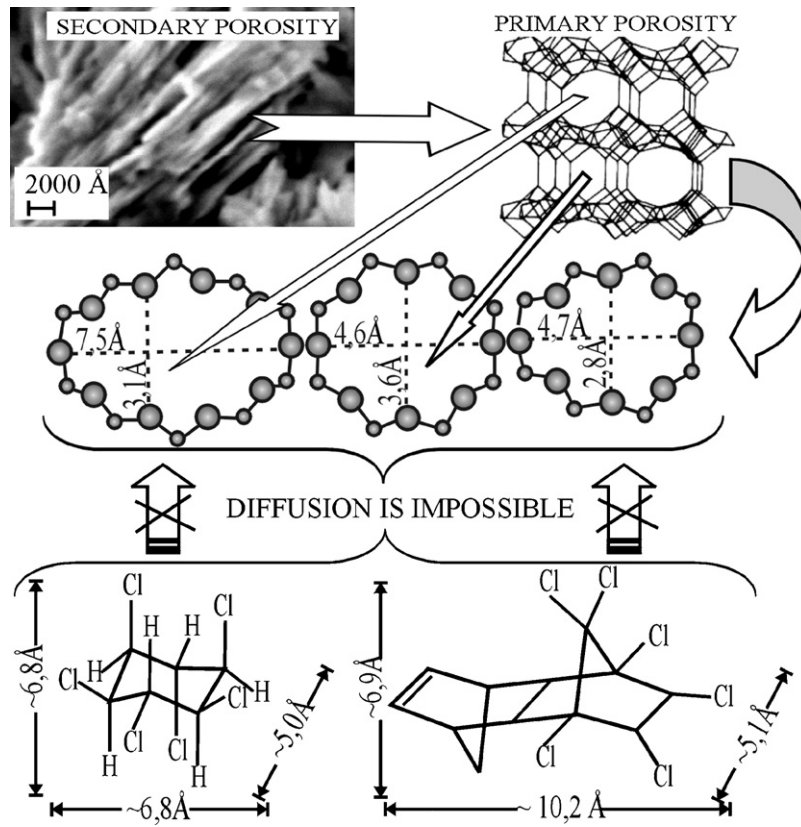*R*—the correlation coefficients; *S*—the standard errors.

Fig. 5. The primary porous structure of the clinoptilolite and its accessibility for lindane and aldrin diffusion.
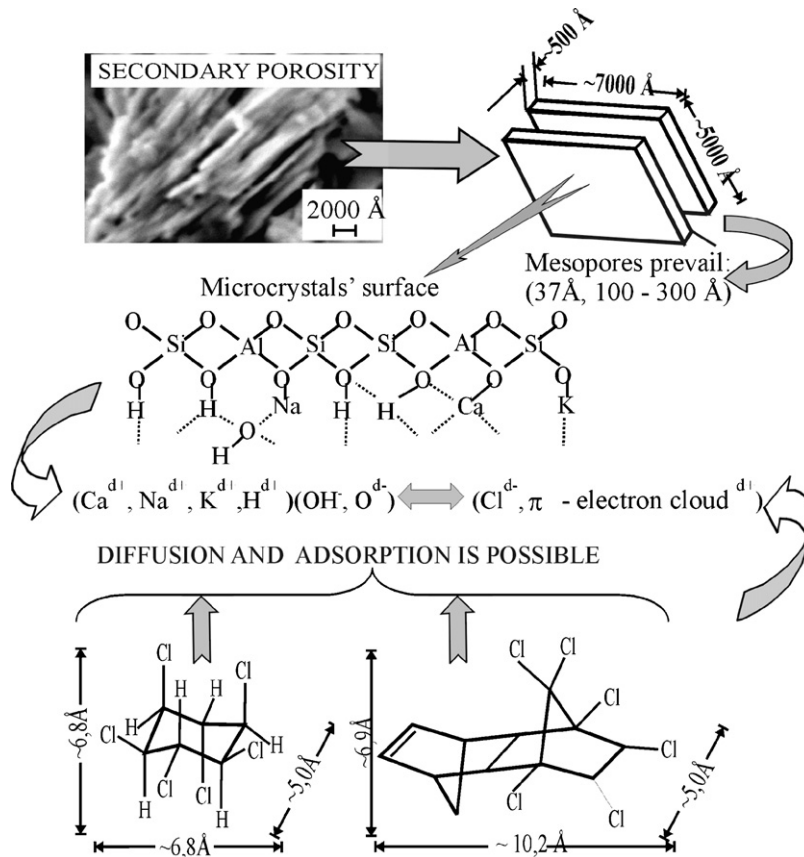

Fig. 6. The secondary porous structure of the clinoptilolite and probable active surface centers of interaction with lindane and aldrin.

and adsorption. This surface of the clinoptilolite microcrystals is available for adsorption by diffusion through the developed mesoporous system (Fig. 6).

Nature of the pesticides adsorption mechanisms on the clinoptilolite surface is also of great interest. It is important to clear what active centers of the clinoptilolite microcrystals' surface and what active centers of the pesticides molecules could interact. In our opinion, this interaction may occur through involving electrostatic bonding mechanisms. The particle charges caused by inductive effect of chlorine atoms in aromatic rings may appear in the role of the mentioned active centers of the pesticides molecules. According to its electronegativity value chlorine can create a negative inductive effect with the residual particle negative charge (d−) for chlorine proper and rising of particle positive charge (d+) of p-cloud aromatic ring. Consequently, the pesticide adsorption may occur through interaction between positive dipole charge of p-cloud aromatic rings of the pesticides with OH^--groups of the clinoptilolite surface as well as through interaction between negative dipole charge of Cl^- with the clinoptilolite exchangeable cations.

Possibility of ion–dipole interaction of organic compounds with exchangeable cations on clay surfaces is pointed out by Bowman [28], Jaynes and Boyd [29], Laird and Fleming [30], and Johnston et al. [31]. Coker et al. [32] discussed adsorption of benzene and benzene derivatives onto zeolite H–Y through interaction between the sorbate and small numbers of residual Na^+-ions. According to the results of Li et al. [12] ion–dipole interactions may be enhanced with increasing charge valence of exchangeable cations.

4. Conclusions

The pseudo-first and pseudo-second-order kinetic models satisfactory describe adsorption kinetics of lindane and aldrin onto the clinoptilolite from aqueous solutions. The best fitting of the experimental data to the pseudo-second-order kinetic model points to the complicated mechanism of interaction of the pesticides with the zeolite active surface. The higher values of the rate constants of the mentioned models for aldrin in comparison with lindane may be connected with more effective interaction of polar–dipole centers of aldrin with the active positions of the clinoptilolite surface. These active centers of sorption in the pesticide molecules are probably presented by dipole charges resulted from inductive effect of chlorine atoms in aromatic rings (Cl (d−) and π-cloud (d+)). OH^--groups and the coordinated exchangeable cations of calcium, magnesium, sodium and potassium are probably the main active positions for the pesticide sorption on the clinoptilolite surface.

According to the evaluated rate constants of intraparticle diffusion model the both pesticides are removed from aqueous solutions most intensively for the first several hours of the sorption process. The main part of the aldrin amount and near a half part of the lindane was sorbed for this period. The sorption equilibria with removal of 95% of aldrin and about 68% were set in for 48 h.

Adsorption isotherms for the low concentrations of lindane and aldrin are linear in shape and fit well to the Freundlich as well as the Liner models. The adsorption capacities of the clinoptilolite calculated by the batch experiments make up 5.60 and 4.99 μg/g for lindane and aldrin, respectively. The distribution coefficients are close to one another for the both models and evaluated as 50 and 89 L/kg by the Linear model and 57 and 78 L/kg by the Freundlich model for lindane and aldrin, respectively.

Only 10% of lindane sorbed and about 60% of aldrin sorbed was desorbed from the clinoptilolite using *n*-hexane under static conditions. Hence, a more effective desoprtion methods are necessary for the zeolite regeneration for the recurring utilization.

It may be concluded that clinoptilolite is an effective and inexpensive adsorbent for low concentration of lindane and aldrin removal from wastewater as well as from some other solutions.

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