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Predicting bentonite sorption properties toward selected hydrocarbons based on certain physical properties

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ABSTRACT

Three hydrocarbons (benzene, toluene, and *p*-xylene) and methylene were subjected to sorption on natural and homoionic forms of three bentonites of different origin (SWy–2, Stx–1b, and bentonite from Slovakia). The obtained results analysis shows that the bentonites saturated with polyvalent cations Ca^{2+}lub Fe^{3+} manifest the best sorption properties. The sorption of *p*-xylene was the sole exception to this rule, occurring most efficiently on potassium forms. The sorption ability of a natural bentonite toward a given sorbate can be predicted by means of a logarithmic function of plasticity limit, representing the water content at which clay loses its plastic properties. Using a linear function of plasticity limit of bentonite natural form (i.e., before the modification), it is possible to predict its sorption ability after cation exchange. The relative error of the prediction in wide range of concentrations was between 0.09% for sorption of *p*-xylene on K-form and 10.4% for sorption of toluene on natural bentonite. The method permits a preliminary a priori assessment of the sorption properties after a possible clay modification.

Keywords: Hydrocarbons; Benzene; Toluene; *p*-Xylene; Sorption; Clays; Bentonites

1. Introduction

Because of their high toxicity and persistence in environment, the aromatic hydrocarbons are viewed as significantly dangerous pollutants. There are various sources of their emissions to the atmosphere and soil. Sources of benzene atmosphere emission considered as important are petroleum refining operations, petrochemical manufacturing, oil storage tanks, urban industrial areas, service stations, certain foods, groundwater contamination, and underground gasoline leaks [1]. However, according to Wallace [1], “the most important source of exposure for 50 million smokers is the mainstream smoke from their cigarettes, which accounts for about half of the total population burden of exposure to benzene.” Other sources are vehicle exhaust and industrial emissions as well as emissions from consumer products, building materials, paints, and adhesives. The main sources of toluene emissions are traffic, filling stations, and tobacco smoking. In enclosed areas, high concentrations may occur when toluene is used in solvents or thinners [2]. As reported by Niaz et al. [3], major sources of xylene emission into the atmosphere are fugitive emissions from petrochemical industries, fire, cigarette, and vehicles.

The assessment of using clays as hydrocarbons removing agents has recently been a subject of intensive research [4–12]. In laboratory conditions, sorption of organic pollutants on natural sorbents is in most cases carried out on water solutes [13–15]. Recently, Shah et al. [16] discussed the removal of organic pollutants from contaminated wastewater by sorption on montmorillonite clay converted to organoclays. A vital structural property relationship for selective adsorption of pollutants from aqueous solutions was observed. Pazos et al. [17] presented results of sorption of benzene, toluene, and phenol on surface-functionalized synthetic micas, their

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adsorption performance being a function of the alkylammonium properties such as the chain length, the mass fraction, and the organization of the organic cation in the interlayer space. Xiang et al. [18] investigated the environmental fate of aniline aerofloat (AAF) by sorption to four types of agricultural soils at low concentrations (1–10 mg/L) using batch experiments. AAF sorption was remarkably affected by soil constituents, positively correlating with the contents of organic matter and clay. Only a few investigations examine sorption of vapors of organic pollutants [19]. However, due to a poor solubility of most organic compounds in water, they may evaporate in specific environmental conditions, for example, from wet soils, the contact with a sorbent leading only to vapor sorption, which will also occur in the case of using natural sorbents in the purification of gas streams.

The aim of the presented studies was to assess the sorption ability of selected model bentonites (i.e., clays with montmorillonite as the major mineral constituent), both natural and modified by introducing exchangeable cations Na^+, K^+, as well as Ca^{2+} and Fe^{2+} in exchange sites. The effects of the kind of clay, the specific cation, and the kind of sorbate on the sorption magnitude were examined. The sorption ability was assessed with regards to polar substances such as water and methanol as well as to nonpolar organic compounds including benzene and its two homologues, toluene and *p*-xylene.

A model to predict sorption properties of homoionic bentonites toward selected hydrocarbons based on a physical property of the same bentonites in natural state (i.e., prior to the modification) is presented. The model was derived based on a statistical analysis without taking into account the theoretic isotherms equations. Such an approach yields solutions not laden with assumptions and more useful in engineering applications.

2. Experimental studies

2.1. Materials

The following three bentonites were used as the materials: St from Texas (USA), Wy from Wyoming (USA), and JP from JelsovyPotok (Slovakia). The main mineral constituent of all the bentonites is montmorillonite [20]. The major properties of the bentonites are collected in Table 1.

The American clays were obtained from the Source Clay Repository of the Clay Mineral Society. The experiments were carried out on both natural and homoionic forms. Four homoionic forms (Fe^{3+}, Ca^{2+}, Na^+, and K^+) were fabricated by the repeated saturation of the fraction less than 0.063 mm with an appropriate chloride and the subsequent purifying from chlorine anion by diffusion, until the disappearance of the characteristic reaction with $AgNO_3$.

Table 1
Natural clays properties

Clay	MEC	CF, %	SF, %	PL, %	LL, %	S, m²/g	w_{95}, %	*d*(001) Ǻ
Wy	Na^+	45	55	35	519	333	23	11.4
St	Ca^{2+}	16	84	55	142	593	29	14.9
JP	Ca^{2+}	15	85	46	112	633	30	14.9

MEC, main exchangeable cation; PL, plasticity limit; LL, liquid limit; CF, clay fraction; SF, silt fraction, w_{95}, hygroscopic water content at $p/p_0 = 0.95$; *S*, specific surface accessible for water; *d*(001), basal spacing.

2.2. Sorbates

The sorption properties were analyzed toward the following hydrocarbons: benzene, toluene, and *p*-xylene (BTEX). In addition, distilled water and methylene were used as reference sorbates. These hydrocarbons were selected in view of their high concentrations in the environment, significant mobility and toxicity, creating the necessity to remove them from the environment.

2.3. Method

The adsorption experiments were carried out at 20°C at the relative humidity RH ranging between 0 and 0.96 p/p_0, using a dynamic vapor sorption instrument Advantage (DVS-A) manufactured by Surface Measurement System, USA. The basic parameters of this instrument are presented in Table 2.

The masses of the clay samples were 10–15 mg. The initial heating was carried out at 150°C.

3. Results

The obtained sorption isotherms of BTEX hydrocarbons, methylene and water indicate significant differentiation, both quantitative and qualitative. It results from the fact that the sorption magnitude depends on the structure and surface properties of the sorbents, such as the specific surface area, the pore volume and size distribution, the number and kind of the surface functional groups affecting the polarity, and the kind of interaction with adsorbed particles. On the other hand, the sorbates properties are important, including the particle size, the spatial microstructure, the presence of functional groups, and the polarity. In Fig. 1, isotherms obtained for Ca-form of bentonite St from Texas are shown as an example.

Table 2
Specification of the dynamic vapor sorption instrument advantage (DVS-A)

Sample mass, g	1
Dynamic range, mg	150
Minimum suggested sample mass, mg	1
Sensitivity, μg	0.1
Sample pre-heater temperature range, °C	up to 150
Temperature range, °C	5–60
Humidity range, % RH	0–98
Relative humidity (RH) accuracy (+/– σ), % RH	+/– 0.5
Vapor concentration range, % p/p_0	0–90
Vapor pressure accuracy (+/– σ), % p/p_0	+/– 0.7

The shapes of the obtained isotherms suggest that, regardless of the adsorbent kind, the sorption of methanol is described by Type II adsorption isotherms according to Brunauer, while the sorption of water goes in accordance with Type IV or V adsorption isotherms [21]. These isotherms are characteristic of the sorption on microporous adsorbates.

Further, only the values of sorption obtained at RH = 0.96 (i.e., the maximum relative humidity applied in this study) were analyzed. Such results are presented in Tables 3 and 4 and in Fig. 2. The analysis of the plots in Fig. 1 leads to the following conclusions:

- Modifications by bivalent cation Ca^{2+} cause multiple increases in sorption properties toward toluene, benzene, and methanol.
- Basically, sorption of water proceeds differently than sorption of the other solvents.
- The significant decrease in sorption observed for K-forms is in agreement with the up-to-date knowledge about the clay–water systems [22].
- In contrast to water, the potassium cation significantly increases the sorption ability toward *p*-xylene, which is particularly strongly manifested in the case of bentonite St from Texas.
- For all the clays, the profile of the cation dependency was identical for water and methanol, both having similar physical–chemical properties.

The differences in sorption of water and organic solvents are shown in Table 3. Being exceptionally onerous and time-consuming, the cation exchange into ferric form Fe^{3+} was performed only in the case of bentonite Wy from Wyoming. For this reason, it was impossible to make general statistical analyses including this form. Table 4 shows a comparison only with other forms of bentonite Wy from Wyoming.

Apparently, water sorption on clays is twice more intensive. In relation to organic solvents, the exchange to the polyvalent cations Ca^{2+} and Fe^{3+} most significantly improves the sorption properties of bentonites, yielding in each case the highest values of sorption (with the exception of *p*-xylene). The values in Table 4 indicate high effectiveness of ferric cation compared with other cations used in the present investigation. However, it should be noticed that the mean sorption properties toward toluene, benzene, and *p*-xylene in Table 3 are the highest for the calcium forms. In the case where specific clays are used as a sorbent toward *p*-xylene, the best solution is a modification by potassium cation, although a modification to calcium forms also improves the sorption properties toward *p*-xylene.

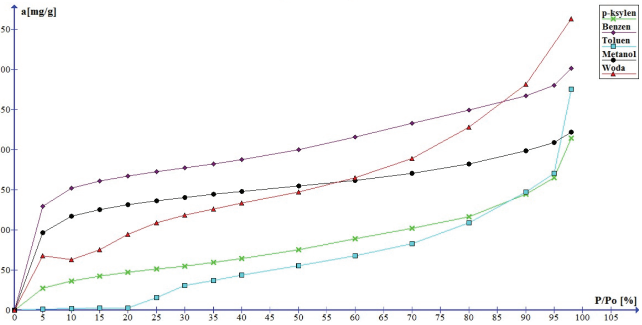

Fig. 1. Sorption isotherms obtained for Ca-form of bentonite St from Texas.

In view of practical use, an important fact is the high effectiveness of calcium homoionic form toward benzene and toluene as well as potassium form toward *p*-xylene. Hence, searching for a model toward sodium and natural forms seems useless. In addition, the most significant issue may be a possible relationship between the properties of natural clays and their subsequent sorption properties as Ca- and K-forms. It would enable an efficient selection of clay material.

Table 3
Mean sorption of water, methanol, and BTEX on natural and modified clays (the best sorptions toward a specific sorbate are underlined)

Compound	Sorption (mg/g) on form			
	Natural	Ca^{2+}	Na^{+}	K^{+}
BTEX + CH_3OH	128.0	172.5	129.9	129.1
Water	327.2	328.2	319.5	217.2
Methanol	180.3	230.4	170.0	134.0
Toluene	94.3	181.2	123.6	119.0
Benzene	115.7	143.8	97.7	94.6
p-Xylene	121.8	134.5	128.2	168.6

Table 4
Mean sorption of water, methanol, and hydrocarbons on natural and modified forms of bentonite SWy-2 (the best sorptions toward a specific sorbate are underlined)

Compound	Sorption (mg/g) on form				
	Natural	Ca^{2+}	Na^{+}	K^{+}	Fe^{3+}
BTEX + CH_3OH	63.1	110.1	71.4	82.1	132.9
Water	276.8	277.5	276.0	205.6	294.7
Methanol	140.7	237.3	157.0	135.4	184.0
Toluene	35.9	82.4	46.3	70.3	128.8
Benzene	42.3	51.6	33.6	48.3	93.4
p-Xylene	33.5	69.0	48.6	74.3	125.6

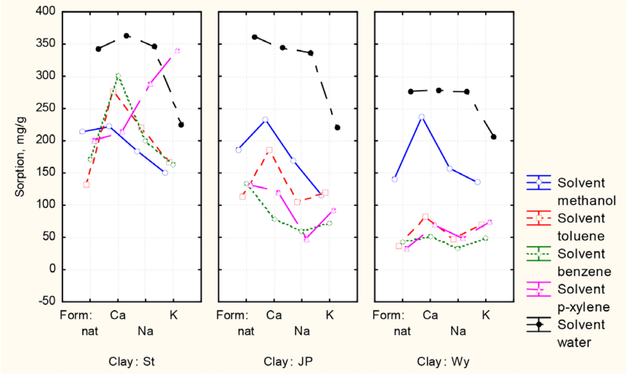

Fig. 2. Effect of clay and form on sorption of individual solvents.

4. Predictive models

4.1. Models derivation

In order to find a model enabling a prediction of the sorption properties of natural or modified clay in function of natural clay parameters, several functions were analyzed using the nonlinear estimation method in the following general form:

$$\mathrm{SP} = f\left(x_i, x_j, a_k \ldots a_n\right) \tag{1}$$

where SP—sorption of a given solvent on a clay of a given form, mg/g; x_i, x_j—selected initial parameters of natural clay (j = 1 lub$j$ = 0); and a_k … a_n—constants dependent on a given solvent and a given form of clay.

In view of the above, particular attention was paid to natural and calcium forms of clays. In the case of *p*-xylene, the potassium form was taken into account. Keeping in mind the postulate of the model simplicity, priority was given to models with $j = 0$ (i.e., with one parameter describing natural clay). All the possible combinations were tested, introducing a given parameter to linear, power, logarithmic, and exponential segment. Finally, the following model was proposed for predicting the sorption properties of natural clays:

$$\mathrm{SP} = a \bullet \ln\left(w_P\right) + b \tag{2}$$

where w_p is the plasticity limit, %.

The fitting parameters of the model given by Eq. (2) are shown in Table 5. It is apparent that the model exhibits high values of the correlation coefficients and high statistical significance of the estimates of the parameters *a* and *b*. The model can be used for rough predictions of sorption properties of clays in the case where cation exchange is not planned.

The plasticity limit w_p is a common clay characteristic and can be easily determined experimentally without a special equipment. The plasticity limit is considered an important soil parameter, determining the quantity of the so-called poly-layers and the hygroscopic water [23]. Ipso facto, it depends on properties of the pore space and on the size and the surface properties of the particles [24].

In order to predict the sorption properties of calcium forms, the following model is proposed:

$$\mathrm{SP} = a \bullet w_P + b \tag{3}$$

where w_p is the plasticity limit of natural clay (i.e., prior to modification), %.

Fitting parameters of the model given by Eq. (3) are presented in Table 6. It is easy to notice that the model exhibits high values of the correlation coefficients and high statistical significance of the estimates of the parameters *a* and *b*. The model can be used for rough predictions of sorption properties of clays in the case where cation exchange to the calcium form is taken into consideration.

Because sorption of *p*-xylene was most efficient on potassium forms, it is reasonable to use the best developed model in this case:

$$\mathrm{SP} = a \bullet \ln\left(w_P\right) + b * w_{95} + c \tag{4}$$

where SP—sorption magnitude, mg/g; w_P—plasticity limit of the natural form of a given clay, %; w_{95}—water content of the natural form of a clay obtained after 14-day keeping of dry samples under 10% solution of H_2SO_4 (i.e., at relative humidity equal to 0.95); and *a*, *b*, *c*—constant parameters.

Fitting parameters of the model given by Eq. (4) are presented in Table 7.

The model given by Eq. (4) can be used to predict benzene sorption on calcium forms (fitting parameters in Table 8). Table 3 shows clearly that in this sole case one of the estimates of Eq. (3) proves to be less statistically significant.

Table 5
Fitting parameters of the model given by Eq. (2)—natural forms of bentonites

Model for:		Estimate	Standard	*t*-Value	*p*-Level	Lower confidence	Upper confidence
Methanol							
	a	162.137	3.37695	48.0130	0.000001	152.761	171.513
$R = 0.999$	b	–435.356	12.83798	–33.9115	0.000005	–471.000	–399.712
Toluene							
	a	219.952	25.25303	8.70993	0.000957	149.84	290.066
$R = 0.975$	b	–740.919	96.00327	–7.71764	0.001517	–1,007.47	–474.371
Benzene							
	a	289.742	16.57513	17.4805	0.000063	243.72	335.762
$R = 0.994$	b	–984.439	63.01292	–15.6228	0.000098	–1,159.39	–809.487
p-Xylene							
	a	369.30	5.19517	71.0856	0.000000	354.88	383.73
$R = 0.999$	b	–1,280.43	19.75024	–64.8312	0.000000	–1,335.27	–1,225.60
BTEX + CH_3OH							
	a	260.283	40.6451	6.40381	0.000002	175.99	344.576
$R = 0.807$	b	–860.286	154.5185	–5.56753	0.000013	–1,180.74	–539.835

Table 6
Fitting parameters of the model given by Eq. (3)—calcium forms of bentonites

Model for:		Estimate	Standard	*t*-Value	*p*-Level	Lo. Conf	Up. Conf
Methanol							
	a	–0.7639	0.117929	–6.47769	0.002927	–1.0913	–0.4365
$R = 0.956$	b	265.0796	5.432401	48.79602	0.000001	249.9968	280.1623
Toluene							
	a	9.648	0.106751	90.3824	0.000000	9.352	9.945
$R = 0.999$	b	–256.241	4.917507	–52.1079	0.000001	–269.894	–242.588
Benzene							
	a	12.108	3.1675	3.82257	0.018737	3.314	20.90234
$R = 0.886$	b	–405.102	145.9112	–2.77636	0.050004	–810.216	0.01278
p-Xylene							
	a	7.181	0.84071	8.54110	0.001031	4.846	9.5147
$R = 0.974$	b	–191.046	38.72727	–4.93312	0.007855	–298.570	–83.5220
BTEX + CH_3OH							
	a	9.646	1.23654	7.80052	0.000001	7.024	12.267
$R = 0.890$	b	–284.130	56.96137	–4.98811	0.000134	–404.882	–163.377

Table 7
Fitting parameters of the model given by Eq. (4)—prediction of *p*-xylene sorption on potassium form of bentonite

$R = 0.9999$	Estimate	Standard	*t*-Value	*p*-Level	Lo. Conf	Up. Conf
a	1,178.82	6.30293	187.027	0.000000	1,158.76	1,198.88
b	–44.00	0.37995	–115.797	0.000001	–45.21	–42.79
c	–3,118.99	15.83828	–196.927	0.000000	–3,169.39	–3,068.58

Table 8
Fitting parameters of the model given by Eq. (4)—predicted benzene sorption on calcium form of bentonite

$R = 0.9999$	Estimate	Standard	*t*-Value	*p*-Level	Lo. Conf	Up. Conf
a	1,064.95	6.32396	168.400	0.000000	1,044.83	1,085.08
b	–38.14	0.38122	–100.038	0.000002	–39.35	–36.92
c	–2,869.76	15.89112	–180.589	0.000000	–2,920.33	–2,819.18

Fig. 3 presents the plots generated using Eqs. (2) and (3). An analogous plot for Eq. (4) cannot be produced, because in real clays the parameters w_p and w_{95} are strongly dependent on each other. The plasticity limit of natural clays considerably predetermines their sorption properties toward toxic solvents, both in natural state and after modification to the most effective calcium form. In the latter case however, methanol sorption proceeds rather differently, being somewhat dependent on the plasticity limit of the natural form.

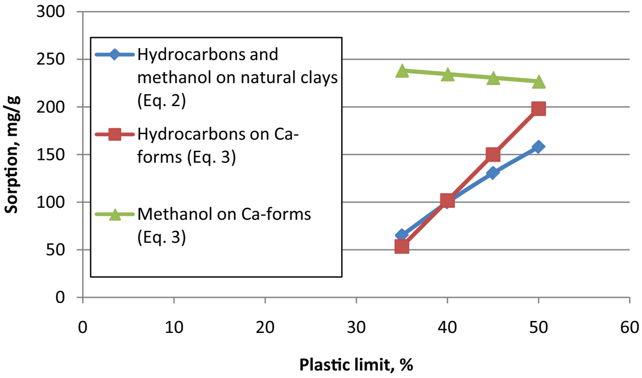

Fig. 3. Dependence of the toxic solvents sorption on the plasticity limit.

4.2. Models validation

The validation of the proposed model was performed by calculating the mean relative error (MRE) as the mean of absolute difference values between the calculated and measured values, for each group of results related to a given model. The results are collected in Table 9.

MRE in individual cases, that is, for specific solutes, does not exceed 12%, which can be considered a fully satisfying result. Similarly, the prediction of the sorption properties toward all the toxic solvents at a level of MRE equal to 25%–30% seems acceptable. The results indicate the usefulness of the plasticity limit as a parameter indirectly describing the sorption ability of bentonites. It should be kept in mind that the proposed models express the sorption ability of the natural

Table 9
Mean relative error for the proposed models, %

	Sorption of form		
	Natural	Ca	K
Methanol	0.4[a]	0.7[c]	
Toluene	10.4[a]	0.9[c]	
Benzene	5.7[a]	0.01[b]	
p-Xylene	1.7[a]	11.2[c]	0.09[b]
Hydrocarbons and methanol	30.3[a]	25.0[c]	

[a]Model given by Eq. (2).
[b]Model given by Eq. (3).
[c]Model given by Eq. (4).

and modified forms, in both cases in function of properties of the natural form, prior to modification. It enables a preliminary selection of bentonites to environmental applications.

Despite the excellent results obtained for the model given by Eq. (4), it should be stressed that such models usually yield better fitting to experimental data when more parameters are taken into account. They may appear unreliable, however, if the population in question is broadened to include clays that are not taken into account in the experiments.

Therefore, the prediction based on the simplest models, Eqs. (2) and (4), seems more worthy of recommendation at the sorbent pre-selection stage, and the model given by Eq. (4) should be used only in those cases where the two analyzed models apparently fail, that is, while predicting benzene sorption on calcium forms and *p*-xylene sorption on potassium forms (according to Table 8).

5. Conclusions

- The obtained results indicate high effectiveness of natural and modified homoionic bentonites as sorbents of aromatic hydrocarbons.
- The sorption properties significantly depend on the kind of clay, its form (natural vs. homoionic), the main exchangeable cation, and the kind of hydrocarbon.
- The most appropriate option seems to be using bentonites modified by a polyvalent cation (Ca^{2+} or Fe^{3+}), with the exception of *p*-xylene, the sorption of which was most efficient on potassium forms.
- In order to predict sorption properties of a specific bentonite in natural state, the model given by Eq. (2) should be used, in which predicted sorption properties are related to the plasticity limit w_p.
- In order to predict sorption properties of a specific bentonite after modification to the Ca-form, the model given by Eq. (3) should be used, in which predicted sorption properties after the modification are related to the plasticity limit value prior to modification (i.e., in the natural state). This model should not be used to predict the sorption of benzene on calcium forms.
- A separate model, given by Eq. (4), can be used in order to predict the sorption properties of a specific bentonite after modification to potassium form toward *p*-xylene or after modification to calcium form toward benzene.
- The MRE values yielded by the proposed model vary depending on the kind of exchangeable cation and the kind of hydrocarbon; however, in some cases they are surprisingly low, less than 0.1% (toluene and benzene on Ca-forms), which indicates that sorption properties of natural clays prior to their modification can be successfully applied in preliminary prediction.

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