

Paweł MUSZYŃSKI¹

**SORPTION OF TRITON X-100
IN SOILS WITH VARIOUS GRAIN SIZE COMPOSITIONS:
KINETICS, EFFECT OF pH, ELECTROLYTE
AND TEMPERATURE**

**SORPCJA TRITONU X-100 W GLEBACH O RÓŻNYM UZIARNIENIU:
KINETYKA, WPLYW pH, ELEKTROLITU I TEMPERATURY**

Abstract: A study was conducted on the sorption of the surfactant Triton X-100, with a static method, through shaking of 2 g of soil (Albic Luvisols, Haplic Luvisols, Haplic Cambisols) in 10 cm³ of solution during 24 hours. The kinetics was also studied of the process and the efficiency of sorption of triton X-100 from solutions with different values (1–12) of pH, in the presence of electrolytes: KCl, NH₄Cl and CaCl₂, and at temperatures of 20, 25, 30, 35 and 50 °C. Experimental results showed good agreement with results calculated from the Langmuir's equation and from a pseudo quadratic equation of kinetics. In the loamy soil, sorption of TX-100 increased in a nearly linear manner within the whole range of concentrations studied, while in the loess and sandy soils it had a linear course in the range of low initial concentrations. A high rate of sorption was found within the initial 30 min of TX-100 contact with the soils, following which the sorption increased more slowly and to a lesser degree. The value of pH had no effect on the sorption of the surfactant from solution with concentration of 250 mg · dm⁻³. At concentrations of 1000 and 2000 mg · dm⁻³ significantly higher sorption was observed for solutions with pH = 1, in all of the soils under study, and from solution with pH = 12 – in the loess and sandy soils. The presence of electrolyte caused an increase in triton sorption, but in a degree dependent on the type of electrolyte and on the soil properties, and on the concentration of the surfactant. A slight effect of temperature on the sorption of TX-100 in the soils was observed.

Keywords: triton X-100, sorption, kinetics, soil

Surfactants, or surface-active agents, are the basic components of cleaning agents, emulsions, and foaming agents. Due to their capacity for reducing surface tension, they are extensively used in various branches of industry, in construction, and in the production of pharmaceuticals, paints, and pesticides. Uncontrolled disposal of sewage from households and industry, with simultaneous mass-scale use of surfactants, causes that more and more of those substances penetrate to waters and soils [1, 2].

¹ Faculty of Chemistry, University of Life Sciences, ul. Akademicka 15, 20–950 Lublin, Poland, phone 81 445 65 56.

Surfactants are noxious compounds that at high concentrations may constitute a hazard to human health and have a toxic effect for aquatic organisms. Certain surfactants have also an effect on the sorption, mobility and degradation of many dangerous compounds, eg pesticides, or chloric derivatives of hydrocarbons [3].

Processes of sorption of surfactants in soils are not known in depth. This is due, among other things, to the specific structure of surfactants that are composed of a non-polar part (hydrophobic) and a polar part, with ionic (cation and anion surfactants) or dipole (non-ionic surfactants) character.

It is commonly known that sorption of non-ionic surfactants shows a relation with their structure, ie with the number of oxyethylene groups and the length of hydrocarbon chain [4]. Also in studies a relation has been observed on the level of sorption of the compounds with the content of organic carbon, clay minerals, and Fe and Al oxides in soils [5, 6].

The objective of this study was to acquire knowledge on the course of sorption of a non-ionic surfactant, Triton X-100, in three soils – Albic Luvisols, Haplic Luvisols, Haplic Cambisols – in connection with the duration of the surfactant – soil contact, pH of solution, presence of electrolyte, and temperature.

Material and methods

Soil samples for the study were taken from the A_p horizon of a grey-brown podzolic soil with grain size composition of weakly-loamy silty sand (Albic Luvisols), grey-brown podzolic soil developed from loess, with grain size composition of clay silt (Haplic Luvisols), and brown soil developed from boulder loam, with grain size composition of heavy loam (Haplic Cambisols) (acc. to Polish Society of Soil Science), further referred to in this report, due to the character of the parent rock, as a sandy soil, a loess soil and a loamy soil. The soil samples were air-dried, screened through a sieve with 1 mm mesh, and averaged.

The basic physicochemical properties of the sandy, loess and loamy soils were as follows: grain size composition (fraction: share): 1.0–0.1 mm – 80, 1, 29 %; 0.1–0.02 mm – 14, 63, 19 %; 0.02–0.002 mm – 2, 27, 34 %; < 0.002 mm: 4, 9, 18 %; pH in 1 mol KCl · dm⁻³ – 3.9, 4.3, 5.6; organic carbon content – 5.0, 21.3, 17 g · kg⁻¹; specific surface area – 8.67, 20.05, 49.09 m² · g⁻¹; hydrolytic acidity (H_h) – 35.8, 41.7, 9.2 mmol H⁺ · kg⁻¹; sum of exchangeable bases (S) – 0, 30, 332.4 mmol(+) · kg⁻¹; the sorptive capacity – 35.8, 71.7, 341.6 mmol(+) · kg⁻¹.

Grain size composition was determined with the Cassagrande method as modified by Prószyński, organic carbon content with the Tiurin method, pH in 1 mol KCl · dm⁻³ – electrometrically, specific surface area with the method of water vapour adsorption, hydrolytic acidity acc. to procedure PB-38 and sum of exchangeable cations acc. to procedure PN-R-04027:1997 and sorptive capacity as sum H_h and S.

Triton X-100 (abbreviation TX-100) was used in the study, produced by Sigma-Aldrich (Germany), with the following parameters: mean molar mass 628 g · mol⁻¹, mean number of oxyethylene groups 9.5, CMC (*critical micelle concentration*) 167 mg · dm⁻³ [7]. Sorption was conducted with the static method: 2 g of soil were shaken

in 10 cm³ of Triton solutions with concentrations of 50–2000 mg · dm⁻³ for 24 h. Soil suspension was centrifuged at 4000 rpm for 25 min. In the obtained solutions, after suitable dilution, intensity of emission was measured on the fluorescence spectrophotometer Varian Cary Eclipse ($\lambda_{Ex} = 275$ nm, $\lambda_{Em} = 302$ nm), and then Triton concentration was read from the calibration curve. Determinations of sorption were conducted in water solutions solutions with pH in the range of 1–12, in 0.1 mol · dm⁻³ solutions of KCl, NH₄Cl and CaCl₂, at temperatures from 20 to 50 °C and in the time interval from 5 to 2880 min. In studies of sorption in the presence of electrolyte the concentrations of TX-100 solutions were from 50 to 2000 mg · dm⁻³. In the remaining experiments the solutions used had concentrations of 250, 750, 1000 and 2000 mg · dm⁻³. The amount of sorbed Triton (q_e , [mg · kg⁻¹]) was calculated from the formula:

$$q_e = (C_{in} - C_{eq}) \cdot V/m \quad (1)$$

where: C_{in} and C_{eq} – the initial and equivalent concentrations of triton [mg · dm⁻³],
 V – volume of solution [dm³],
 m – mass of soil [kg].

For the description of relations between the sorbed amounts of TX-100 and the equivalent concentration in solution the Langmuir isotherm was applied. The linear form of the Langmuir isotherm is represented by the following equation:

$$C_{eq}/q_e = 1/q_L \cdot K_L + C_{eq}/q_L \quad (2)$$

where: q_e – the amount of triton sorbed by unit mass of soil [mg · kg⁻¹],
 C_{eq} – equivalent concentration of Triton [mg · dm⁻³],
 q_L – the amount of triton sorbed by unit mass of soil required to cover the sorptive surface with a monolayer [mg · kg⁻¹],
 K_L – a constant related with the energy of sorption [dm³ · mg⁻¹].

The values of q_L and K_L are determined from the slope and intersection of the linear graph of C_{eq}/q_e in the function of C_{eq} [8]. The kinetics of the process of sorption was analysed using a pseudo-secondorder equation:

$$t/q_t = 1/k_2 \cdot q_{cal}^2 + t/q_{cal} \quad (3)$$

where: q_t – the amount of Triton sorbed during time t [min],
 k_2 – the rate constant [kg · mg⁻¹ · min⁻¹],
 q_{cal} – the value of Triton sorption calculated from the equation of kinetics [mg · kg⁻¹].

All experiments were made in three replications, and the reported values are arithmetic means of the results. The results concerning the effect of pH, electrolyte and temperature were compared with the results of Triton sorption from water solutions

with natural pH and analysed with the method of variance to determine whether there exists a statistically significant difference at $p = 0.05$.

Results

Fig. 1 presents changes in the level of sorption of TX-100 as a function of equivalent concentration.

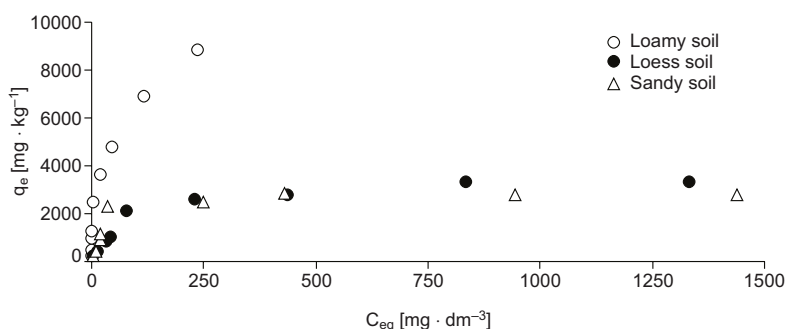


Fig. 1. The sorption of TX-100 in soils

In the loamy soil, sorption of TX-100 increased in a linear manner with increasing concentration of initial solution, but at a degree that decreased as the value of C_{eq} approached the level of $238 \text{ mg} \cdot \text{dm}^{-3}$. In the loess and sandy soils, the sorption was initially also linear in character. Above the equivalent concentration, $248 \text{ mg} \cdot \text{dm}^{-3}$ in the sandy soil and $230.6 \text{ mg} \cdot \text{dm}^{-3}$ in the loess soil, the sorption increased slightly and attained a constant value in the range of the highest concentrations of C_{eq} . Comparison of the slope of graphs permitted the soils to be arranged in the following series of decreasing sorptive capacity with relation to TX-100: loamy soil > loess soil > sandy soil.

The value of sorption of TX-100 in the soils under study is expressed by percentage sorption that decreased with increase in the initial concentration of the surfactant solution and depended also on the sorptive capacity of the soil. At the maximum initial concentration of $2000 \text{ mg} \cdot \text{dm}^{-3}$ the percentage sorption of TX-100 was notably lower in the sandy soil (28.7 %) and in the loess soil (33.2 %), compared with the loamy soil (88.3 %) that was characterised by the highest sorptive capacity. At the initial concentration of $50 \text{ mg} \cdot \text{dm}^{-3}$ the percentage sorption of TX-100 was also the highest in the loamy soil (99.5 %), while in the sandy and loess soils it was at a similar level – at 91.4 % and 91.9 %.

Table 1 gives the parameters for the linear form of Langmuir's isotherm of sorption, and the values of coefficient R^2 . High values of the coefficient of correlation R^2 (≥ 0.97) suggest that the Langmuir equation is suitable for the description of TX-100 sorption balance in the soils used in the experiment and within the range of concentrations under study. In the Langmuir equation the value of TX-100 sorption is expressed by the constant q_L . For the sandy, loess and loamy soils the values of constant q_L calculated

from the Langmuir equation were comparable to the values of q_e obtained experimentally. Coefficient K_L , that defines the energy of sorption, had the highest value for the sorption of TX-100 in the loamy soil. This may indicate that interactions between TX-100 and the sorptive complex of the loamy soil were stronger than in the case of the loess and sandy soils.

Table 1

Langmuir constants for the sorption of TX-100 in soils

| Soil | K_L | q_L | R^2 |
|-------|--------------------------------------|------------------------------------|-------|
| | $[\text{dm}^3 \cdot \text{mg}^{-1}]$ | $[\text{mg} \cdot \text{kg}^{-1}]$ | |
| Sandy | 0.0269 | 2932.6 | 0.99 |
| Loess | 0.012 | 3533.6 | 0.99 |
| Loamy | 0.0696 | 8849.6 | 0.97 |

The graphs given in Fig. 2 present the relation of TX-200 sorption from solutions of various concentrations as a function of duration of contact of the surfactant with the soils. In the graphs, two sections can be distinguished: one, with steeper slope, corresponds to fast sorption, while the other, with notably gentler slope, characterises slow sorption leading to the attainment of the state of saturation. It was found that the rate of sorption was the highest at the beginning of the experiment and decreased gradually with the passage of time. The rate of sorption depended also on the sorptive capacity of the soils and on the concentration of the surfactant. Within the time interval of 5–30 minutes, the rate of sorption (q_t/t) of TX-100 from solution with concentration of $250 \text{ mg} \cdot \text{dm}^{-3}$ decreased from 44.8 to $25.6 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ in the sandy soil, from 167.1 to $33.5 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ in the loess soil, and from 216.5 to $38.7 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ in the loamy soil. In the case of solution with concentration of $2000 \text{ mg} \cdot \text{dm}^{-3}$ the dynamics of sorption decreased from 85.4 to $34.1 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ in the sandy soil, from 468 to $92.9 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ in the loess soil, and from 1635 to 282.4

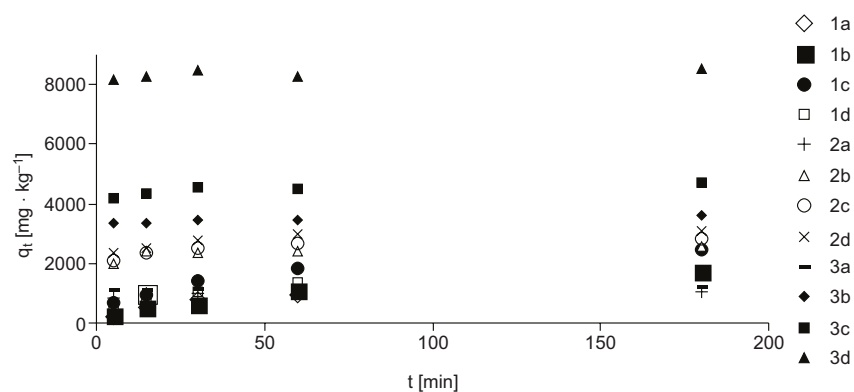


Fig. 2. Kinetics of TX-100 sorption in sandy soil (1), loess soil (2) and loamy soil (3) from solutions with concentrations of: a – $250 \text{ mg} \cdot \text{dm}^{-3}$, b – $750 \text{ mg} \cdot \text{dm}^{-3}$, c – $1000 \text{ mg} \cdot \text{dm}^{-3}$, d – $2000 \text{ mg} \cdot \text{dm}^{-3}$; q_t – is the amount of TX-100 sorbed at time t

Table 2
Kinetics parameters for the sorption of TX-100 in soils

| C_{in} [mg · dm ⁻³] | Sandy soil | | | Loess soil | | | Loamy soil | | |
|--------------------------------------|-----------------------------------|-----------|---|-----------------------------------|---------------------------------------|---|-----------------------------------|-----------|---|
| | q_e [mg · kg ⁻¹] | q_{cal} | k_2 [kg · mg ⁻¹ · min ⁻¹] | q_e [mg · kg ⁻¹] | q_{cal} [mg · kg ⁻¹] | k_2 [kg · mg ⁻¹ · min ⁻¹] | q_e [mg · kg ⁻¹] | q_{cal} | k_2 [kg · mg ⁻¹ · min ⁻¹] |
| 250 | 1147.8 | 1171 | $4.3 \cdot 10^{-5}$ | 1041.1 | 1052.6 | $5.2 \cdot 10^{-4}$ | 1246 | 1259.4 | $8.1 \cdot 10^{-5}$ |
| 750 | 2502.7 | 2652.5 | $0.3 \cdot 10^{-5}$ | 2581.4 | 2611 | $1.1 \cdot 10^{-4}$ | 3662.1 | 3703.7 | $3.2 \cdot 10^{-5}$ |
| 1000 | 2851.9 | 2857.1 | 10^{-5} | 2777.8 | 2824.9 | $1.9 \cdot 10^{-4}$ | 4782.7 | 4854.4 | $2.7 \cdot 10^{-5}$ |
| 2000 | 2871.9 | 2949.8 | $0.5 \cdot 10^{-5}$ | 3323 | 3367 | $2.4 \cdot 10^{-4}$ | 8833.6 | 8928.6 | $1.3 \cdot 10^{-5}$ |
| | | | R^2 | | | R^2 | | | R^2 |
| | | | 0.99 | | | 0.99 | | | 0.99 |
| | | | 0.99 | | | 0.99 | | | 0.99 |
| | | | 0.99 | | | 0.99 | | | 0.99 |
| | | | 0.99 | | | 0.99 | | | 0.99 |

$\text{kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ in the loamy soil. After the 30th minute, until the end of the experiment changes in the rate of TX-100 sorption were notably smaller. This was observable, among other things, in the slight slope of the graphs in the section for the time interval of 30–2280 minutes, and in the low, compared with the 30th minute, rate of sorption in the 48th hour, that amounted to $0.4 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ (sandy soil), $0.36 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ (loess soil) and $0.44 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ (loamy soil) for TX-100 solution with concentration of $250 \text{ mg} \cdot \text{dm}^{-3}$, and $0.99 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ (sandy soil), $1.17 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ (loamy soil) and $3.1 \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ (loamy soil) for TX-100 solution with concentration of $2000 \text{ mg} \cdot \text{dm}^{-3}$. Also the efficiency of sorption displayed a relation to the duration of Triton-soil contact. For example, in the 5th minute the level of sorption of TX-100 from solution with concentration of $250 \text{ mg} \cdot \text{dm}^{-3}$ was $234 \text{ mg} \cdot \text{kg}^{-1}$ (sandy soil), $835.5 \text{ mg} \cdot \text{kg}^{-1}$ (loess soil) and $1082.6 \text{ mg} \cdot \text{kg}^{-1}$ (loamy soil). With relation to the amount of TX-100 absorbed after 24 hours, those values constituted 20 %, 80 % and 86 %, respectively. In the 30th minute the sorption was at the level of $767.4 \text{ mg} \cdot \text{kg}^{-1}$ (sandy soil), $1005 \text{ mg} \cdot \text{kg}^{-1}$ (loess soil) and $1162.5 \text{ mg} \cdot \text{kg}^{-1}$ (loamy soil), and in comparison with the sorption in the 5th minute it increased by 227.9 % in the sandy soil, 20.4 % in the loess soil, and by 7.4 % in the loamy soil. After 60 minutes the sorption attained the level of $1055.4 \text{ mg} \cdot \text{kg}^{-1}$ in the sandy soil, $1053 \text{ mg} \cdot \text{kg}^{-1}$ in the loess soil, and $1196 \text{ mg} \cdot \text{kg}^{-1}$ in the loamy soil, and was 37.5 %, 4.75 % and 2.5 % higher, respectively, with relation to sorption after the 30th minute.

Table 2 gives the parameters of the pseudo-quadratic equation of kinetics. Values of q_{cal} calculated from the equation of kinetics were higher than values of q_e obtained from the experiments, with maximum difference between the values not exceeding 6 %.

Fig. 3 presents sorption of TX-100 from solutions with pH from 1 to 12. In the soils under study, at Triton concentration of $250 \text{ mg} \cdot \text{dm}^{-3}$, within the range of pH values from 1 to 12 no statistically significant differences were observed compared with sorption from a solution with natural pH. Also for the concentrations of 750, 1000 and $2000 \text{ mg} \cdot \text{dm}^{-3}$ at pH from 5 to 10 the changes were practically equal to zero. In all the soils, sorption of TX-100 from solutions with concentrations of 1000 and $2000 \text{ mg} \cdot \text{dm}^{-3}$ was significantly greater under strongly acidic conditions ($\text{pH} = 1$), and in the

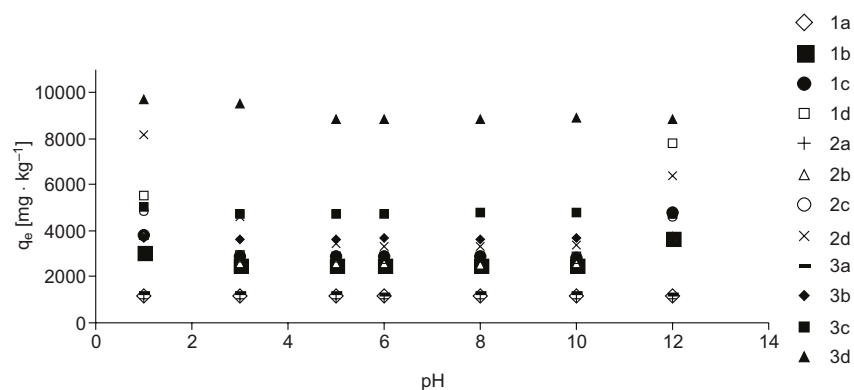


Fig. 3. Effect of pH on the sorption of TX-100 in soils (explanations see Fig. 2)

case of the loess and sandy soil also under strongly alkaline conditions ($\text{pH} = 12$). Moreover, in the loess and loamy soils, at $\text{pH} = 3$ there appeared a significant increase of sorption from the solution with concentration of $2000 \text{ mg} \cdot \text{dm}^{-3}$.

The effect of electrolyte was ambiguous: both an increase and a lack of change in the level of Triton sorption were observed (Fig. 4–6) with relation to sorption from solutions without any admixture of KCl , NH_4Cl and CaCl_2 .

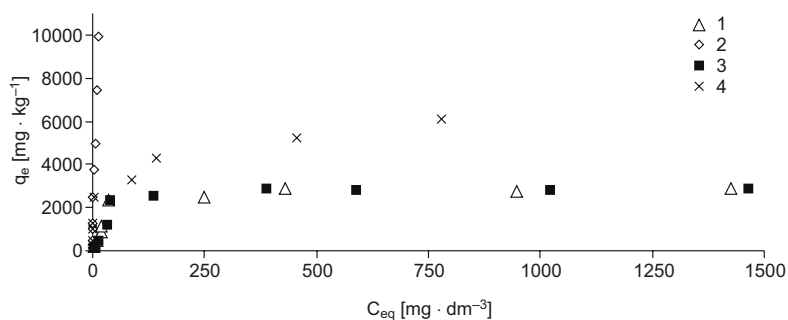


Fig. 4. The sorption of TX-100 in sandy soil: in the absence of electrolyte (1), in the presence of electrolyte: 2 – KCl , 3 – NH_4Cl , 4 – CaCl_2

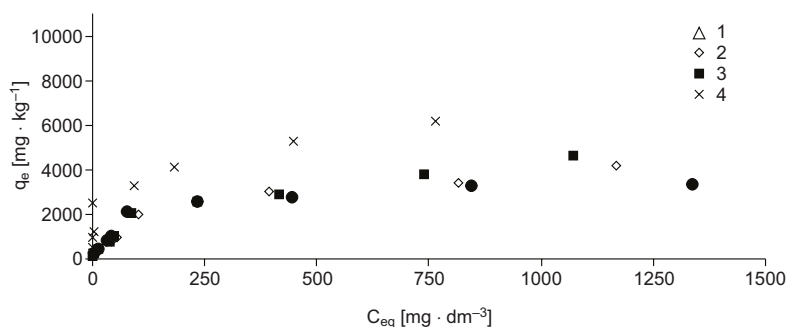


Fig. 5. The sorption of TX-100 in loess soil: in the absence of electrolyte (1), in the presence of electrolyte: 2 – KCl , 3 – NH_4Cl , 4 – CaCl_2

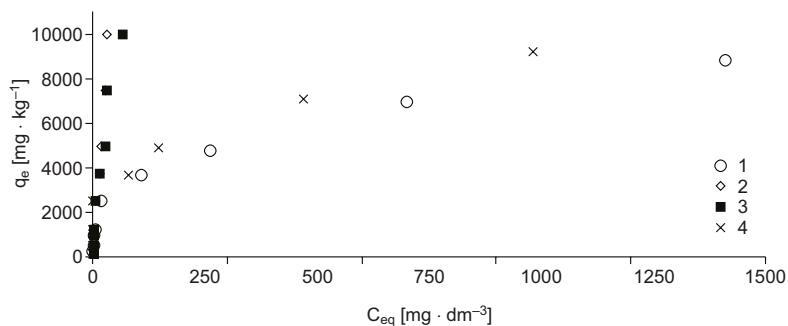


Fig. 6. The sorption of TX-100 in loamy soil: in the absence of electrolyte (1), in the presence of electrolyte: 2 – KCl , 3 – NH_4Cl , 4 – CaCl_2

In the loamy soil, a significant increase was observed in Triton sorption from solutions with the highest initial concentrations, ie 1500 and $2000 \text{ mg} \cdot \text{dm}^{-3}$. For the solution with the concentration of $1500 \text{ mg} \cdot \text{dm}^{-3}$, the sorption increased by 8 % in the presence of KCl and NH_4Cl , and by 2.7 % in the presence of CaCl_2 .

For the solution with concentration of $2000 \text{ mg} \cdot \text{dm}^{-3}$, on the other hand, the increase in sorption was ca 13 % in the presence of KCl and NH_4Cl , and 4 % in that of CaCl_2 . In the loess soil the presence of KCl and CaCl_2 caused a significant increase of sorption within nearly the whole range of initial concentrations, the greatest changes being observed for the solutions with concentrations of 1500 and $2000 \text{ mg} \cdot \text{dm}^{-3}$. In the presence of NH_4Cl there was a notable increase of sorption from solutions with concentrations of 1500 and $2000 \text{ mg} \cdot \text{dm}^{-3}$, while at lower concentration no significant changes were found. The effect of electrolytes on Triton sorption from solutions with concentrations of 1500 and $2000 \text{ mg} \cdot \text{dm}^{-3}$ decreased in the sequence of $\text{CaCl}_2 > \text{NH}_4\text{Cl} > \text{KCl}$. In the sandy soil, NH_4Cl had no effect on the sorption of Triton. In the same soil, in the presence of KCl and CaCl_2 , as in the loess soil, a significant increase was noted in triton sorption from all initial solutions. Compared with Triton sorption from solutions without any content of KCl and CaCl_2 , the greatest differences were observed at concentrations of 1500 and $2000 \text{ mg} \cdot \text{dm}^{-3}$. The increase in Triton sorption from solutions of those electrolytes was not uniform. In the presence of KCl, sorption of TX-100 from solution with concentration of $1500 \text{ mg} \cdot \text{dm}^{-3}$ was 1.4-fold higher, and from solution with concentration of $2000 \text{ mg} \cdot \text{dm}^{-3}$ – 1.6-fold higher than from solutions with an addition of CaCl_2 .

Fig. 7 presents the effect of temperature on Triton sorption from solutions with various concentrations. In the sandy and loamy soils, Triton sorption at temperatures $> 20^\circ\text{C}$ was at the same level as at 20°C or displayed a slight increase of 3–4 %. In the loess soil a few more notable changes were recorded, related with Triton sorption increases within the range of from 8 to 39 %.

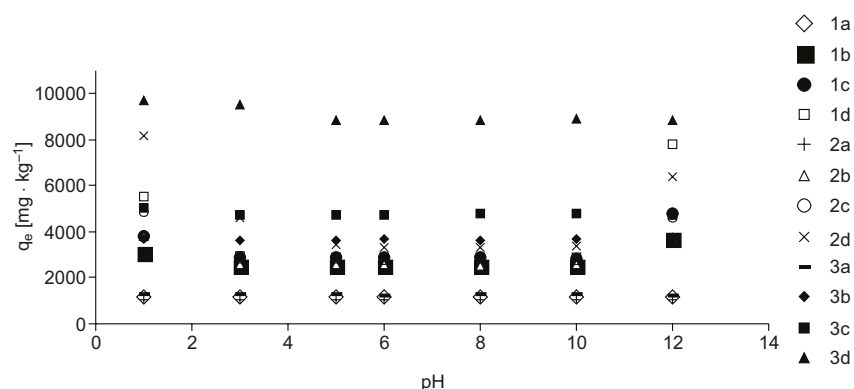


Fig. 7. Effect of temperature on the sorption of TX-100 in sandy soil (1), loess soil (2) and loamy soil (3) from solutions with concentrations of: a – $250 \text{ mg} \cdot \text{dm}^{-3}$, b – $750 \text{ mg} \cdot \text{dm}^{-3}$, c – $1000 \text{ mg} \cdot \text{dm}^{-3}$, d – $2000 \text{ mg} \cdot \text{dm}^{-3}$

Discussion

The study showed that sorption of TX-100 in the soils was the highest from solutions with low concentrations of the surfactant. This could have been caused by the fact that the amount of TX-100 in solutions with the lowest concentrations was insufficient for the saturation of the soils under study. For this reason the number of sorption sites potentially available for the sorption of TX-100 from solutions with low concentrations was greater than during sorption from solutions with higher concentrations.

The shape of curves representing the relation of q_e to C_{eq} indicates that the degree of TX-100 sorption in the sandy and loess soils decreased notably when the equivalent concentration of Triton in the solution was close to the value of 1.5 CMC, ie ca 250 $\text{mg} \cdot \text{dm}^{-3}$. Similar behaviour of surfactants in soils was also observed in other studies [9] and attributed to aggregation of molecules of those compounds [10]. In the loamy soil the equivalent concentration did not exceed the value of 1.5 CMC, and therefore the shape of the sorption curve for that soil was different from those for the sandy and loess soils.

Greater sorption of TX-100 (expressed in %) in the loamy soil with relation to the sandy and loess soils indicates notable differentiation in the sorptive capacity between those soils, resulting from the different physicochemical properties of the soils. The loamy soil showed the greatest affinity to Triton and was characterised by the highest content of clay fractions. The loess soil had the highest content of organic carbon, but a lower share of clay fractions relative to the loamy soil. In the loess soil the sorption of triton oscillated around the same level as in the sandy soil that had the lowest content of organic carbon and of clay fractions. This suggests the supposition that Triton sorption in the soils under study depended to a greater degree on the content of clay fractions than on that of organic carbon.

As follows from the study, sorption of TX-100 from solutions with concentrations of 1500 and 2000 $\text{mg} \cdot \text{dm}^{-3}$ was significantly higher at $\text{pH} = 1$ and 12 with relation to sorption from solutions with natural pH . Dependence of TX-100 sorption on pH was demonstrated also by Khan and Zareen [8]. According to Paria et al [11], this may indicate participation of hydrogen bonds in the binding of a non-ionic surfactant. In the case of Triton, hydrogen bonds may be formed between oxygen atoms of oxyethylene groups $-\text{OCH}_2\text{CH}_2-$ of the surfactant and $-\text{OH}$ groups on the surface of oxides and on the edges of clay minerals. In an acid environment, $-\text{OH}$ groups are non-dissociated and thus capable of forming hydrogen bonds with strongly electronegative atoms of oxygen. In this study, bonding of Triton molecules by soil colloids by means of hydrogen bonds could have been the cause of increased sorption of TX-100 from solutions with low pH . The cause of greater sorption of Triton from a solution with $\text{pH} = 12$ is not known. As it is known, under strongly alkaline conditions there takes place dissociation of $-\text{OH}$ groups, and formation of negative charge and dissolution of organic matter. Studies conducted with the use of various surfactants showed both a positive correlation between the level of sorption of those compounds and the content of organic matter [12], and a lack of any distinct effect of that soil component on their sorption [13, 14]. Increase in Triton sorption under conditions in which organic matter was dissolved may

suggest that that soil component had only a slight effect on TX-100 sorption in the soils under study.

The effect of KCl, NH₄Cl and CaCl₂ on Triton sorption depended on the sorptive capacity of the soil and on the electrolyte cation, and was especially notable in the case of sorption from solutions with the highest concentrations. In principle, the presence of electrolyte caused an increase in Triton sorption, but in certain cases the increase was slight and statistically insignificant. In the loamy soil, electrolytes had a less pronounced effect on Triton sorption. It appears that this resulted from two reasons: firstly, the sorption of TX-100 from solutions without any addition of electrolytes was the highest in the loamy soil, and secondly, K⁺, NH₄⁺ or Ca²⁺ cations could have been subject to sorption themselves, and to a degree much higher in the loamy soil than in the other soils. This could have been due to the specific physicochemical properties of the loamy soil, and especially to its large specific surface area and the related capacity of the sorptive complex. In the opinion of Zhao and Brown [15], the presence of electrolytes causes removal of water film encasing molecules of a non-ionic surfactant. At the same time there is a reduction in the ease with which hydrocarbon chains dissolve, which may lead – at suitable concentration of the surfactant – to aggregation of its molecules and, consequently, to decrease in the sorption. As in this study an increase was generally observed in the sorption of TX-100 from solutions containing KCl, NH₄Cl and CaCl₂, it should be assumed that in the presence of those electrolytes formation of aggregated forms of Triton did not take place.

In the study presented herein, only a slight effect of temperature on the sorption of TX-100 was observed. Kronberg and Silveston [16] are of the opinion that increase in temperature causes a reduction in the degree of hydration of the hydrophilic part of surfactant molecules, which facilitates the formation of aggregates. On the other hand, increase in temperature entails disturbance in the ordered structures of water surrounding the hydrophobic part of surfactants, and that in turn inhibits the formation of aggregates. The relative value of those opposing effects, that display a dependence on the degree of covering of the sorption sites of the sorbent, determines whether surfactant aggregation will take place or not.

Conclusions

1. The level of Triton sorption depended on the capacity of the sorption complex of soil and decreased in the sequence: loamy soil > loess soil > sandy soil.
2. The process of Triton sorption was fast during the initial 30 minutes, following which its dynamics decreased notably.
3. Generally, KCl, NH₄Cl and CaCl₂ caused an increase in Triton sorption. The effect of the electrolytes depended on the type of the electrolyte cation, sorptive capacity of the soil, and concentration of the surfactant.
4. Sorption of Triton from solutions with low initial concentrations did not display any relation with the value of pH. The highest increase in Triton sorption was recorded for pH = 1 and 12, for solutions with concentration of 1000 and 2000 mg · dm⁻³.
5. Temperature had only a slight effect on the sorption of Triton in the soils.

References

- [1] Jia L.Q., Ou Z.Q. and Ouyang Z.Y.: *Pedosphere* 2005, **15**, 216–224.
- [2] Karagunduz A., Pennell K.D. and Young M.H.: *Soil Sci. Soc. Amer. J.* 2001, **65**, 1392–1399.
- [3] Krogh K.A., Halling-Sørensen B., Mogensen B.B. and Vejrup K.V.: *Chemosphere* 2003, **50**, 871–901.
- [4] Brownawell B.J., Chen H., Zhang W. and Westall J.C.: *Environ. Sci. Technol.* 1997, **31**, 1735–1741.
- [5] Dai S.G., Dong L. and Wang Z.: *China Environ. Sci.* 1999, **19**, 392–396.
- [6] Shen Y.H.: *Chemosphere* 2000, **41**, 711–716.
- [7] Kile D.E. and Chiou C.T.: *Environ. Sci. Technol.* 1989, **23**, 832–838.
- [8] Khan M.N. and Zareen U.: *J. Iran. Chem. Soc.* 2004, **1**(2), 152–158.
- [9] Zhu L., Yang K., Lou B. and Yuan B.: *Water Res.* 2003, **37**, 4792–4800.
- [10] Chin Y., Kimble K.D. and Swank C.R.: *J. Contam. Hydrol.* 1996, **22**, 83–94.
- [11] Paria S., Manohar C. and Khilar K.C.: *Colloids Surfaces A* 2005, **252**, 221–229.
- [12] Paterson L.F., Chowdhry B.Z., Carey P.J. and Lehrane S.A.: *J. Contam. Hydrol.* 1999, **40**, 37–51.
- [13] Cano M.L. and Dorn P.B.: *Environ. Toxicol. Chem.* 1996, **15**, 684–690.
- [14] Rodriguez-Cruz M.S., Sanchez-Martin M.J. and Sanchez-Camazano M.: *Chemosphere* 2005, **61**, 56–64.
- [15] Zhao J. and Brown W.: *J. Phys. Chem.* 1996, **100**, 3775–3782.
- [16] Kronberg B. and Silveston R.: *Progr. Colloid Polym. Sci.* 1990, **83**, 75–81.

SORPCJA TRITONU X-100 W GLEBACH O RÓŻNYM UZIARNIENIU: KINETYKA, WPLYW pH, ELEKTROLITU I TEMPERATURY

Katedra Chemii
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Przeprowadzono badania sorpcji surfaktantu tritonu X-100 metodą statyczną przez wytrząsanie 2 g gleby płowej z piasku słabogliniastego, płowej z lessu, brunatnej z gliny ciężkiej w 10 cm³ roztworu w ciągu 24 godz. Badano także kinetykę procesu i efektywność sorpcji tritonu X-100 z roztworów o różnej wartości (1–12) pH, w obecności elektrolitów: KCl, NH₄Cl i CaCl₂ w temperaturach: 20, 25, 30 35 i 50 °C. Wyniki doświadczalne wykazywały dobrą zgodność z wynikami obliczonymi z równania Langmuira i równania kinetyki pseudodrugiego rzędu. W glebie gliniastej sorpcja TX-100 wzrastała prawie liniowo w całym przedziale badanych stężeń, natomiast w glebie lessowej i piaszczystej wykazywała liniowy przebieg w zakresie małych stężeń wyjściowych. Stwierdzono dużą szybkość sorpcji w pierwszych 30 min kontaktu TX-100 z glebami, po tym okresie sorpcja zwiększała się wolniej i w mniejszym stopniu. Wartość pH nie miała wpływu na sorpcję surfaktantu z roztworu o stężeniu 250 mg · dm⁻³. Przy stężeniach 1000 i 2000 mg · dm⁻³ obserwowano znacznie większą sorpcję z roztworów o pH = 1 we wszystkich badanych glebach, a z roztworu o pH = 12 w glebie lessowej i piaszczystej. Obecność elektrolitu powodowała wzrost sorpcji tritonu, ale w stopniu zależnym od rodzaju elektrolitu i właściwości gleby oraz stężenia surfaktanu. Stwierdzono niewielki wpływ temperatury na sorpcję TX-100 w glebach.

Słowa kluczowe: triton X-100, sorpcja, kinetyka, gleba