



© 2023. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike 4.0 International Public License (CC BY SA 4.0, <https://creativecommons.org/licenses/by-sa/4.0/legalcode>), which permits use, distribution, and reproduction in any medium, provided that the article is properly cited.

The influence of chlorine substitution on the adsorption of chlorophenols on HDTMA-modified halloysite in aqueous solutions

Beata Szczepanik^{1*}, Anna Kołbus¹, Piotr Słomkiewicz¹, Marianna Czaplicka²

¹Institute of Chemistry, Jan Kochanowski University, Kielce, Poland

²Institute of Environmental Engineering Polish Academy of Sciences, Zabrze, Poland

*Corresponding author's e-mail: beata.szczepanik@ujk.edu.pl

Keywords: adsorption, mechanism, chlorophenols, HDTMA-halloysite adsorbent; computational calculation

Abstract: This article focuses on discussing the adsorption process of phenol and its chloro-derivatives on the HDTMA-modified halloysite. Optimized chemical structures of phenol, 2-, 3-, 4-chlorophenol, 2,4-dichloro-, and 2,4,6-trichlorophenol were obtained with computational calculation (the Scigress program). Charge distributions and the hypothetical structure of the system HDTMA-modified halloysite are among their key features. The above-mentioned calculations are applied in order to explain adsorption mechanism details of chlorophenols on the HDTMA-modified halloysite in aqueous solutions. The results of electron density distribution and solvent accessible surface area calculations for phenol and chlorophenols molecules illustrate the impact of chlorine substitution position in a phenol molecule, both on the mechanism and the kinetics of their adsorption in aqueous solutions. Experimental adsorption data were sufficiently represented using the Langmuir multi-center adsorption model for all adsorbates. In addition, the relations between adsorption isotherm parameters and the adsorbate properties were discussed. This study also targets at explaining the role of *meta* position as a chlorine substituent for mono-chloro derivatives. Given the above findings, two possible mechanisms were utilized as regards chlorophenol adsorption on the HDTMA-modified halloysite, i.e., electrostatic and partition interactions when the chlorophenols exist in a molecular form.

Introduction

Phenols are used in a wide range of applications. Petrochemical, pharmaceutical, pesticide, plastic, coal conversion, and paper industries are the main sources of phenolic wastewaters (Czaplicka 2004, Garba et al. 2019, Issabayeva et al. 2018). A high level of toxicity of phenols causes critical environmental problems (Garba et al. 2019, Issabayeva et al. 2018). Because of their potential harmful effects on aquatic organisms, plants, and human beings, even at low concentrations, phenolic compounds are listed as priority pollutants by the US Environmental Protection Agency (USEPA) and the U.S. Agency for Toxic Substances and Disease Registry (Garba et al. 2019, Honda and Kannan 2018). Removing phenols from wastewaters before they appear in the aquatic environment is important to ensure the safety of water supplies. Various technologies, including adsorption, membrane separation, oxidation, and biological treatment, are used to remove phenols from wastewaters (Ali et al. 2012, Bodzek et al. 2021, Lin et al. 2003, Park et al. 2013, Rawajfih and Nsour 2006, Sinha et al. 2006). Adsorption emerges as an effective, simple, and economical technique (Park et al. 2013) as phenols are hydrophobic compounds and have poor biological activity. Moreover, many adsorbents have

limited ability to adsorb phenols (Wu and Yu 2006, Yousef and El-Eswed 2009). Among others, carbonaceous and polymeric adsorbents, zeolites, and clays are used to remove phenol and chlorophenols from water (Damjanović et al. 2010, Chen et al. 2017, Huang et al. 2012, Hu et al. 2012, Madannejad et al. 2018, Majlesi and Hashempour 2017, Qiu et al. 2014, Sarkar et al. 2010, Su et al. 2011, Yu et al. 2004, Xie et al. 2012).

Naturally abundant clays can function as adsorbents due to their low cost, chemical stability, high adsorption capacity, and ion exchange properties (Sarkar et al. 2010). Montmorillonite and bentonite have been commonly used as adsorbents of phenolic compounds (Djebbar et al. 2012, Ocampo-Perez et al. 2011, Park et al. 2013, Su et al. 2011, Yang et al. 2017, Yu et al. 2004, Zhang et al. 2015). Adsorption properties of montmorillonite and bentonite have been improved by modifying the mineral surface with a cationic surfactant (Ocampo-Perez et al. 2011, Park et al. 2013, Su et al. 2011, Yang et al. 2017). Replacing inorganic exchangeable cations with cationic surfactants changes the hydrophilic clay surface into a hydrophobic one. The obtained complex is an organoclay (Ocampo-Perez et al. 2011, Yang et al. 2017). Organoclays can be used as adsorbents for removing organic contaminants (Ocampo-Perez et al. 2011, Yang et al. 2017). Improving

the adsorption properties of organoclays corresponds to the charge density of clay layers and the molecular arrangement of surfactants within the organoclays themselves. Examining the surfactant arrangement and surface properties of synthesized organoclays plays a major role in terms of their adsorption applications (Cruz-Guzmán et al. 2005, Paul et al. 2005, Smith and Galan 1995, Zhou et al. 2007, Yuan 2004).

Halloysite is an aluminosilicate dioctahedral 1:1 clay mineral with tubular nanostructure. The outer surface of halloysite nanotubes consists of siloxane groups and is negatively charged, while the inner lumen contains aluminol groups and is positively charged. This feature facilitates modifying its surface properties (charge, hydrophilicity) by physically adsorbing some specific cations, e.g., cationic surfactants (Joussein et al. 2005, Pasbakhsh et al. 2013, Tana et al. 2016, Pandey et al. (a) 2022). The properties of halloysite nanotubes enable them to be used also as the nano-support system for other different compounds (Pandey et al. 2017, Pandey et al. (b) 2022, Tharmavaram et al. 2021, 2023), or as the carriers for drugs (Setter et al. 2022).

In our previous work, we presented the application of the hexadecyltrimethylammonium (HDTMA) modified halloysite as an adsorbent of phenol and chlorophenols. 2-, 3-, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol were chosen as model pollutants (Słomkiewicz et al. 2020).

This study, in turn, provides a new possibility for understanding the influence of surfactant arrangement on the halloysite surface and other properties of the HDTMA modified halloysite on the mechanism of the chlorophenols adsorption from aqueous solutions. Quantum chemical calculations were performed for phenol, 2-, 3-, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. Theoretical calculations were also conducted to obtain halloysite structure modified with HDTMA. Following quantum chemical calculations, we provided a detailed description of chemical activity concerning chlorophenol molecules on the adsorption process onto organo-halloysite. Our analysis of the relations between the adsorbate properties and adsorption parameters allowed us to clarify the role of chlorine substituent in the adsorption of chlorophenols.

Materials and Methods

Chemicals and materials

Halloysite was obtained from the “Dunino” strip mine, Intermark Company, Legnica, Poland. 2-, 3-, 4-chlorophenol $\geq 99\%$ as well as 2,4-dichlorophenol $\geq 99\%$ were obtained from Sigma-Aldrich. Hexadecyltrimethylammonium bromide ($[(C_{16}H_{33})N(CH_3)_3]Br$) and 2,4,6-trichlorophenol $\geq 98\%$ were purchased from MERCK. Sodium chloride (95%) was provided by Avantor Performance Materials Poland S.A. Deionized water ($1.74 \mu S \cdot cm^{-1}$, temp. $25^\circ C$) was applied throughout all experiments.

Preparation of HDTMA- modified halloysite

Pre-cleaned raw halloysite (HAL) samples were placed in a sodium chloride solution to obtain Na-halloysite. Preparing the HDTMA-Na-halloysite was conducted according to the procedure described in detail in Ref. Słomkiewicz et al. 2020. Raw halloysite was pre-cleaned with deionized water. Next, the halloysite sample was placed in a sodium chloride solution to obtain Na-halloysite. The HDTMA solution was shaken

with Na-halloysite at an ambient temperature for 24 h. Finally, the obtained samples were labelled as HDTMA-HAL.

Adsorption experiments

Adsorption measurements were conducted in two systems: using the Peak Division Inverse Liquid Chromatography (PD ILC) method and in the batch system. The first method was presented in Ref. Słomkiewicz et al. 2020. Batch adsorption experiments were carried out by adding 1g of an adsorbent to an aqueous solution (15 cm^3) placed in a 100 cm^3 Erlenmeyer's flask. The experiment was conducted following the change in time of the adsorbate concentration. The flasks were put into the Biosan ES-20 incubator and shaken for 3 hours at different temperatures ($20^\circ C$, $30^\circ C$, and $40^\circ C$) and at a mixing rate of 100 rpm. The concentrations of chlorophenols were determined with the spectrophotometric method, using a UV Shimadzu UV-1800 spectrophotometer. Wavelengths used to determine the concentrations had the following values: 270, 274, 274, 280, 284, and 294 nm, respectively for absorption maxima of the studied chlorophenols.

Computational calculations

Theoretical calculations were completed using the Scigress program, version FJ 2.7. The geometry of the studied phenol and its chloro-derivatives molecules was optimized with the B88-LYP GGA functional containing the DZVP basis. In the calculations, the model was taken into account in which the same forces were assumed to act on all molecules. The GGA of the DFT method did not include long range interactions (Berland et al. 2015, Czaplicka 2004, Grimme 2006, Tamijani et al. 2016). However, this model allowed for gaining an insight into the general trends in the adsorbate behavior.

The system composed of HDTMA and halloysite was calculated using molecular mechanics with augmented MM3 parameters. This method was selected as it provides large system size. The length of chemical bonds was less than 2 \AA in both the halloysite and the HDTMA molecule. Finally, the distance between the HDTMA molecule and halloysite was within the range of $2.5\text{--}3 \text{ \AA}$.

Taking into account that phenol and its chloro-derivatives were dissolved in water, the solvent accessible surface area (SASA) parameter was calculated in the Scigress Program. The SASA parameter was calculated at an optimized geometry in water.

Results and discussion

Characterization of the HDTMA/Halloysite Adsorbent

Morphological and structural changes of the HDTMA/halloysite nanocomposite were characterized with the use of scanning and transmission electron microscopy (SEM, TEM), Fourier-transform infrared spectrometry (FT-IR), and the low-temperature nitrogen adsorption method. Details were provided in. Słomkiewicz et al. 2020. The results proved that the obtained sample belongs to the group of mesoporous materials. After modifying halloysite with the HDTMA, the adsorbent specific surface area (S_{BET}) decreased from $47 \text{ m}^2 \cdot \text{g}^{-1}$ to $43 \text{ m}^2 \cdot \text{g}^{-1}$, total pore volume (V_t) decreased from $0.1773 \text{ cm}^3 \cdot \text{g}^{-1}$ to $0.1716 \text{ cm}^3 \cdot \text{g}^{-1}$, whilst the pore diameter slightly increased from 16.8 nm to 17.6 nm . ATR FT-IR spectra of halloysite

and HDTMA/halloysite in the 4000–650 cm^{-1} region show characteristic bands for the kaolin-group minerals. Moreover, two new bands at 2924 and 2852 cm^{-1} appear in the HDTMA/halloysite sample spectrum, which can be assigned to the CH_2 stretching vibrational bands in the alkyl chain of HDTMA. They are almost the same bands as in the HDTMA micelles. SEM and TEM images illustrate that modifying halloysite with HDTMA does not significantly change the tubular mineral structure (Słomkiewicz et al. 2020).

Characteristics of adsorbates

Phenol and its chloro-derivatives are weak organic acids, therefore pH is an important factor, which affects the ionization

degree and the charge of their molecules. These compounds can exist in the solution in a molecular form (non-ionic, undissociated) for a pH value lower than pK_a . On the other hand, the deprotonated form (dissociated, anionic) is formed if pH is higher than their pK_a values (see Table 1). Figure 1 illustrates the distribution of ionized and non-ionized forms of their molecules with respect to the pH value.

Electrostatic potential maps were prepared (Figure 2) as regards optimized molecule structures. Phenol and its chloro-derivatives were placed in aqueous solutions, which promoted the formation of hydrogen bonds (Czaplicka and Czaplicki 2006). Therefore, in the next step, the structures with the hydrogen bond between the studied molecules and

Table 1. pK_a and $\log K_{ow}$ values for phenol and its chloro derivatives (Czaplicka 2004)

Compound	phenol	2-chlorophenol	3-chlorophenol	4-chlorophenol	2,4-chlorophenol	2,4,6-chlorophenol
pK_a^*	9.99	8.52	9.12	9.41	7.89	6.23
$\log K_{ow}^{**}$	1.46	2.12	2.48	2.35	2.75	3.60

* K_a – dissociation constant at 20°C ** $\log K_{ow}$ – *n*-octanol/water partition coefficient

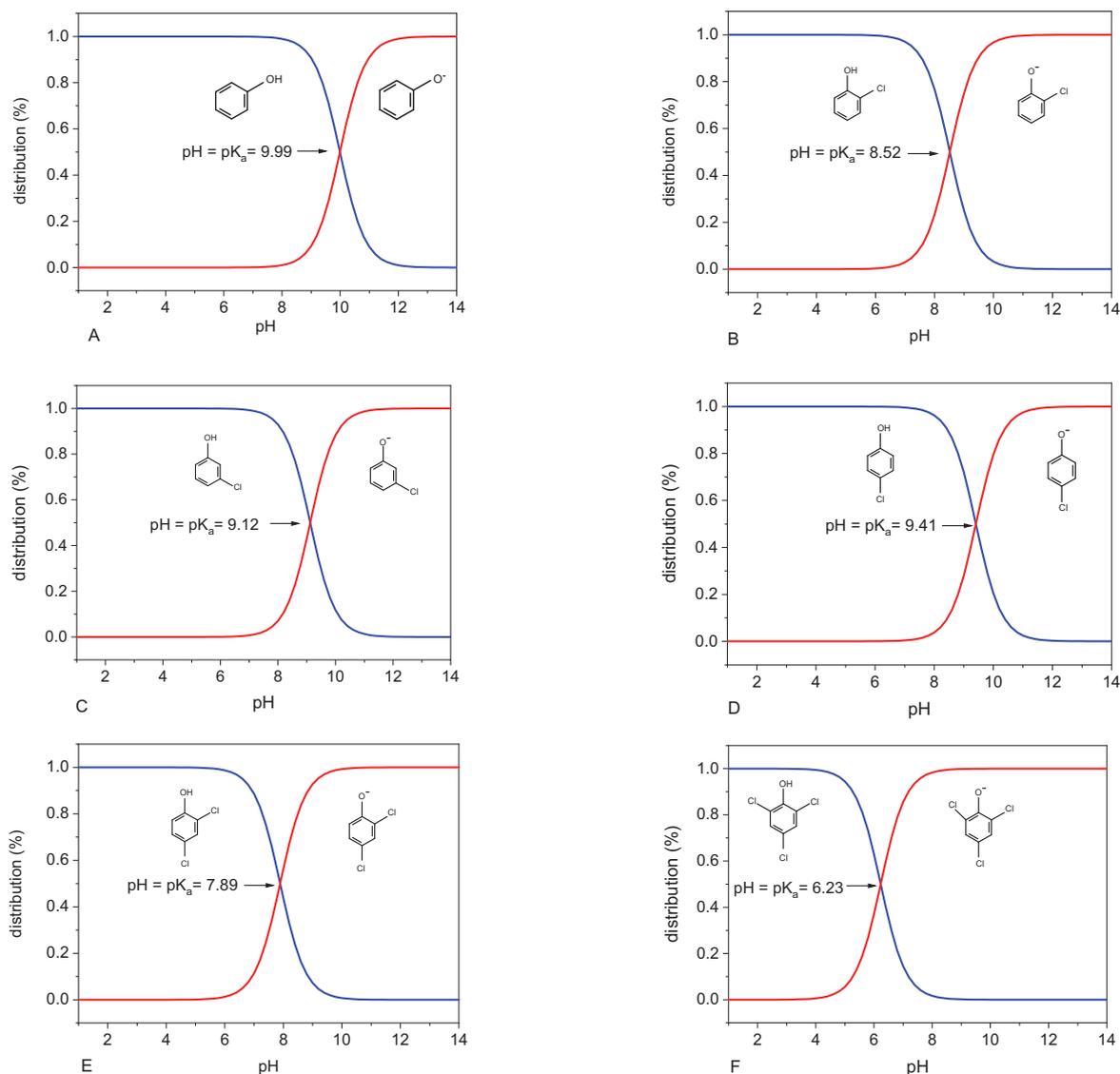


Fig. 1. The distribution of ionized and non-ionized forms of phenol and chlorophenols depending on solution pH value (Raczyńska-Żak 2018)

the water molecule were calculated. General electron density distribution did not change, contrary to the values of the partial charges. Table 2 includes the values of partial charges on oxygen and chlorine atoms in molecules – with and without hydrogen bonds. Larger differences in the values of partial charges occur for the molecules with hydrogen bonds. The

largest negative charge is in the vicinity of an oxygen atom for both phenol and its chloro-derivatives. It can be seen that for the molecules with the hydrogen bond, the value on the oxygen atom becomes less and less negative according to the following order: 4-chlorophenol, 2-chlorophenol, 3-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol.

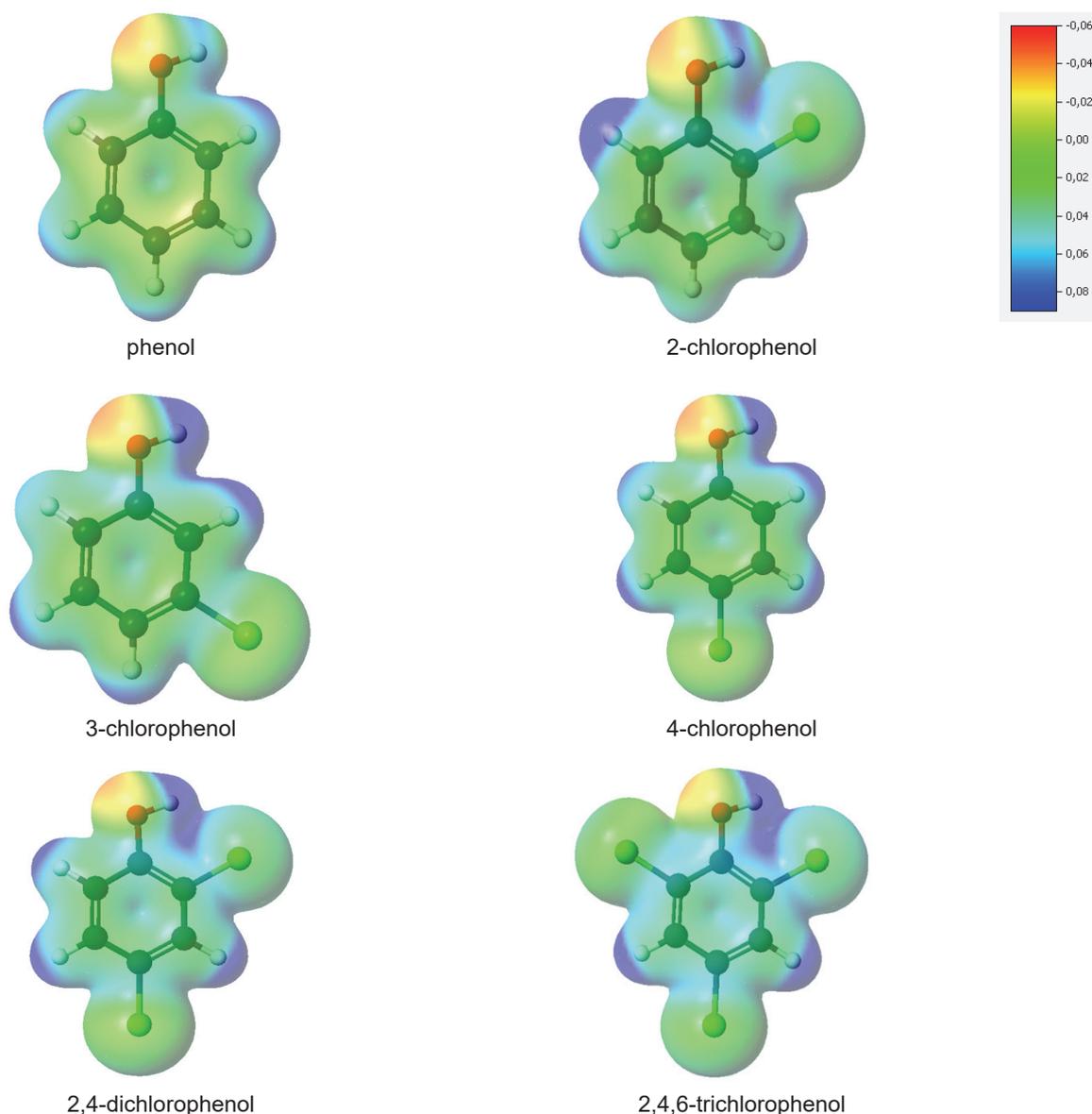


Fig. 2. Electrostatic potential energy maps for phenol and chlorophenols. Blue surface indicates positive value of electrostatic potential (localized positive charge) and the red one – the negative value (localized negative charge) – surface legend can be found in the upper right corner. Electron density at the surface is $0.01 \text{ e}/\text{\AA}^3$.

Table 2. The values of partial charge for phenol and chlorophenols

Molecule	Atom	Value of partial charge [charge a.u.]	Value of partial charge for the molecule with hydrogen bond [charge a.u.]
phenol	O	-0.478	-0.521
4-chlorophenol	O / Cl	-0.473 / -0.073	-0.512 / -0.075
2-chlorophenol	O / Cl	-0.463 / -0.074	-0.502 / -0.067
3-chlorophenol	O / Cl	-0.473 / -0.071	-0.496 / -0.069
2,4-dichlorophenol	O / Cl2 / Cl4	-0.459 / -0.059 / -0.059	-0.496 / -0.051 / -0.059
2,4,6-trichlorophenol	O / Cl2 / Cl4 / Cl6	-0.442 / -0.049 / -0.047 / -0.016	-0.479 / -0.043 / -0.050 / -0.031

The SASA parameter calculated at an optimized geometry in water can provide some information about the real surface available for the solvent which differs from the total particle area. The lowest value of SASA was obtained for phenol and it equaled 129.9 Å². The highest values of SASA could be found among di- and trichloro-derivatives, equal to 166.2 Å² and 183.8 Å², for 2,4-dichlorophenol and 2,4,6-trichlorophenol, respectively. Among the chlorophenols, 3-chloro-phenol had the highest SASA value (149.4 Å²), followed by 4-chlorophenol (148.9 Å²), and 2-chlorophenol (146.6 Å²).

The results of electron density distribution as well as solvent accessible surface area calculations for phenol and chlorophenols molecules indicate a clear influence of substituting chlorine position in a phenol molecule, which may have a significant impact on the mechanism and kinetics of their adsorption in aqueous solutions.

Adsorption experiments

The adsorption of phenol, 2-,3-,4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol on HDTMA/halloysite nanocomposite was studied in the batch system in aqueous solutions with the pH value reaching 6. The compatibility of the results was checked with the nonlinear regression method (Levenberg-Marquardt least square method) with the Origin Microcal software (Program Origin User's Manual; Microcal Software Inc.: Northampton, MA, USA, 2018). Furthermore, the check was performed with the Langmuir, Freundlich, Temkin, Elovich and Dubinin-Raduszkiewicz equations and referred to the adsorption of phenol and its chloro-derivatives on the HDTMA-modified halloysite adsorbent. The results indicate no correlation of the experimental data for the Temkin, Elovich, and Dubinin-Raduszkiewicz models. The best fitting of experimental data was obtained for the Langmuir (multi-center, Langmuir adsorption model on multiple active centers without dissociation) isotherm model (Słomkiewicz et al. 2020) with the highest values of correlation coefficients for phenol and all the studied chlorophenols. Adsorption constant values for 298 K decreased in the following order: phenol > 4-chlorophenol > 2-chlorophenol > 3-chlorophenol > 2,4-dichlorophenol > 2,4,6-trichlorophenol. An increase in temperature caused a decrease in constant values, indicating the exothermic nature of the adsorption process (see Table 3).

In the Langmuir equation, describing the multi-center adsorption (equation 1), the value of the n exponent determines the number of active centers participating in the phenol adsorption process (together with its chlorine derivatives) on HDTMA/HAL. Moreover, the determined values of n are not whole numbers for phenol and its derivatives. These values equal 1.12 for phenol, 1.28 for 2-chlorophenol, 1.43 for 3-chlorophenol, 1.51 for 4-chlorophenol, 1.22 for 2,4-dichlorophenol, and 1.38 for 2,4,6-trichlorophenol.

$$a = a_m \frac{Kc^{1/n}}{(1 + Kc^{1/n})} \quad (1)$$

where: c_e – equilibrium concentration of a solute in an aqueous solution (mg·dm⁻³); a – the amount of a solute adsorbed per gram of the adsorbent at equilibrium (mg·g⁻¹), a_m – maximum monolayer coverage capacity (mg·g⁻¹); K – adsorption equilibrium constant (cm³/mg)^{1/n}, n – adsorption model index (dimensionless).

The adsorption of phenol and chlorophenols on HDTMA/halloysite nanocomposite was also studied with the use of the Inverse Liquid Chromatography methods (the Peak Division and the Breakthrough Curves Inverse Liquid Chromatography) in aqueous solutions at pH about 6 (Słomkiewicz et al. 2020). Experimental adsorption data were represented with the Langmuir (multi-center) adsorption model, similar to the adsorption studies in the batch system. Adsorption constant values also change similarly for phenol and mono-chlorophenols from the highest to the lowest value: phenol > 4-chlorophenol > 3-chlorophenol, and for other chloro-derivatives: 2,4-dichlorophenol > 2,4,6-trichlorophenol (Table 4). The value of the n exponent, which determines the numbers of active centers in the adsorption, was similar to the values obtained for the batch method (1.09 for phenol; 1.25 for 2-chlorophenol; 1.39 for 3-chlorophenol; 1.47 for 4-chlorophenol; 1.19 for 2,4-dichlorophenol, and 1.42 for 2,4,6-trichlorophenol) (Słomkiewicz et al. 2020).

Adsorption mechanism

Modifying halloysite with surfactants prevents aggregating of its particles. HDTMA molecules can create a steric barrier between the surface of halloysite and water molecules, which

Table 3. Adsorption constants (for different temperatures), adsorption enthalpy, and adsorption capacities calculated on the basis of Langmuir (multi-center) equation using *Batch Method* for the adsorption of phenol and chlorophenols on HDTMA-modified halloysite adsorbent

Adsorbate	PH	2CPH	3CPH	4CPH	24DCPH	246TCPH
$T(K)$	$K (dm^3 \cdot mg^{-1})$					
298	0.016	0.0067	0.0052	0.0086	0.0048	0.0032
303	0.015	0.0057	0.0039	0.0071	0.0039	0.0027
313	0.014	0.0043	0.0030	0.0055	0.0028	0.0023
Adsorption enthalpy, $\Delta H_a (kJ \cdot mol^{-1})$	-8.3	-22.5	-27.3	-22.1	-27.4	-16.5
$T(K)$	$a_m (mg \cdot g^{-1})$					
298	42.7	17.2	7.25	9.24	6.0	4.1
303	30.5	13.1	6.19	8.36	5.4	3.9
313	25.1	10.2	5.82	7.12	5.1	3.8

enhances nanotube dispersion in the solution (Tharmavaram et al. 2018). The outer halloysite surface is negatively charged. Therefore, it can be modified with a cationic surfactant, e.g., HDTMA. The presence of surfactant molecules on the halloysite surface favors forming reverse micelles formed when the positive head group of the surfactants were specifically absorbed, followed by the formation of inorganic tubular nanoparticles, which consist of a hydrophilic core and a hydrophobic shell (Cavallaro et al. 2015).

The hydrophilic character of the halloysite surface can be changed into the hydrophobic one through this modification. On the other hand, reverse micelles with positively charged surfaces can act as adsorptive centers for organic compounds with an acidic character, which adsorb poorly on the negatively charged outer surface of halloysite.

Theoretical calculation carried out by mechanics with the MM3 parameters allowed us to present halloysite structures with HDTMA applied both in the form of micelles and particles arranged in series on the surface (see Figure 3). For such systems, energy calculations were conducted to determine interaction energies between halloysite and HDTMA. Interaction energy for system halloysite and HDTMA (in the form of micelles) equaled ca. 2560 kcal/mol. The value for system halloysite and HDTMA (in the layer form) reached ca. 4621 kcal/mol. The above process illustrates that micelles are the preferred arrangement for HDTMA on the halloysite surface.

The pH value of the solution affects the adsorption of chlorophenols onto different adsorbents, because chlorophenols can exist in both non-ionized and ionized forms, depending on the solution pH. The adsorption of these forms onto the adsorbent surface can be influenced by the surface charge on the adsorbent. When the adsorption process is conducted in deionized water at a pH of ca. 6 phenol, mono-chlorophenols are in a neutral form, whereas the ionic fraction is increasing for di- and trichlorophenols (see Table 1, Fig. 1).

The results of theoretical calculations confirm that the lowest value of the negative partial charge on the phenol O-atom is observed for the neutral form of the phenol molecule. This value is less negative and comparable for the molecules of

3-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. Adsorption constants of the studied compounds calculated for both systems have the values decreasing in the same order on the HDTMA/halloysite adsorbent. This finding leads to a conclusion that adsorption is strongly associated with electron distribution in adsorbate molecules. Data from Table 1 illustrate that the negative charge is more concentrated on the oxygen atom for phenol and its *ortho*- and *para*- derivatives, while for 3-chlorophenol, 2,4-dichloro-, and 2,4,6-trichlorophenol, it is more dispersed throughout the molecule. It can be assumed that electrostatic interactions of phenol and *ortho*- and *meta*-derivatives are stronger with the surface of the micelles on the adsorbent surface as compared to other derivatives. In this manner, these interactions facilitate the adsorption process.

The solvent accessible surface area (SASA) of phenol and its chloro-derivatives dissolved in water is the lowest for phenol and higher for 2-chlorophenol and 4-chlorophenol. The highest values of SASA were found for 3-chlorophenol, di- and trichloro-derivatives. This would indicate a higher possibility of binding to water molecules of the latter derivatives when compared to phenol and *ortho*- and *para*- derivatives. This tendency may hinder the adsorption of these molecules on the adsorbent surface, which is reflected in the adsorption constant values.

The mechanism of phenol and its derivatives adsorption on organoclays depends on various factors, e.g., the surfactant molecule structure, solute concentration, and pH. For organophilic clays (for long chain $R \geq 12$), the adsorption mechanism of phenol and its derivatives from water and wastewater depends on the solubility of organic adsorbates in water. It can continue through the partitioning into the organic phase that is used to modify the clay surface and/or surface adsorption (Nafees and Waseem 2014).

Phenol and chlorophenols, for which $1 < \log K_{ow} < 3$, are average lipophilic and may undergo both mechanisms. Therefore, there are two possible mechanisms for the adsorption of phenol and chlorophenols on the HDTMA-modified halloysite, i.e., the electrostatic interaction and partition interactions when the chlorophenols exist in the molecular form.

Table 4. Adsorption constants (for different temperatures), adsorption enthalpy, and adsorption capacities calculated on the basis of Langmuir (multi-center) equation using *Inverse Liquid Chromatography Method* for the adsorption of phenol and chlorophenols on the HDTMA-modified halloysite adsorbent

Adsorbate	PH	2CPH	3CPH	4CPH	24DCPH	246TCPH
$T(K)$	$K (cm^3 \cdot mg^{-1})^{1/n}$					
298	0.201	0.031	0.018	0.067	0.051	0.031
303	0.184	0.025	0.014	0.055	0.041	0.025
313	0.160	0.019	0.011	0.043	0.030	0.021
Adsorption enthalpy, $\Delta H_a (kJ \cdot mol^{-1})$	-11.6	-23.3	-26.3	-22.9	-26.1	-18.4
$T(K)$	$a_m (mg \cdot g^{-1})$					
298	34.5	18.6	8.1	11.8	6.9	3.8
303	29.8	14.3	7.9	10.2	6.4	3.6
313	17.6	12.9	7.1	9.3	6.2	3.3

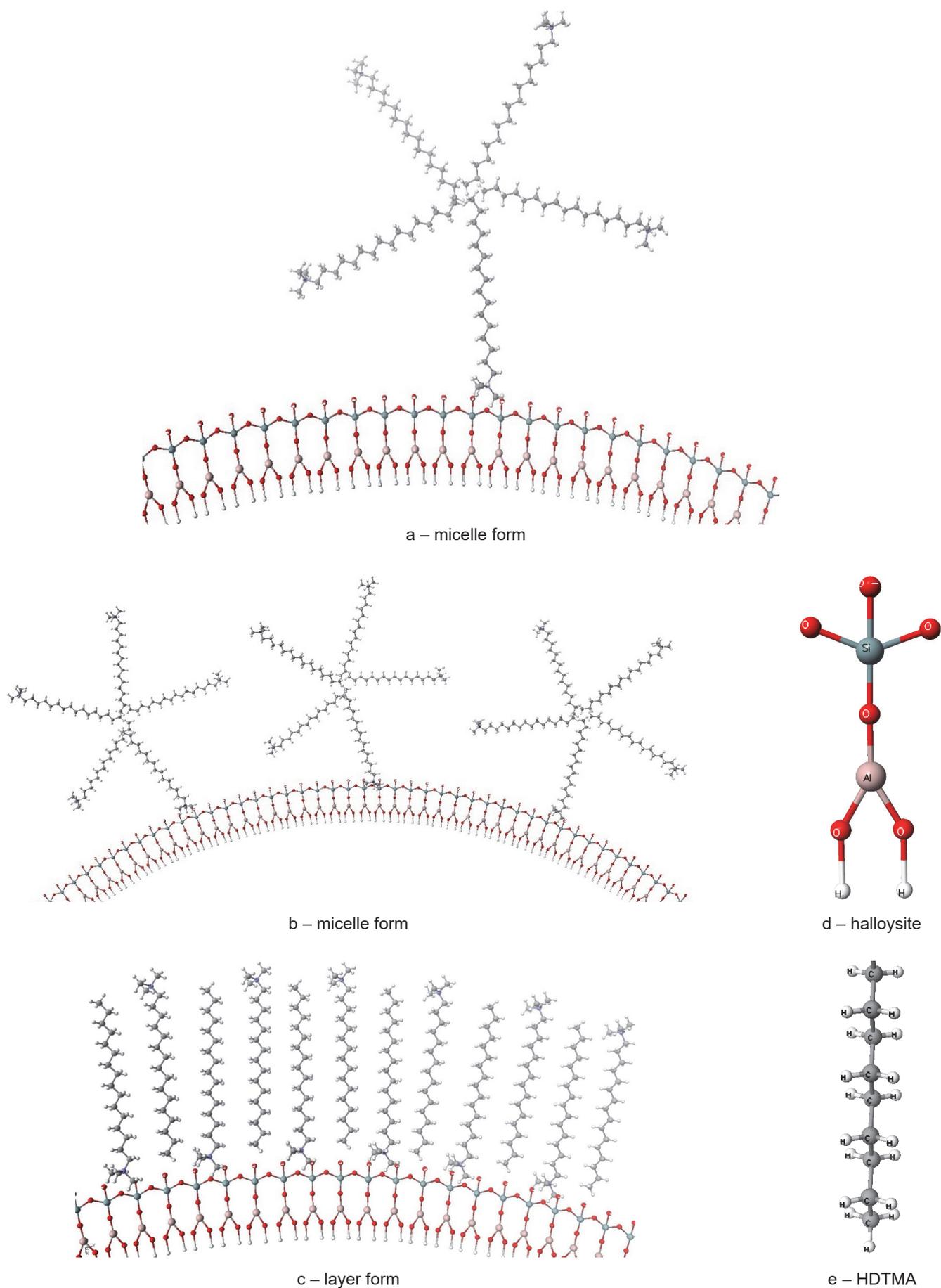


Fig. 3. Hypothetical structure of system HDTMA-modified halloysite where HDTMA is attached in the form of micelles (a, b) and a layer (c)

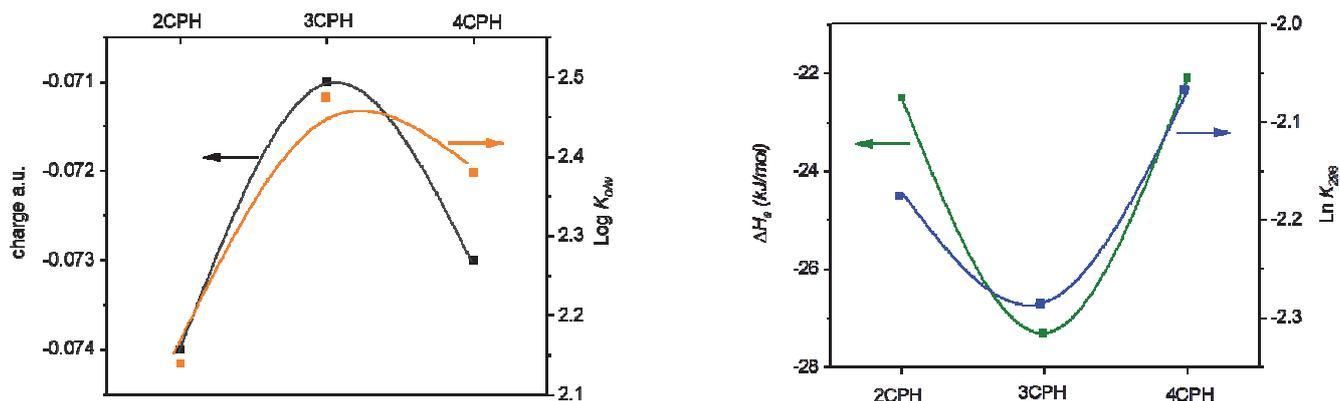


Fig. 4. Correlation between the values of partial charge for oxygen and chlorine atoms in: mono-chlorophenols molecules; $\log K_{ow}$ with logarithms of adsorption constants $\ln K$ at 298K and adsorption enthalpy ΔH_a for *ortho*-, *meta*- and *para*-chlorophenol

In Fig. 4 we compared adsorption constant logarithms $\ln K$ at 298K and adsorption enthalpy ΔH_a with: the values of partial charge for oxygen and chlorine atoms in chlorophenol molecules as well as $\log K_{ow}$ for *ortho*-, *meta*-, and *para*-chlorophenol. The course of the relationship illustrates that the isomer for which the values of charge and K_{ow} are the highest has, at the same time, the poorest adsorption properties.

Conclusions

1. This paper presents adsorption data analysis of several phenol chloro-derivatives from aqueous solutions in batch and flow systems on the HDTMA-modified halloysite.
2. Experimental adsorption data well represented with the Langmuir (multi-center) adsorption model enable determining the value of factor n , indicating adsorption mechanisms of phenol and chlorophenols with a different number of adsorptive centers on the HDTMA/halloysite surface.
3. The adsorption mechanism is discussed with regard to the properties of the adsorbate molecules: electron density distribution, solvent accessible surface area, the values of pK_a and $\log K_{ow}$.
4. Analyzing the relations between the adsorbate properties and adsorption parameters (adsorption equilibrium constants and adsorption enthalpy) facilitated an explanation of chlorine substituent's role for the mono-chlorophenols adsorption and a weaker adsorption of di- and tri-chlorophenols in comparison to mono-derivatives.
5. The results of theoretical calculations prove that the lowest value of negative partial charge on the phenol O-atom is observed for the neutral form of the phenol molecule. The negative charge decreases for chloro-derivatives, especially for *m*-chlorophenol, di-, and trichlorophenol, according to the electron withdrawing nature of the chlorine substituent.

Acknowledgements

This work was funded from resources of Ministry of Science and Higher Education as research project SUPB.RN.21.188

References

- Ali, I., Asim M. & Khan, T.A. (2012). Low cost adsorbents for the removal of organic pollutants from wastewater. *J. Environ. Manag.* 113, 170. DOI: 10.1016/j.jenvman.2012.08.028
- Berland, K., Cooper, V.R., Lee, K., Schröder, E., Thonhauser, T., Hyldgaard, P. & Lundqvist, B.I. (2015). Van der Waals forces in density functional theory: A review of the vdW-DF method. *Rep. Prog. Phys.* 78, 066501. DOI: 10.1088/0034-4885/78/6/066501
- Bodzek, M., Konieczny, K. & Kwiecińska-Mydlak A. (2021). New generation of semipermeable membranes with carbon nanotubes for water and wastewater treatment: Critical review. *Arch. Environ. Protect.* 47, pp. 3–27. DOI: 10.24425/aep.2021.138460
- Cavallaro, G., Lazzara, G., Milioto, S. & Parisi, F. (2015). Hydrophobically Modified Halloysite Nanotubes as reverse Micelles for Water-in-Oil Emulsion. *Langmuir* 31, 7472–8. DOI: 10.1021/acs.langmuir.5b01181
- Chen, C., Geng, X. & Huang W. (2017). Adsorption of 4-chlorophenol and aniline by nanosized activated carbons. *Chem. Eng. J.* 327, 941. DOI: 10.1016/j.cej.2017.06.183
- Cruz-Guzmán, M., Celis, R., Hermosin, M.C., Koskinen, W.C. & Cornejo, J. (2005). Adsorption of pesticides from water by functionalized organobentonites. *J. Agric. Food. Chem.* 53, pp. 7502–7511. DOI: 10.1021/jf058048p
- Czaplicka, M. (2004). Sources and transformations of chlorophenols in the natural environment. *Sci. Total Environ.* 322, 21. DOI: 10.1016/j.scitotenv.2003.09.015
- Czaplicka M. & Czaplicki, A. (2006). Photodegradation of 2,3,4,5-tetrachlorophenol in water/methanol mixture. *J. Photochem. Photobiol. A* 178, 90. DOI: 10.1016/j.jphotochem.2005.07.005
- Damjanović, L., Rakić, V., Rac, V., Stošić, D. & Auroux, A. (2010). The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. *J. Hazard. Mater.* 184, 477. DOI: 10.1016/j.jhazmat.2010.08.059
- Djebbar, M., Djafri, F., Boucekara, M. & Djafri, A. (2012). Adsorption of phenol on natural clay. *Appl. Water Sci.* 2, 77. DOI: 10.1007/s13201-012-0031-8
- Garba, Z.N., Zhou, W., Lawan, I., Xiao, W., Zhang, M., Wang, L., Chen, L. & Yuan Z. (2019). An overview of chlorophenols as contaminants and their removal from wastewater by adsorption: A review. *J. Environ. Manage.* 241, 59. DOI: 10.1016/j.jenvman.2019.04.004
- Grimme, S. (2006). Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* 27, 1787. DOI: 10.1002/jcc.20495
- Honda, M. & Kannan, K. (2018). Biomonitoring of chlorophenols in human urine from several Asian countries, Greece and the

- United States. *Environ. Pollut.* 232, 487. DOI: 10.1016/j.envpol.2017.09.073
- Hu, X., B. Wang, Yan, G. & Ge B. (2012). Simultaneous removal of phenol and Cu(II) from wastewater by tallow dihydroxyethyl betaine modified bentonite. *Arch. Environ. Protect.* 48, pp. 37–47. DOI: 10.24425/aep.2022.142688
- Huang, J., Jin, X. & Deng, S. (2012). Phenol adsorption on an N-methylacetamide-modified hypercrosslinked resin from aqueous solutions. *Chem. Eng. J.* 192, 192. DOI: 10.1016/j.cej.2012.03.078
- Issabayeva, G., Hang, S.Y., Wong M.C. & Aroua, M.K. (2018). A review on the adsorption of phenols from wastewater onto diverse groups of adsorbents. *Rev. Chem. Eng.* 34, pp. 855–873. DOI: 10.1515/revce-2017-0007
- Joussein, E., Petit, S., Churchman, G.J., Theng, B.K.G., Righi, D. & Delvaux, B. (2005). Halloysite clay minerals—a review. *Clay Clay Miner.* 40, 383. DOI: 10.1180/0009855054040180
- Lin, S.S., Chang, D.J., Wang, C.H. & Chen, C.C. (2003). Catalytic wet air oxidation of phenol by CeO₂ catalyst—effect of reaction conditions. *Water Res.* 37, pp. 793–800. DOI: 10.1016/s0043-1354(02)00422-0
- Madannejad, S., Rashidi, A., Sadeghassani, S., Shemirani, F. & Ghasemy, E. (2018) Removal of 4-chlorophenol from water using different carbon nanostructures: a comparison study. *J. Mol. Liq.* 249, 877. DOI: 10.1016/j.molliq.2017.11.089
- Majlesi, M. & Hashempour Y. (2017). Removal of 4-chlorophenol from aqueous solution by granular activated carbon/nanoscale zero valent iron based on Response Surface Modeling. *Arch. Environ. Protect.* 43, pp. 13–25. DOI: 10.1515/aep-2017-0035
- Nafees, M. & Waseem, A. (2014). Organoclays as Sorbent Material for Phenolic Compounds: A Review. *Clean – Soil, Air, Water* 41, pp. 1–9. DOI: 10.1002/clen.201300312
- Ocampo-Perez, R., Leyva-Ramos, R., Mendoza-Barron, J. & Guerrero-Coronado, R.M. (2011). Adsorption rate of phenol from aqueous solution onto organobentonite: Surface diffusion and kinetic models. *J. Colloid Interf. Sci.* 364, 195. DOI: 10.1016/j.jcis.2011.08.032
- Pandey, G., Munguambe, D.M., Tharmavaram, M., Rawtani, D. & Agrawal, Y.K. (2017). Halloysite nanotubes – An efficient ‘nano-support’ for the immobilization of α -amylase. *App. Clay Sci.* 136, pp. 184–191. DOI: 10.1016/j.clay.2016.11.034
- Pandey, G., Tharmavaram, M., Khatri, N. & Rawtani, D. (2022). Mesoporous halloysite nanotubes as nano-support system for cationic dyes: An equilibrium, kinetic and thermodynamic study for latent fingerprinting. *Micropor. Mesopor. Mat.* 346, 112288. DOI: 10.1016/j.micromeso.2022.112288
- Pandey, G., Tharmavaram, M., Phadke, G., Rawtani, D., Ranjan, M. & Sooraj K.P. (2022). Silanized halloysite nanotubes as ‘nano-platform’ for the complexation and removal of Fe(II) and Fe(III) ions from aqueous environment. *Sep. Purif. Technol.* 29, 121141. DOI: 10.1016/j.seppur.2022.121141
- Park, Y., Ayoko, G.A., Kurdi, R., Horváth, E., Kristóf, J. & Frost, R.L. (2013). Adsorption of phenolic compounds by organoclays: Implications for the removal of organic pollutants from aqueous media. *J. Colloid Interf. Sci.* 406, 196. DOI: 10.1016/j.jcis.2013.05.027
- Pasbakhsh, P., Churchman, G.J. & Keeling, J.L. (2013). Characterisation of properties of various halloysites relevant to their use as nanotubes and microfibre fillers. *Appl. Clay Sci.* 74, 47. DOI: 10.1016/j.clay.2012.06.014
- Paul, D.R., Zeng, Q.H., Yu, A.B. & Lu, G.Q. (2005). The interlayer swelling and molecular packing in organoclays. *J. Colloid Interface Sci.* 292, pp. 462–468. DOI: 10.1016/j.jcis.2005.06.024
- Qiu, X., Li, N., Ma, X., Yang, S., Xu, Q., Li, H. & Lu, J. (2014). Facile preparation of acrylic ester-based crosslinked resin and its adsorption of phenol at high concentration. *J. Environ. Chem. Eng.* 2, 745. DOI: 10.1016/j.jece.2013.11.016
- Raczyńska-Żak, M. PhD Thesis, supervisor P. Słomkiewicz, Kielce, Poland, 2018
- Rawajfih, Z. & Nsour, N. (2006). Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite. *J. Colloid Interface Sci.* 298, pp. 39–49. DOI: 10.1016/j.jcis.2005.11.063
- Sarkar, B., Xi, Y., Megharaj, M., Krishnamurti, G.S.M., Rajarathnam, D. & Naidu, R. (2010). Remediation of hexavalent chromium through adsorption by bentonite based Arquad® 2HT-75 organoclays. *J. Hazard. Mater.* 183, 87. DOI: 10.1016/j.jhazmat.2010.06.110
- Setter, O.P., Dahan, L., Hamad, H.A. & Segal, E. (2022). Acid-etched Halloysite nanotubes as superior carriers for ciprofloxacin. *App. Clay Sci.* 228, 106629. DOI: 10.1016/j.clay.2022.106629
- Sinha, B., Ghosh, U.K., Pradhan, N.C. & Adhikari, B. (2006). Separation of phenol from aqueous solution by membrane pervaporation using modified polyurethaneurea membranes. *J. Appl. Polym. Sci.* 10, pp. 1857–1865. DOI: 10.1002/app.23566
- Słomkiewicz, P., Szczepanik, B. & Czaplicka, M. (2020). Adsorption of Phenol and Chlorophenols by HDTMA Modified Halloysite Nanotubes. *Materials* 13, 3309. DOI: 10.3390/ma13153309
- Smith, J.A. & Galan, A. (1995). Sorption of nonionic organic contaminants to single and dual organic cation bentonites from water. *Environ. Sci. Technol.* 29, pp. 685–692. DOI: 10.1021/es00003a016
- Su, J., Lin, H.-F., Wang, Q.-P., Xie, Z.M. & Chen, Z.L. (2011). Adsorption of phenol from aqueous solutions by organomontmorillonite. *Desalination*, 269, 163. DOI: 10.1016/j.desal.2010.10.056
- Tamijani, A.A., Salam, A. & de Lara-Castells, M.P. (2016). Adsorption of Noble-Gas Atoms on the TiO₂(110) Surface: An Ab Initio-Assisted Study with van der Waals-Corrected DFT. *J. Phys. Chem. C* 120, 18126. DOI: 10.1021/acs.jpcc.6b05949
- Tana, D., Yuan, P., Liu, D. & Du, P. Modifications of Halloysite, Chapter 8 in *Developments in Clay Science*, December 2016.
- Tharmavaram, M., Pandey, G. & Rawtani, D. (2018). Surface modified halloysite nanotubes: A flexible interface for biological, environmental and catalytic applications. *Adv. Colloid Interface Sci.* 261, 82–101. DOI: 10.1016/j.cis.2018.09.001
- Tharmavaram, M., Pandey, G., Bhatt, P., Prajapati, P., Rawtani, D., Sooraj, K.P. & Ranjan, M. (2021). Chitosan functionalized Halloysite Nanotubes as a receptive surface for laccase and copper to perform degradation of chlorpyrifos in aqueous environment. *Int. J. Biol. Macromol.* 191, pp. 1046–1055. DOI: 10.1016/j.ijbiomac.2021.09.098
- Tharmavaram, M., Pandey, G., Khatri, N. & Rawtani, D. (2023). L-arginine-grafted halloysite nanotubes as a sustainable excipient for antifouling composite coating. *Mater. Chem. Phys.* 293, 126937. DOI: 10.1016/j.matchemphys.2022.126937
- Wu, J. & Yu, H.Q. (2006). Biosorption of 2,4-dichlorophenol from aqueous solution by *Phanerochaete chrysosporium* biomass: isotherms, kinetics and thermodynamics. *J. Hazard. Mater.* 137, pp. 498–508. DOI: 10.1016/j.jhazmat.2006.02.026
- Xie, J., Meng, W., Wu, D., Zhang, Z. & Kong, H. (2012). Removal of organic pollutants by surfactant modified zeolite: Comparison between ionizable phenolic compounds and non-ionizable organic compounds. *J. Hazard. Mater.* 231, 57. DOI: 10.1016/j.jhazmat.2012.06.035
- Yang, Q., Gao, M. & Zang, W. (2017). Comparative study of 2,4,6-trichlorophenol adsorption by montmorillonites functionalized with surfactants differing in the number of head group and alkyl chain. *Colloid. Surf. Physicochem. Eng. Asp.* 520, 805. DOI: 10.1016/j.colsurfa.2017.02.057

- Yousef, R.I. & El-Eswed B. (2009). The effect of pH on the adsorption of phenol and chlorophenols onto natural zeolite. *Colloid Surf. A* 334, pp. 92–99. DOI: 10.1016/j.colsurfa.2008.10.004
- Yu, J.-Y., Shin, M.Y., Noh, J.-H. & Seo, J.J. (2004). Adsorption of phenol and chlorophenols on Ca-montmorillonite in aqueous. *Geosci. J.* 8, 185. DOI: 10.1007/BF02910194
- Yuan, G. (2004). Natural and modified nanomaterials as sorbents of environmental contaminants. *J. Environ. Sci. Health. Part A* 39, pp. 2661–2670. DOI: 10.1081/ESE-200027022
- Zhang, L., Zhang, B., Wu, T., Sun, D. & Li, Y. (2015). Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution. *Colloids Surf. A Physicochem. Eng. Asp.* 484, 118. DOI: 10.1016/j.colsurfa.2015.07.055
- Zhou, Q., Frost, R.L., He, H., Xi, Y. & Zbik, M. (2007). TEM, XRD, and thermal stability of adsorbed paranitrophenol on DDOAB organoclay. *J. Colloid Interface Sci.* 311, pp. 24–37. DOI: 10.1016/j.jcis.2007.02.039