

## Physical-chemical properties and possible applications of clay minerals and humic acid composite materials

M. Jemeljanova\*, R. Ozola and M. Klavins

Department of Environmental Science, University of Latvia, Raina Blvd. 19, LV-1586 Riga, Latvia

\*Correspondence: [marta.jemeljanova@gmail.com](mailto:marta.jemeljanova@gmail.com)

**Abstract.** Pollution caused by pharmaceuticals has become an increasingly serious issue, therefore innovative and cost – effective methods of pharmaceutical’s removal must be studied. Clay – humic acid composite materials can be considered as prospective and low cost sorbents for contaminants. The aim of this study is to develop clay mineral and humic acid composite materials and to characterise their possible applications. For this research, three types of clay minerals (montmorillonite, kaolinite and bentonite) were modified with three types of humic substances: technical humic acid from lignite, humic substances extracted from raised bog peat and technical K humate from lignite. The sorption was characterised according to the chosen clay mineral and humic acid type and concentration. The obtained material was characterised by Fourier Transform Infrared spectroscopy and Scanning Electron microscopy. The composite materials were tested for sorption of pharmaceuticals (chlorpromazine hydrochloride). The obtained results characterise clay mineral and humic acid composite materials’ possible applications as sorbents for removal of pharmacologically active substances.

**Key words:** clay composites, humic acids, sorption, environmentally friendly technologies.

### INTRODUCTION

Clay minerals are phyllosilicates and their crystal structure consists of tetrahedral  $[\text{SiO}_4]^{4-}$  and octahedral  $[\text{AlO}_3(\text{OH})_3]^{6-}$  sheets in either a 1:1, 2:1 or 2:1:1 proportion. The arrangement and composition of octahedral and tetrahedral sheets mostly determine the physical and chemical properties of clay minerals. Commonly known clay mineral kaolinite’s structure consists of a single tetrahedral sheet and a single octahedral sheet with little or no permanent charge. The structure of montmorillonite consists of two tetrahedral sheets with a central octahedral sheet with a charge from 0.5 to 1.2 e/uc per unit cell (Murray, 2007; Lee & Tiwari, 2012). The negative charge is due to isomorphous substitution in octahedral (e.g.,  $\text{Al}^{3+}$  for  $\text{Mg}^{2+}$ ) sheet and it is compensated with exchangeable cations ( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$  etc.) present in the interlayer space of the clay mineral. Due to isomorphous substitution, montmorillonite has a higher cation exchange capacity and surface area than kaolinite (Schulze, 2005; Zhu et al., 2016).

Humic substances is a group of naturally occurring organic substances which results from long-term physical, microbial and chemical transformations of organic matter. Humic substances are high-molecular weight polycationites and can be used for

clay modification to obtain a sorbent for the removal of organic and inorganic pollutants (Jin et al., 2016; Wang et al., 2018). Nowadays humic substances from different sources are produced in quantities of tons and can be considered as low cost natural material.

Natural clay minerals have received a lot of attention as potential sorbents, because of high sorption and ion-exchange properties as well as their abundance and low cost (Zhang et al., 2015). Clay minerals can be modified using different approaches to obtain innovative materials for their application as sorbents in the removal of different types of pollutants (Lee & Tiwari, 2012). In the last two decades most studies have concentrated on using organoclays to remove organic and inorganic contaminants from wastewater (Ozola et al., 2018). Organoclays are prepared by intercalating specific organic molecules in the interlayer space of a clay mineral through an ion exchange reaction. The surfactants, known as quaternary alkylammonium salts, are the most commonly used organic compounds for the preparation of organoclays (Yariv & Cross, 2002). For example, kaolinite modified with hexadecyltrimethylammonium bromide, has been used to remove significant quantities of nitrates, arsenate and chromates from aqueous solutions (Li & Bowman et al., 2001), while montmorillonite, kaolinite or palygorskite modified with octadecyltrimethylammonium bromide has been used as an efficient sorbent of various pesticides (linuron, atrazine and metalaxyl) in a sandy soil (Rodríguez-Cruz et al., 2007). However, cationic surfactants, such as hexadecyltrimethylammonium bromide and octadecyltrimethylammonium bromide can be environmentally hazardous; they are toxic to soil microbially mediated processes (dehydrogenase and nitrification) and earthworms (Sarkar et al., 2013).

The aim of the present study is to develop clay mineral and humic acid composite materials and to characterise their possible applications.

## MATERIALS AND METHODS

### Materials

Three types of industrially produced clay minerals were used – kaolinite (*Kaolin heavy*, Sigma – Aldrich Chemie GmbH), montmorillonite (*Montmorillonite K10*, Sigma – Aldrich Chemie GmbH) and bentonite (*Bentonite pure*, AppliChem Panreac GmbH) – as well as three types of humic substances – technical humic acid from lignite (Sigma – Aldrich Chemie GmbH), technical K humate from lignite (Czech Republic) and humic substances from raised bog peat (Latvia).

### Characterisation of materials

**FTIR.** In order to characterise changes of functional groups, infrared spectra were taken for modified and unmodified clay samples. 10 mg of clay sample was mixed with 200 mg of KBr, 30 mg of the obtained powder was pressed into a tablet. Fourier Transform Infrared Spectrophotometer *Shimadzu IR- Tracer 100* was used with following settings – wave number 4000–400  $\text{cm}^{-1}$ ; resolution 2  $\text{cm}^{-1}$ ; the number of scans 20.

**SEM.** SEM was performed on *Hitachi S-4800* Scanning Electron Microscope with 3.0 kV voltage. *Image J* programme was used for data processing.

### Sorption experiments

Batch system was used to conduct sorption experiments. Three types of humic substances and 0.1 M NaOH were used for preparation of humic substances stock solutions with varied concentrations (5, 10, 25, 50, 100, 200, 500, 1,000 mg L<sup>-1</sup>). 0.3 g of clay minerals were weighed in a glass vessel and 50 mL of humic substances concentrate was added. Vessels were subsequently shaken for 24 hours at room temperature at 150 rpm with orbital shaker *BioSan PSU U-20*. Suspensions were afterwards filtered into 50 mL plastic test tubes and then the concentrations of filtrates were measured with *Shimadzu UV Spectrophotometer UV-1800* at the 410 nm wavelength.

The concentration after sorption was calculated using the equation of the calibration graph and the following formula:

$$C = (A + b_0) \div b_1, \quad (1)$$

where  $C$  – the concentration after sorption, mg L<sup>-1</sup>;  $A$  – absorption;  $b_0$  – the y-intercept;  $b_1$  – the coefficient of slope. The sorbed amount was calculated with the following formula:

$$q_e = (C_1 - C_2) \times V \div m, \quad (2)$$

where  $q_e$  – the sorbed weight, mg g<sup>-1</sup>;  $C_1$  – the concentration before sorption, mg L<sup>-1</sup>;  $C_2$  – the concentration after sorption, mg L<sup>-1</sup>;  $V$  – the volume of added solution, mL;  $m$  – the weight of clay minerals, g.

### Sorption of chlorpromazine hydrochloride

*Standard solutions preparation.* Stock solution of reference standard was prepared by dissolving accurate weighed sample of a compound in 50 mM ammonium acetate solution at a concentration of 10,000 mg mL<sup>-1</sup>. Working standard solutions (5.0–550 µg mL<sup>-1</sup>) containing chlorpromazine hydrochloride (≥ 98% (TLC) Sigma-Aldrich) was prepared by diluting the stock solutions. A sample of 2.0 µl was injected with an autosampler. The straight-line regression was not forced to a zero intercept. Linear least squares regression of the peak areas as a function of the concentrations was performed to determine the correlation coefficients ( $R^2 > 0.9995$ ). The equation parameters (slope and intercept) of standard curve were used to obtain the concentration values ( $y = 20495x + 23$ ;  $y$  – peak area, mV·s;  $x$  – conc., µg mL<sup>-1</sup>). The precision of the method was assessed by triplicate analysis of standard solutions at eight concentrations (5.0, 10.0, 50.0, 100.0, 200.0, 300.0, 400.0 and 550.0).

*UPLC analysis of chlorpromazine.* Chromatography of chlorpromazine compounds in clay samples was carried out using the methods of Larsimon et al (1998) and Takahashi (1980) with slight modification. Acidified (5 mM CH<sub>3</sub>COONH<sub>4</sub>) clay (100 mg) extract was filtered through an nylon syringe filter with 0.22 µm pore size (Membrane Solutions, Plano, TX, USA) straight to 1.5 mL glass vials and right away analyzed using the UPLC system. The chromatographic separation was carried out using the *Waters Acquity UPLC H-class* consisting of a ultra high-pressure gradient unit (*Quaternary Solvent Manager*), an auto injector (*FTN*), a column oven (*CHA*), and a fluorescence detector (*FLR*). Chromatographic data was collected via *Waters Empower*

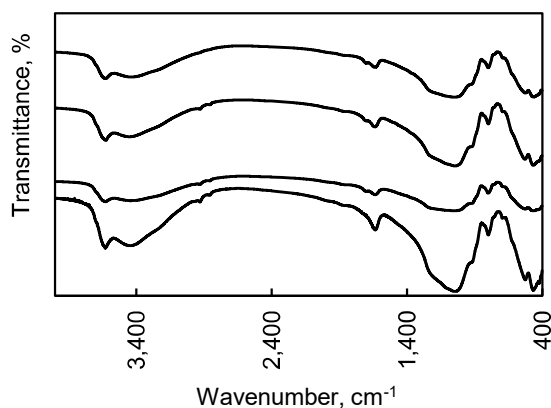
chromatography software. Chromatography was carried out at 30 °C using a Acquity UPLC HSS CYANO column (1.7  $\mu\text{m}$ , 2.1  $\times$  450 mm) and a mobile phase consisting of acetonitrile and 50 mM  $\text{CH}_3\text{COONH}_4$  (9:1 v/v) running a constant flow-rate of 0.50 mL  $\text{min}^{-1}$ . The total separation time was 3.5 min. The identification and quantification of chlorpromazine was estimated using a fluorescence detector at an excitation wavelength of 280 nm and emission wavelength of 450 nm.

*Sorption of chlorpromazine on clay samples.* The concentrate of chlorpromazine hydrochloride was obtained by dissolving 0.3 g of chlorpromazine hydrochloride in 500 mL 0.1% ammonia acetate. 0.1 g of each obtained type of sorbent as well as each type of raw clay minerals was weighed and 20 mL of chlorpromazine concentrate was added. The samples were shaken in *Biosan PSU U-20 (Latvia)* shaker for 24 hours in room temperature. The samples were subsequently filtered with paper filter and 0.45  $\mu\text{m}$  membrane filter and analysed in the UPLC system.

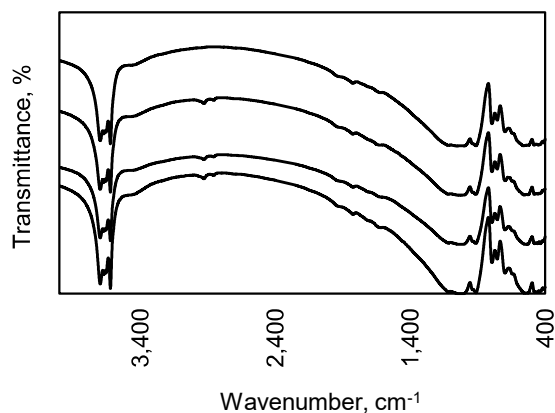
## RESULTS AND DISCUSSION

### Characterisation of the materials

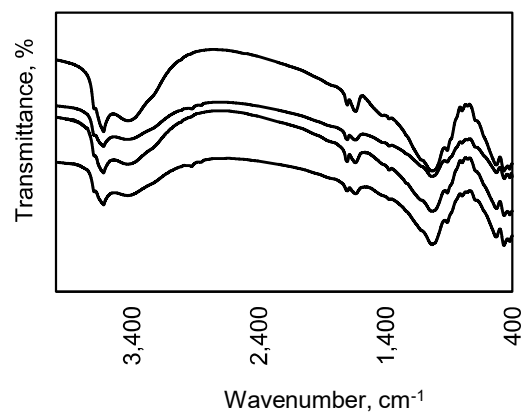
*FTIR.* In order to characterize the changes of obtained clay – humic acid sorbents' functional groups, FTIR spectra were taken and the differences between raw and modified clays were analysed. All of the modified samples apart from bentonite modified with technical K humate (Figs 1, 2, 3) had peaks at wave number 2,850–2,950  $\text{cm}^{-1}$ , that can be assigned to C-H aliphatic stretch. Common peaks were observed that can be assigned to clay mineral structure, such as peak at the wavenumber 3,620  $\text{cm}^{-1}$  (approximately) that refers to hydroxyl groups between tetrahedral and octahedral sheets. Samples had peaks at the wavenumbers 3,653  $\text{cm}^{-1}$  and 3,669  $\text{cm}^{-1}$  that can be assigned to Si-O-Si and O-H stretch. The samples of bentonite and kaolinite had a peak at the wavenumber interval 950–800  $\text{cm}^{-1}$  that refers to O-H bend and tri-valent central atoms in octahedral sheets. Bentonite samples had a peak in the wavenumber interval 1,400–1,300  $\text{cm}^{-1}$  that can be assigned to Si-O stretch and bend as well as O-H bend. Kaolinite samples had a peak in the wavenumber interval 695–698  $\text{cm}^{-1}$  that can be assigned to O-H bend and two-valent central atoms.



**Figure 1.** Montmorillonite FTIR spectra (from top to bottom: Mt\_A – modified with technical humic acid; Mt\_CH – modified with technical K humate; Mt – raw montmorillonite; Mt\_HS – modified with raised bog peat humic substances).

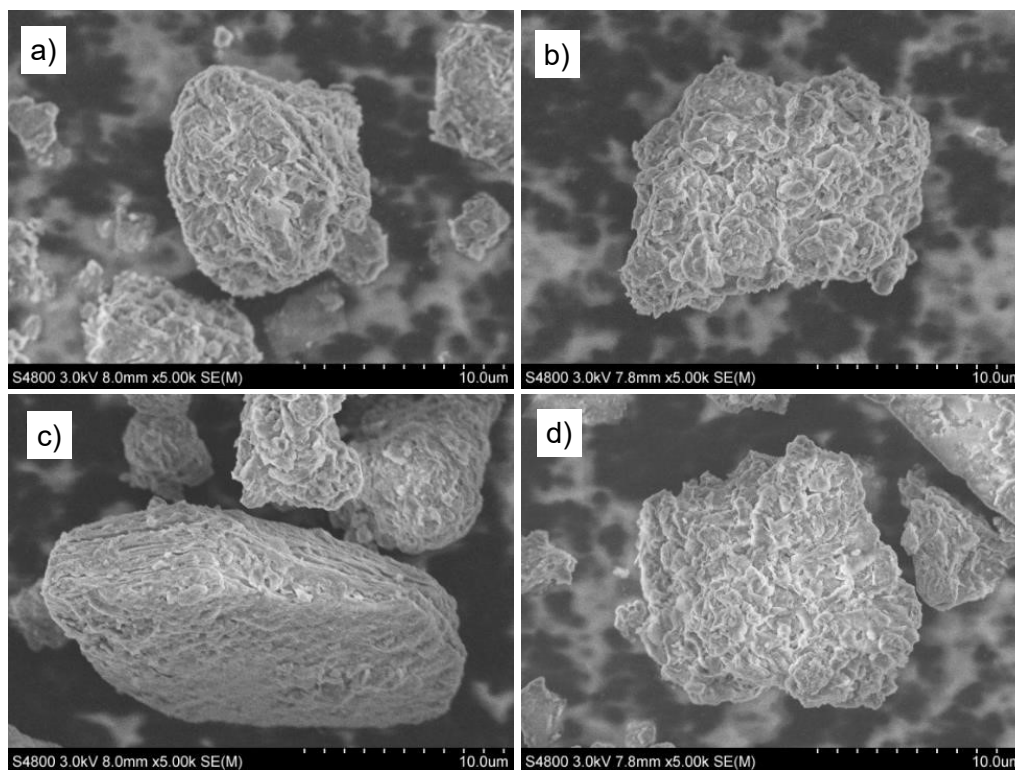


**Figure 2.** Kaolinite IR spectra (from top to bottom: K\_A – modified with technical humic acid; K\_CH – modified with technical K humate; K – raw kaolinite; K\_HS – modified with raised bog peat humic substances).



**Figure 3.** Bentonite IR spectra (from top to bottom: Bt\_A – modified with technical humic acid; Bt\_CH – modified with technical K humate; Bt – raw bentonite; Bt\_HS – modified with raised bog humic substances).

*SEM.* SEM images can be seen in Fig. 4. Montmorillonite had an irregular surface both pre – (Fig. 4, a) and post (Fig. 4, b, c, d) modification. No significant changes in morphology were noted.

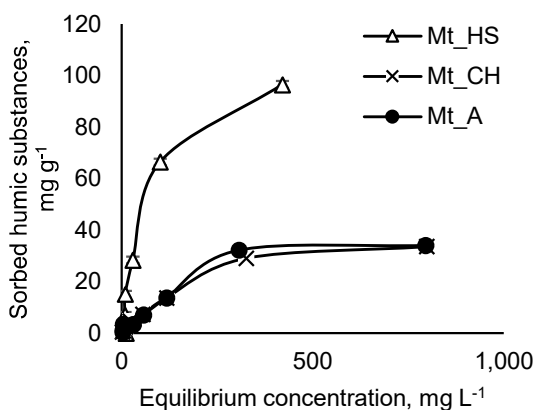


**Figure 4.** SEM images of a) raw montmorillonite; b) montmorillonite modified with high bog peat humic substances; c) montmorillonite modified with technical humic acid; d) montmorillonite modified with technical K humate.

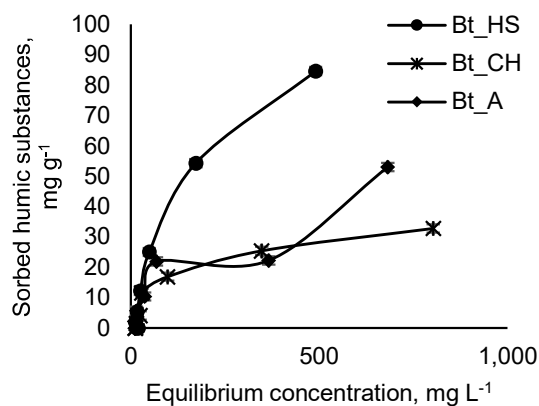
## Sorption experiments

In order to obtain the optimal conditions of clay minerals and humic substances composite materials synthesis, the initial concentration of humic substances was varied while maintaining other sorption parameters, e.g., the sorption time, pH value, the weight of clay minerals sample.

Comparing the isotherms of the sorbent montmorillonite, it can be seen that the highest sorption capacity by a significant margin was attained modifying with raised bog peat humic substances ( $96.5 \text{ mg g}^{-1}$ ), but the sorption capacities of the remaining sorbates were almost the same –  $34.1 \text{ mg g}^{-1}$  with technical humic acid as a sorbate and  $33.6 \text{ mg g}^{-1}$  with technical K humate as a sorbate (Fig. 5).



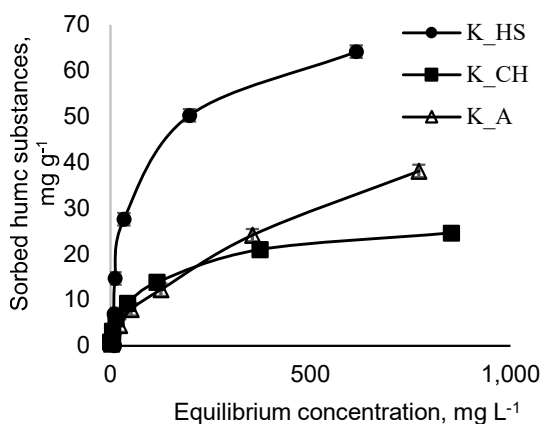
**Figure 5.** The sorption isotherms of montmorillonite samples (Mt\_HS – modified with raised bog peat humic substances; Mt\_CH – modified with technical K humate; Mt\_A – modified with technical humic acid).



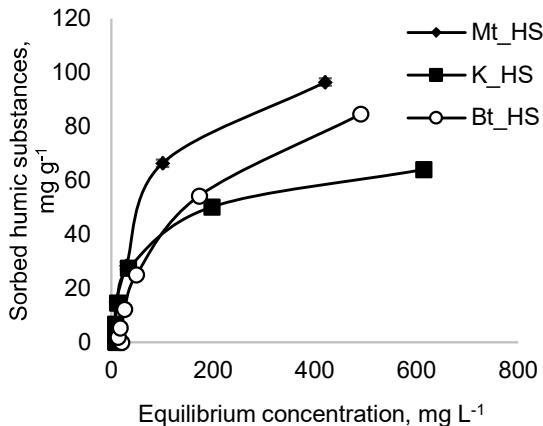
**Figure 6.** The sorption isotherms of bentonite samples (Bt\_HS – modified with raised bog peat humic substances; Bt\_CH – modified with technical K humate; Bt\_A – modified with technical humic acid).

Similar results were obtained using bentonite as a sorbent – the raised bog peat humic substances sorption capacity was higher by a significant margin ( $84.6 \text{ mg g}^{-1}$ ) (Fig. 6). By contrast, the sorption capacities of remaining samples varied significantly – the sorption capacity of technical humic acid was  $53.0 \text{ mg g}^{-1}$ , and the lowest sorption capacity of bentonite was observed when K humate ( $32.8 \text{ mg g}^{-1}$ ) was used. Similarly, modifying kaolinite with raised bog peat humic substances, the highest sorption capacity was obtained ( $64.1 \text{ mg g}^{-1}$ ) (Fig. 7). The sorption capacity of kaolinite modified with technical humic acid was  $38.1 \text{ mg g}^{-1}$ , but kaolinite modified with technical K humate had the lowest sorption capacity ( $24.6 \text{ mg g}^{-1}$ ). Comparing the results of chosen sorbates, it can be concluded that the highest sorption capacity was found when raised bog peat humic substances were used as a sorbate.

Comparing isotherms of a common sorbate – raised bog peat humic substances – it can be concluded that montmorillonite had the highest sorption capacity ( $96.5 \text{ mg g}^{-1}$ ) followed by bentonite ( $84.6 \text{ mg g}^{-1}$ ). The lowest sorption capacity was found when kaolinite was used ( $64.1 \text{ mg g}^{-1}$ ) (Fig. 8).

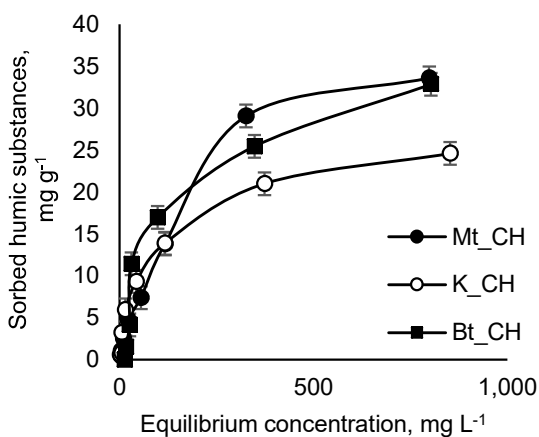


**Figure 7.** The sorption isotherms of kaolinite samples (K\_HS – modified with raised bog peat humic substances; K\_CH – modified with technical K humate; K\_A – modified with technical humic acid).

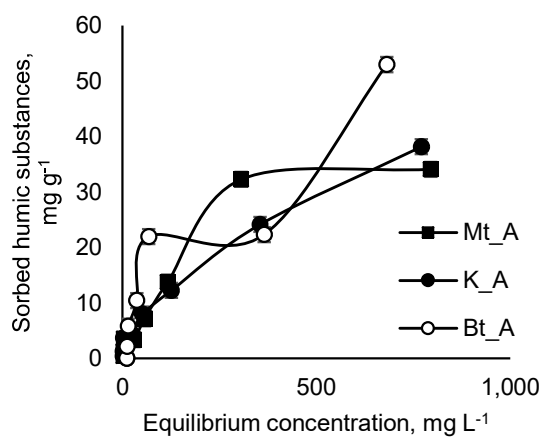


**Figure 8.** The sorption isotherms of sorbents modified with raised bog peat humic substances (Mt\_HS – montmorillonite; K\_HS – kaolinite; Bt\_HS – bentonite).

A similar order can be seen when clay minerals were modified with technical K humate, although the sorption capacity of bentonite was almost the same as that of montmorillonite (32.8 mg g<sup>-1</sup> and 33.6 mg g<sup>-1</sup>, respectively) (Fig. 9). Kaolinite modified with technical K humate had the lowest sorption capacity (24.6 mg g<sup>-1</sup>). The results differed when modifying clay minerals with technical humic acid – bentonite had the highest sorption capacity (52.9 mg g<sup>-1</sup>) (Fig. 10). The sorption capacity of kaolinite was 38.13 mg g<sup>-1</sup>. Montmorillonite had the lowest sorption capacity (34.07 mg g<sup>-1</sup>), although modified with raised bog peat humic substances or technical K humate it had the highest sorption capacity.



**Figure 9.** The sorption isotherms of sorbents modified with technical K humate (Mt\_CH – montmorillonite; K\_CH – kaolinite; Bt\_CH – bentonite).



**Figure 10.** The sorption isotherms of sorbents modified with technical humic acid (Mt\_A – montmorillonite; K\_A – kaolinite; Bt\_A – bentonite).

Chotzen et al. (2016) observed that kaolinite had higher sorption capacity than montmorillonite in the natural pH of the respective clay minerals, and it was argued to be because of kaolinite's low natural pH. In acidic pHs, higher adsorption of humic substances can be achieved (Derakhshani & Naghizadeh, 2018). For this study an acidified montmorillonite was used and an identical pH was set, therefore the sorption capacity of montmorillonite in this study was higher than that of kaolinite. In comparison, while adjusting the humic acid solution to pH 7, Zhang et al. (2012) observed higher sorption capacity for smectite than kaolinite.

### Sorption of chlorpromazine hydrochloride

Sorption experiments were done by adding 20 mL of chlorpromazine hydrochloride to 1 g of clay minerals and subsequently shaking the samples for 24 hours in room temperature on *Biosan* shaker. The filtrates were filtered through 45 µm membrane filter and analysed in UPLC system.

The sorption capacity of chlorpromazine by various samples is shown in Table 1. Modified bentonite samples had the highest sorption capacity of chlorpromazine (over 99%). The sorption capacity of montmorillonite samples were in the range of 73.48–93.21%. Kaolinite samples had the lowest sorption capacity (21.12%–59.05%), because of its lower cation exchange capacity and surface layer (Schulze, 2005; Zhu et al., 2016).

Raw bentonite had the lowest sorption capacity of bentonite samples (99.44%), although the approximate difference with modified samples was only 0.5%. The results of modified bentonite samples were identical, therefore studies of higher initial concentration of chlorpromazine should be done. The results of lowest

sorption capacity were coherent with kaolinite samples – raw kaolinite had the lowest sorption capacity (21.12%). The highest sorption capacity of modified kaolinite samples by a significant margin was obtained with kaolinite modified with raised bog peat humic substances (59.05%). Kaolinite modified with technical humic acid and kaolinite modified with technical K humate showed a difference of only 2% (25.79% and 23.46%, respectively).

In contrast, montmorillonite modified with raised bog peat humic substances had the lowest sorption capacity of montmorillonite samples (73.48%). Montmorillonite modified with technical humic acid and modified with technical K humate had the highest sorption capacity (93.21% and 91.02%, respectively). The sorption capacity of raw montmorillonite was 86.13%.

**Table 1.** The sorption capacity of clay - humic acid composite materials (K – kaolinite; Mt – montmorillonite; Bt – bentonite; HS – raised bog peat humic substances; CH – technical K humate; A – technical humic acid)

Sample	Sorbed chlorpromazine amount, µg mL <sup>-1</sup>	Sorbed chlorpromazine amount, %
Bt	596.67	99.4
Bt_CH	599.77	100.0
Bt_A	599.75	100.0
Bt_HS	599.82	100.0
K_A	155.18	25.8
K_HS	354.52	59.1
K_CH	141.18	23.5
K	127.18	21.1
Mt_A	559.29	93.2
Mt_HS	441.01	73.5
Mt_CH	546.18	91.0
Mt	517.92	86.3



To characterise the materials and their possible application comprehensively, X-ray diffraction (XRD) method will be used as well as sorption experiments depending on pH and sorption time.

## CONCLUSIONS

The study of interaction of clay minerals and humic substances is of importance to understand the interaction of clay minerals and natural humic matter at the formation of soils. However clay-humic composites are prospective for development of sorbents for environmental technologies. In this study clay minerals were modified with three types of humic substances and tested for chlorpromazine sorption. Comparing the influence of clay minerals and humic substances on humic substances sorption, it can be concluded that the choice of humic substances affects the sorption capacity more. Modification of clay minerals mostly increased the sorption capacity of chlorpromazine. The highest sorption capacity of chlorpromazine was obtained by using montmorillonite and bentonite samples due to their higher surface area and sorption capacity. Although, in the case of bentonite further sorption experiments of chlorpromazine are needed.

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