

Adsorptive removal of chloroxylenol and chlorophene from aqueous solutions using carbon-halloysite nanocomposites obtained from corrugated cardboard as a carbon precursor

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Received 28 September 2022; Accepted 10 December 2022

ABSTRACT

The adsorption of chloroxylenol and chlorophene on new carbon-halloysite nanocomposites and non-modified halloysite were investigated. The article describes the method of obtaining carbon-halloysite nanocomposites HC1-15, HC1-24, HC2-15, and HC2-24 from corrugated cardboard as a carbon precursor and halloysite as a template (cardboard: halloysite mass ratio 1:1 and 1:2, time of mixing: 15 min and 24 h). Morphological and structural properties of the obtained nanocomposites were investigated by scanning electron microscopy, X-ray diffraction, wavelength dispersive X-ray fluorescence (WDXRF), Fourier-transform infrared spectroscopy (FT-IR), and low-temperature nitrogen adsorption methods. Energy-dispersive X-ray spectroscopy, WDXRF analysis and FT-IR spectra confirmed the presence of carbon on the surface of halloysite. The value of Brunauer–Emmett–Teller specific surface area (S_{BET}) increased for the composites in comparison to unmodified halloysite (51.93 m²/g) reaching the value of 114.50 m²/g for the HC2-24 composite. Pseudo-second-order and intraparticle diffusion models described sufficiently adsorption mechanisms and the adsorption data were represented by the Langmuir adsorption model. Adsorption properties of all the obtained nanocomposites were more satisfactory for both adsorbates compared to the non-modified halloysite. Removal efficiency was the highest for adsorption of both compounds on the HC2-24 composite. The maximum adsorption capacity of HC2-24 composite according to Langmuir isotherm was 14.48 for chloroxylenol and 71.43 mg/g for chlorophene. The adsorption mechanism can be explained mainly by electrostatic interactions between the ionized forms of the adsorbate molecules and the surface of the adsorbent. Based on the basic surface character of the obtained carbon-halloysite nanocomposites, HC2-24 composite could be suggested as a potential adsorbent to eliminate the pollutants with acidic character, including phenol derivatives from water.

Keywords: Cardboard; Carbon precursor; Carbon-halloysite nanocomposites; Chloroxylenol; Chlorophene; Adsorption

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1. Introduction

Environmental micro-pollutants (emerging contaminants) include various compounds, among others: pharmaceuticals, personal care products, and disinfectants. They are not systematically monitored. This can cause negative effects in the environment, especially in the aquatic environment due to its bioaccumulation and creating microbial drug resistance [1]. One group of popular disinfectants (broad-spectrum antibacterial agents) are chlorinated phenol derivatives, which include: triclosan, triclocarban, chloroxylenol (4-chloro-3,5-dimethylphenol), and chlorophene (2-benzyl-4-chlorophenol). These compounds are extensively used in personal care products (PPCs) such as hand soaps, shampoos, shower gels, hand sanitizers, and various cosmetics. The ban of triclosan and triclocarban in personal care products in many countries (except for China) caused an increasing use of chloroxylenol and chlorophene [2]. Initially chloroxylenol was considered safe and non-toxic. However, it is incessantly released into the aquatic environment due to increasing human consumption. Their potential toxicity to aquatic organisms has raised concerns [2]. Moreover, the coronavirus disease 2019 (COVID-2019) pandemic led to a substantial increase in the consumption of antibacterial products, which results in an abundance of the above-mentioned substances in the aquatic environment. In connection with this, removing the residues of such compounds from the environment becomes a major problem. Various methods have been used to remove PPCPs including coagulation, biological methods [3], advanced oxidation, reverse osmosis, and adsorption [4]. Adsorption has many advantages, for example the ease of operation, lack of secondary contaminants, high efficiency, and low-cost [5]. Amongst different adsorbents used for removing PPCPs, there are clay minerals, resins, zeolite [4], cyclodextrin-based adsorbents [5,6], metal-organic frameworks (MOFs) [7], and carbon-based adsorbents [8–14]. Carbon-based materials are most often used due to their oxygen-containing functional groups, large specific surface area, and high efficiency [13]. Despite their wide use in adsorption, they also have disadvantages – high-cost and often a complicated preparation procedure reference [15]. Therefore, there is a growing interest in “low-cost” materials, mainly of natural origin like clay minerals. Among them, halloysite is distinguished as a mineral with a natural nanotube structure, non-toxic, with a well-developed specific surface and porosity, a high chemical and thermal resistance [16,17]. Carbon-halloysite nanocomposites combine the advantages of both materials and show high adsorption potential in relation to organic environmental pollutants. Numerous materials containing carbon are used as the precursors of activated carbon, for example: wood, peat, sawdust, straw, corn cobs, and coconut shells [18–20]. Economic and ecological aspects have an influence on growing interest in the use of plant and industrial waste as carbon precursors. Cardboard belongs to the common municipal solid waste that is mainly used for packing and packaging purposes. The consumption of such packaging has grown steadily in recent times, driven by growing mail order sales during the pandemic time. Recycling of cardboard is important because it causes less

impact on the environment. Activated carbon produced from corrugated cardboard was used as adsorbent of NO₂, CO₂ from air, and oxytetracycline from water [21–23].

In our previous works we presented excellent adsorption properties of carbon-halloysite nanocomposites obtained through liquid phase impregnation and carbonization using saccharose as the carbon precursor for removing ketoprofen, naproxen, diclofenac, and paracetamol from water [24,25]. As a continuation of our interest, the aim of this study was to obtain carbon-halloysite adsorbent from waste difficult to process, that is, corrugated cardboard as a carbon precursor and to determine its ability for removing such phenolic compounds as chloroxylenol and chlorophene from water.

2. Experimental

2.1. Materials and reagents

Halloysite was obtained from strip mine “Dunino”, Intermark Company, Legnica, Poland. Commercial activated carbon AG-5 was purchased from Gryfskand Company, Gryfino, Poland. Chloroxylenol and chlorophene was acquired from Merck KGaA, Darmstadt, Germany, deionized water was used through all experiments. The selected physicochemical properties of the adsorbates are presented in Table 1.

2.2. Preparation of adsorbents

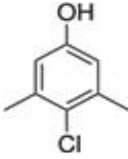
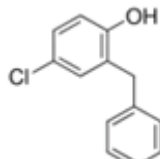
Halloysite (H) was pre-purified as described in ref. [24]. Particle fractions of 0.2–0.32 mm were used to prepare carbon-halloysite composites. Corrugated cardboard was shredded into small pieces and blended together with deionized water. Excess water was filtered off under reduced pressure. The wet cardboard together with deionized water was then homogenized until a homogeneous suspension was obtained and filtered again. Halloysite and deionized water were added to the cardboard and mixed for 15 min (or 24 h) in a shaker. After filtrating, the mixture was transferred to a quartz vessel in a muffle furnace and carbonized at 800°C for 8 h with a heating rate of 5°C/min under N₂ atmosphere. Finally, the black product was milled and sieved. The obtained carbon-halloysite composites were named as follows: HC1-15 (mass ratio halloysite/cardboard 1:1, mixing time: 15 min), HC1-24 (mass ratio halloysite/cardboard 1:1, mixing time: 24 h), HC2-15 (mass ratio halloysite/cardboard 1:2, mixing time: 15 min), and HC2-24 (mass ratio halloysite/cardboard 1:2, mixing time: 24 h).

The corrugated cardboard was also carbonized under the same conditions as the composites: 800°C for 8 h with a heating rate of 5°C/min under N₂ atmosphere.

2.3. Adsorbent characterization

Textural structure of the obtained composites was characterized using the methods of low-temperature nitrogen adsorption-desorption isotherms on a volumetric adsorption analyzer ASAP 2020 by Micromeritics (Norcross, GA, USA) (Structural Research Laboratory of Jan Kochanowski

Table 1
Chemical structures and selected properties of the adsorbates [26]

Compound	Chloroxylenol	Chlorophene
Molecular structure		
IUPAC name	4-chloro-3,5-dimethylphenol	2-benzyl-4-chlorophenol
Chemical formula	C ₈ H ₉ ClO	C ₆ H ₅ CH ₂ C ₆ H ₃ (Cl)OH
Molecular weight	156.61 g/mol	218.68 g/mol
Water solubility	300 mg/dm ³ at 20°C	149 mg/dm ³ at 25°C
pK _a *	9.7	9.81
logK _{ow} **	3.27	4.47

*pK_a – -logK_a (dissociation constant at 20°C), **K_{ow} – octanol-water partition coefficient

University in Kielce). Details of measurements are described by the study of Szczepanik et al. [24].

Scanning electron microscopy (SEM) images of the studied materials were obtained by scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) measurements carried out on a TESCAN VEGA3 microscope with LaB6 filament as electron source. Accelerating voltage was set to 5 kV in order to avoid excessive sample charring. Samples were put on standard SEM studs covered with an adhesive copper tape. In order to carry out elemental analysis, an Oxford Instruments X-act EDS detector was used. Additional high resolution SEM images were recorded after sputtering gold on the sample and using 30 kV accelerating voltage. Infrared spectra were measured using a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer with a smart endurance single bounce diamond, attenuated total reflection (ATR) cell. Spectra in the 4,000–650 cm⁻¹ range were obtained by the co-addition of 40 scans with a resolution of 4 cm⁻¹. X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer, equipped with a copper-based anode (Cu-Kα, λ = 0.154059 nm). Instrument settings were 40 mA and 45 kV and the step of scans and counting time were 0.02 and 2 s per step, respectively. Elemental composition measurements of the composites were carried out with wavelength dispersive X-ray fluorescence (WDXRF) technique using an Axios Spectrometer (PANalytical) equipped with an Rh-anode X-ray tube with maximum power of 2.4 kW. The wavelength dispersive system of the Axios Spectrometer utilizes five crystals (LiF200, Ge111, PE002, PX1, and LiF220) which are automatically selected during the measurement, depending on the analyzed element. All the measurements were performed in vacuum. A quantitative analysis of the spectra was performed with the PANalytical standardless analysis package Omnian. The detection limit of the method used was on the level of about 10 μg/g.

Boehm's titration method was applied to identify functional groups on composite surfaces [24,27]. The pH value at point of zero charge (pH_{pzc}) for all obtained materials was determined by mass titration [24,28].

2.4. Adsorption measurements

Batch adsorption experiments were performed in a 100 cm³ Erlenmeyer's flask containing a composite and the adsorbate solution, which were put into the incubator for 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, 300, 360, and 1,440 min. The temperature during measurement was 25°C and the mixing rate equaled 120 rpm. Next, the adsorbent was separated from the solution with a cup-type centrifuge.

Concentrations of chloroxylenol and chlorophene solutions were determined with the spectrophotometric method (UV Shimadzu UV-1800 spectrophotometer). The wavelengths used to determine solution concentrations were as follows: 242.5 nm for chloroxylenol and 248 nm for chlorophene.

The removal efficiency (*R*, %) and the adsorption capacity (*q_e*, mg/g) were calculated using Eqs. (1) and (2):

$$R(\%) = \frac{C_0 - C_e}{C_0} 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where: *C₀*, *C_e* (mg/dm³) – initial and equilibrium concentrations of adsorbate solutions, *V* (dm³) – the volume of the adsorbate solution, and *m* (g) – the mass of adsorbent.

3. Results and discussion

3.1. Characteristics of adsorbents

Structural parameters were calculated from the adsorption–desorption N₂ isotherms. The values of Brunauer–Emmett–Teller (BET) specific surface area (*S_{BET}*), total pore volume (*V_t*), volume of mesopores (*V_{me}*), micropores (*V_{mi}*), and mesoporosity (%) are presented in Table 2. *S_{BET}* increased for the composites in comparison to unmodified halloysite (H) (51.93 m²/g), which is a different value than in the case of halloysite/carbon composites and was highest

for the HC2-24 sample (114.50 m²/g). Carbon deposition on the halloysite surface caused a decrease of the total pore volume and volume of mesopores, while the volume of micropores increased for composite samples, especially for HC2-15 and HC2-24 against the H sample. S_{BET} , V_{me} , and V_{mi} were the highest for the carbonized cardboard compared to the composites, when the degree of mesoporosity is lower than for the composites.

SEM images of the H sample and composites samples are presented in Fig. 1. In sample H, one can see the tubular, blocky, and platy particles. In the case of composite samples, numerous carbon particles with irregular shapes are deposited on the halloysite surface. The presence of carbon in the obtained composites is confirmed with the EDS analysis (Table 3). Carbon content increased from sample HC1-24 (15.15%) up to sample HC2-15 (27.96%).

Elemental composition of cardboard and halloysite-carbon composites was investigated using the wavelength-dispersive X-ray fluorescence method. The results are presented in Table 4. Main elements present in composite samples are typical for halloysite [29] with the exception of calcium. This element is derived from cardboard and remained in composite samples after pyrolysis.

Diffraction patterns of halloysite (H), halloysite heated at temperature 800°C (H800) and HC1-24, HC2-24 samples of composites are compared in Fig. 2. The main reflections of the halloysite, kaolinite, and hematite are identified for the H sample [29]. The pattern of H800 sample shows broad diffraction maxima owing to dehydroxylation and the formation of an amorphous product – meta-halloysite [30]. The diffractograms of HC1-24 and HC2-24 samples (Fig. 2b) with the main reflection at $2\theta = 22^\circ$ and very weak at 43° are very similar to diffraction patterns of amorphous carbons produced using saccharose [24]. The reflections at 25° and 48° confirm the presence of carbon crystalline structure [24]. Additionally, the reflections at 32° , 37.5° , 55° can be assigned to calcium oxide, and at 29° and 34° to calcium hydroxide according to analysis performed with the HighScore 3.0e program using PDF-2 Release 2019 Database of the International Centre for Diffraction Data.

ATR Fourier-transform infrared spectroscopy (FT-IR) spectra of halloysite (H) and composites HC1-15, HC1-24, HC2-15, and HC2-24 are presented in Fig. 3. The FT-IR spectrum of the H sample shows characteristic bands for the kaolin-group minerals [30–32]. In the case of all composites, the bands in the range 3,700–3,600 cm⁻¹ assigned the

vibrations of the OH groups are not observed, and the intensity of the bands in the range of 1,250–650 cm⁻¹ decreases significantly. These changes suggest the change on the surface of halloysite caused by the presence of carbon on this surface.

Boehm analysis carried out for the composites showed the presence of the functional groups on the carbon surface collected in Table 5. The amount of basic groups was considerably higher than that of acidic groups on the surface of all samples. The point of zero change (pH_{pzc}) of the HC-24 sample equaled 10.04 (Fig. 4).

3.2. Adsorption experiments

Removal efficiencies of chloroxylenol and chlorophene from aqueous solutions using H and HC1-15, HC1-24, HC2-15, HC2-24 composites, carbonized cardboard, and commercial activated carbon AG-5 as adsorbents are showed in Fig. 5. The results showed that composite HC2-24 was better adsorbent of both compounds than other materials. For further research, we chose an adsorbent that showed best possible adsorption abilities – HC2-24 composite.

3.2.1. Effect of adsorbent dose

The influence of HC2-24 adsorbent dose on the adsorption of chloroxylenol and chlorophene was studied. Solutions of adsorbates of 20 mg/dm³ and an adsorbent dose from 0.05 to 0.3 g were applied. The results are presented in Fig. 6. Removal efficiency of both adsorbates was high in whole range of mass used, reaching values above 90% for mass of 0.3 g. The adsorbent mass of 0.2 g for chloroxylenol and 0.05 g for chlorophene were selected for further experiments.

3.2.2. Reusability of adsorbent HC2-24

The ability to reuse the HC2-24 composite was studied for 5 cycles of use (Fig. 7). The adsorption properties of HC2-24 toward chloroxylenol were weakened with the increasing reuse cycles, which indicated that the chloroxylenol molecules could not be completely eluted with deionized water rinsing treatment after each regeneration. The removal efficiency decreased more slowly in the case of chlorophene reaching the value of about 90% after the fifth cycle. Compared with the regeneration methods of activated carbons [33,34] the milder regeneration conditions are beneficial to the reusability of adsorbent.

Table 2
Structural parameters of carbon-halloysite composites

Adsorbent	S_{BET} (m ² /g)	V_t (cm ³ /g)	V_{mi} (cm ³ /g)	V_{me} (cm ³ /g)	Mesoporosity (%)
H	51.93	0.2352	0.0019	0.2333	99
HC1-15	82.44	0.2035	0.0194	0.1841	90
HC1-24	78.47	0.2002	0.0218	0.1784	89
HC2-15	107.85	0.1985	0.0300	0.1685	85
HC2-24	114.50	0.2028	0.0305	0.1723	85
Cardboard	238.87	0.1691	0.0862	0.0829	49

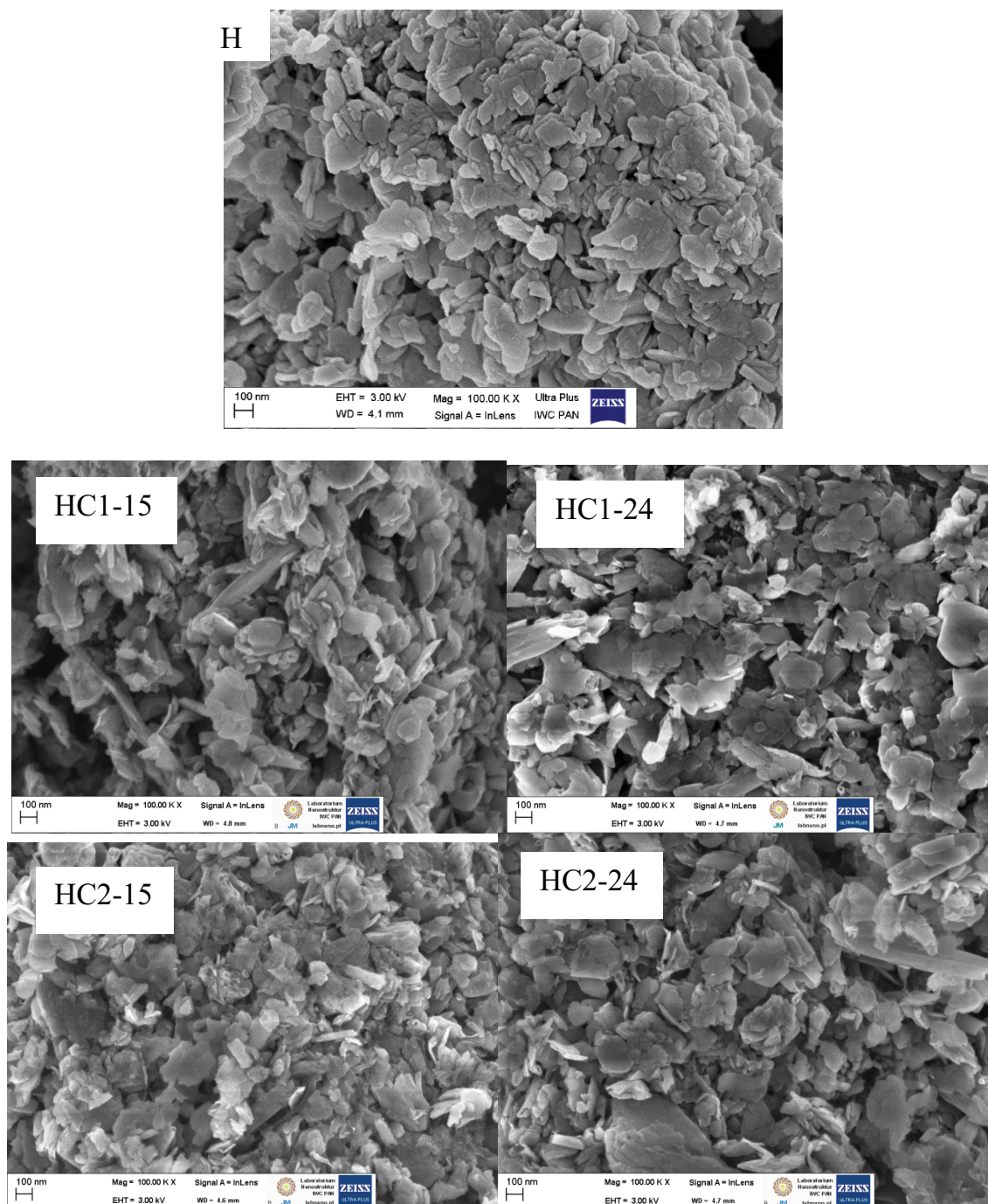


Fig. 1. SEM images of H, HC1-15, HC1-24, HC2-15, and HC2-24 samples.

3.2.3. Kinetic models

The pseudo-first-order, pseudo-second-order kinetic models [35,36], and intraparticle diffusion models [37] were used for the adsorption of chloroxylenol and chlorophene on the HC2-24 adsorbent. The pseudo-first-order and pseudo-second-order rate constants, k_1 and k_2 , and correlation coefficients (R^2) are given in Table 6. Correlation coefficients indicate best possible fit of experimental data to the

pseudo-second-order kinetic model for both adsorbates, suggesting the electrochemical interactions between adsorbate and adsorbent surface. The values of pseudo-second-order rate constant, k_2 , were much higher for chlorophene than for chloroxylenol.

The Weber–Morris diffusion model was used in order to investigate adsorption mechanism of chloroxylenol and chlorophene on the HC2-24 adsorbent. The values of k_{d1} , k_{d2} and c_1 , c_2 determined from the slopes and intercepts of the

first and second linear part of graph presented in Fig. 8 are given in Table 7. The values k_{d1} and k_{d2} decreased and were much lower for chloroxenol compared to chlorophene. The dependency q_t vs. $t_{1/2}$ multi-linear plot shows that at least two steps are involved in the adsorption process. The first faster step was attributed to the diffusion of adsorbate molecules to adsorbent outer surface, while the second one corresponds to slower adsorption, where intraparticle diffusion affects the adsorption process [38].

Table 3
Elemental composition of halloysite (H) and halloysite-carbon composites obtained by EDS

Composite	Content (%)			
	O	Si	Al	C
H	52.71	22.89	21.12	–
HC1-15	40.54	15.42	14.94	23.28
HC1-24	43.85	18.15	16.36	15.15
HC2-15	42.02	12.18	11.30	27.96
HC2-24	41.50	16.38	15.36	20.12

3.2.4. Adsorption isotherm

Fitting experimental adsorption data to the most commonly used adsorption models was checked using non-linear regression (the Levenberg–Marquardt least squares method with the OriginLab software). The results did not completely correlate with the Temkin, Dubinin–Radushkevich, Sips, and Freundlich models. The best

Table 4
Chemical composition (main elements, wt.%) of cardboard, HC1-15 and HC2-15 samples obtained with the WDXRF analysis

Sample element	Cardboard	HC1-15	HC2-15
O	–	49.971	55.791
Na	0.159	0.068	0.094
Mg	0.220	0.195	0.205
Al	1.549	20.586	16.941
Si	1.886	20.664	17.312
Ca	8.493	4.980	6.399
Fe	0.182	2.028	1.656
Ti	0.078	0.830	0.735

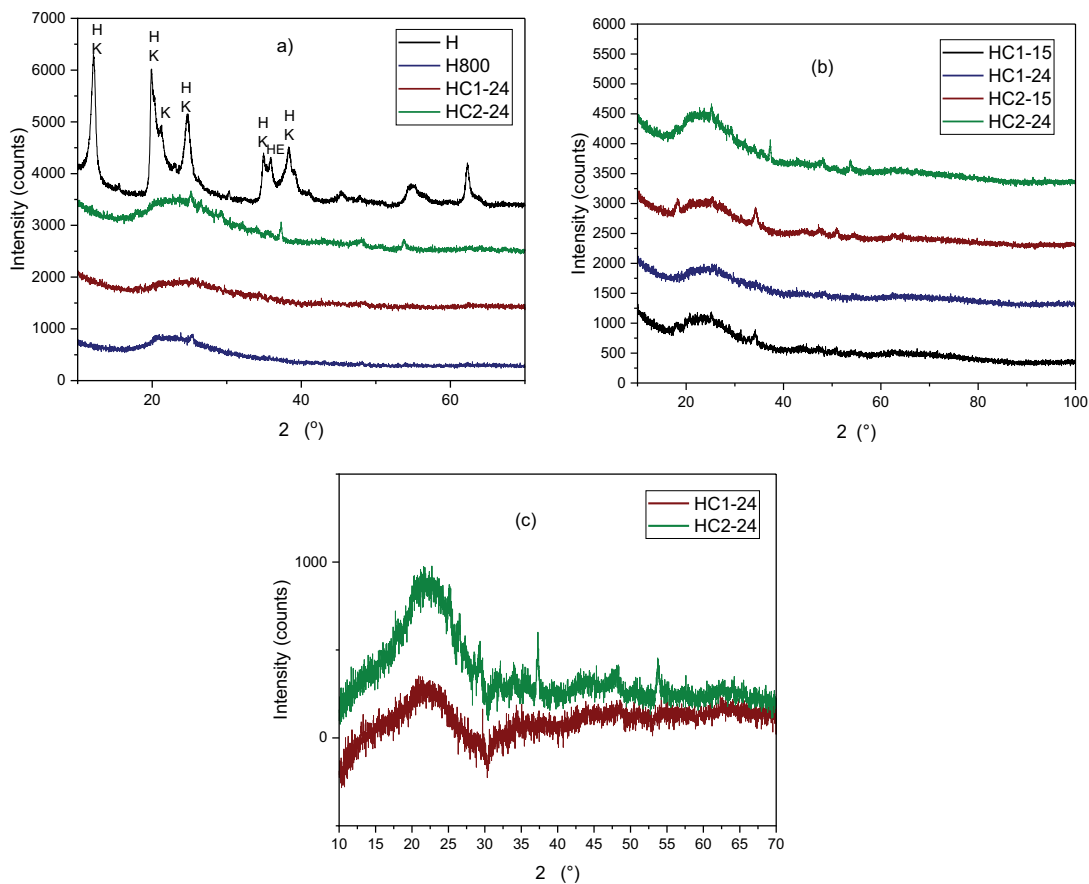


Fig. 2. Diffraction patterns of samples: (a) H, H800, HC1-24, and HC2-24, (b) HC1-15, HC1-24, HC2-15, and HC2-24. In the diffractogram of H sample, the following peaks of the following minerals were identified: H – halloysite; K – kaolinite; He – hematite. (c) Diffractograms of HC1-24 and HC2-24 samples obtained after subtracting the diffractogram of the H800 sample from the original diffractogram of these samples.

correlation of experimental data was obtained for the Langmuir adsorption model as regards both adsorbates. The Langmuir equation [Eq. (3)] parameters, as well as correlation coefficients R^2 for the adsorption of chloroxylenol and chlorophene on the HC2-24 adsorbent are collected in Table 8. Adsorption capacity for chlorophene was three times higher in comparison to chloroxylenol.

$$q_e = q_m = \frac{K_L C_e}{1 + K_L C_e} \quad (3)$$

where: c_e – equilibrium concentration of a solute in an aqueous solution (mg/dm³); q_e – the amount of a solute adsorbed per gram of the adsorbent at equilibrium (mg/g), q_m – maximum monolayer coverage capacity (mg/g); K_L – adsorption equilibrium constant (dm³/mg).

The pH value of the solution is an important parameter affecting phenol derivatives adsorption, because phenols can

exist in non-ionized and ionized forms in aqueous solutions. The amount of these forms depends on the pH value of the solution, and their interaction with adsorbent surface may influence removal efficiency from water.

The HC2-24 composite obtained from corrugated cardboard as carbon precursor was placed in deionized water for 24 h to obtain a constant pH (value of 9.3). An increase in pH is most probably due to the presence of calcium oxide and hydroxide in the resulting composites. These compounds were formed as a result of decomposition mineral various fillers containing such elements as: Ca, Si, Al, Mg, and Na used in producing cardboard. After 24 h of contact of the composites with the adsorbates, the pH value increases by about 0.2 units.

Based on pK_a values of chloroxylenol and chlorophene (Table 1), and using the Henderson–Hasselbalch equation, the amount of ionized and neutral forms of their molecules was calculated for this range of pH values. The ionization degree was 40%–60% for chloroxylenol and 30%–50% for

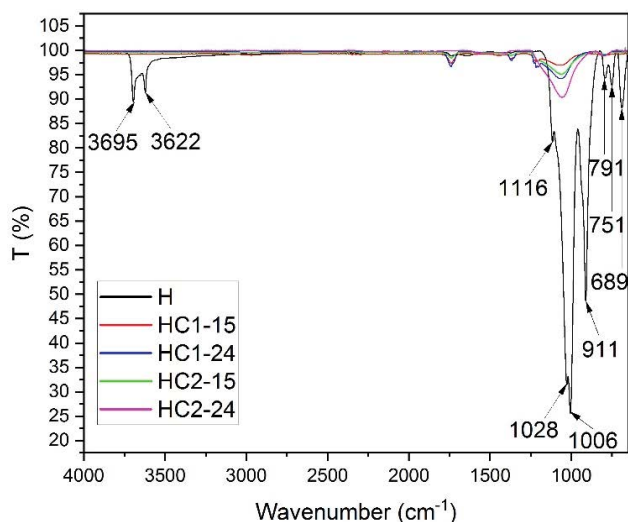


Fig. 3. FT-IR spectra of H, HC1-15, HC1-24, HC2-15, and HC2-24 samples in the 4,000–650 cm⁻¹ region.

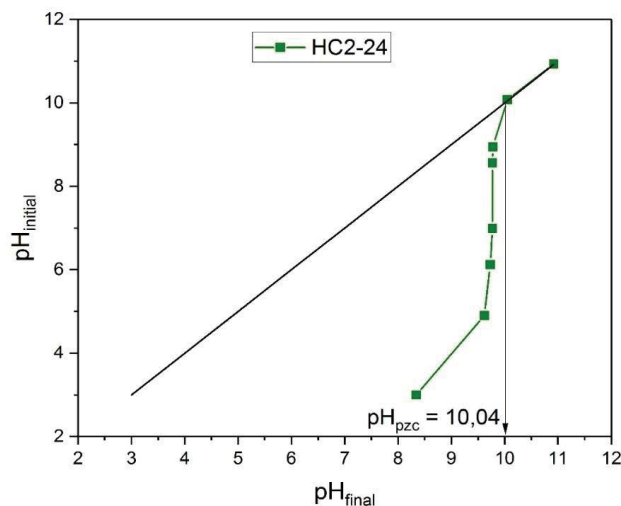


Fig. 4. Determination of $pH_{i,pzc}$ value for HC2-24 adsorbent.

Table 5
Functional groups identified on the studied materials

Functional groups	HC1-15 (mmol/g)	HC1-24 (mmol/g)	HC2-15 (mmol/g)	HC2-24 (mmol/g)
Basic	1.911	1.630	2.740	2.114
Carboxylic	–	–	0.062	–
Lactonic	0.043	0.044	–	0.043
Carbonyl	1.430	1.122	1.324	1.316

Table 6
Kinetic parameters of chloroxylenol and chlorophene adsorption on HC2-24 adsorbent

Adsorbate	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k_1 (min ⁻¹)	R^2	Reduced Chi-Sqr	k_2 (g/mg·min)	R^2	Reduced Chi-Sqr
Chloroxylenol	0.004	0.5621	2.78	0.085	0.9923	0.945
Chlorophene	0.023	0.7143	5.67	0.338	0.9934	0.748

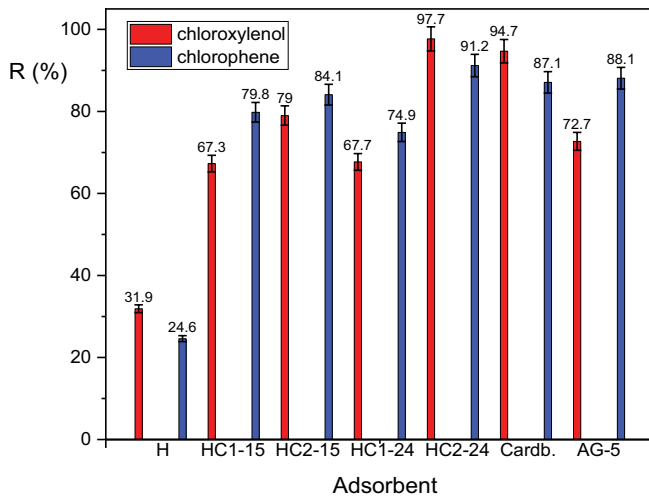


Fig. 5. Removal efficiency of chloroxylenol and chlorophene for halloysite (H) and HC1-15, HC1-24, HC2-15, HC2-24, carbonized cardboard, and commercial activated carbon AG-5 adsorbents (concentration of adsorbate solutions 20 mg/dm³, adsorbent mass: 0.2 g (chloroxylenol), 0.05 g (chlorophene), contact time: 24 h, and temperature: 25°C).

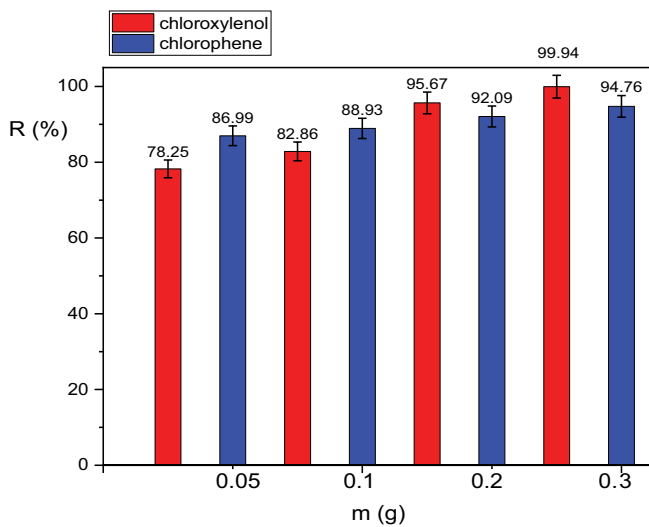


Fig. 6. Removal efficiency of chloroxylenol and chlorophene for different mass of HC2-24 adsorbent (concentration of adsorbate solutions: 20 mg/dm³, contact time: 24 h, temperature: 25°C).

chlorophene. Absorption spectra of chloroxylenol and chlorophene solution measured before and after various times of contact with the HC2-24 adsorbent (Fig. 9) confirmed the presence of anions in the solution for chloroxylenol. In the case of chlorophene the neutral and ionized forms coexist in the solution during the adsorption process.

The value of pH_{PZC} corresponds to the pH of the solution, when the net surface charge is neutral. At pH lower than the pH_{PZC} surface charge will be positive, whereas at a higher pH, it will be negative because of the deprotonation of functional groups present on the carbon surface [39]. The value of pH_{PZC} for the HC2-24 adsorbent equals 10.04, so below this

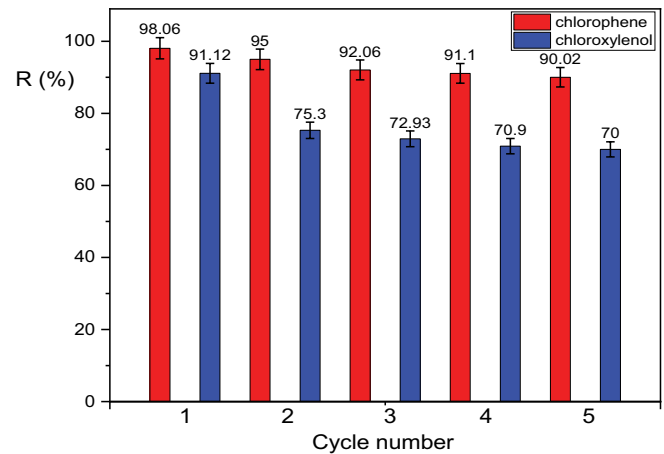


Fig. 7. Removal efficiency of chloroxylenol and chlorophene as a function of adsorption cyclic times (concentration of adsorbate solutions 20 mg/dm³, adsorbent HC2-24 mass: 0.2 g (chloroxylenol), 0.05 g (chlorophene), contact time: 24 h, temperature: 25°C).

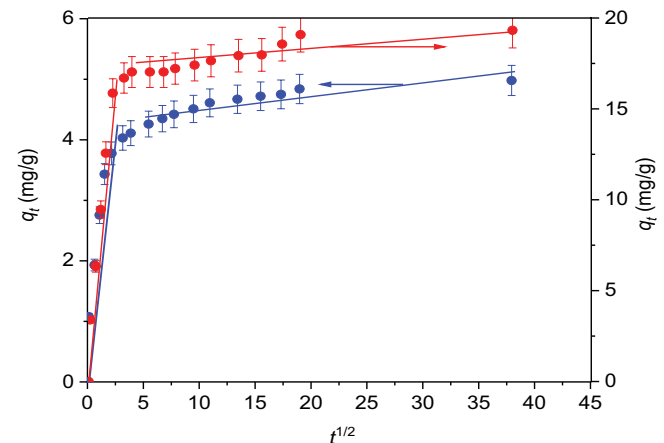


Fig. 8. Intraparticle diffusion of chloroxylenol and chlorophene on HC2-24 adsorbent. ● – chloroxylenol, ● – chlorophene.

value the surface is positively charged and the electrostatic interaction with anions of adsorbates are strong, resulting in higher uptake.

Taking into account the adsorption conditions ($pH > 9$), the values of pK_a for the adsorbates, and the pH_{PZC} of the adsorbent, the adsorption mechanism can be explained mainly by electrostatic interactions between the ionized forms of the adsorbate molecules and the surface of the adsorbent.

4. Conclusions

In this study, the carbon-halloysite nanocomposites were successfully prepared through carbonization in the absence of oxygen using the corrugated cardboard as the carbon precursor.

The removal efficiency of chloroxylenol and chlorophene was compared for halloysite, all composites, carbonized cardboard, and activated carbon AG-5. Removal efficiency was the highest for adsorption of both compounds

Table 7
Intraparticle diffusion model parameters

Adsorbate	k_{d1} (mg/g·min ^{1/2})	c_1 (mg/g)	R_1^2	Reduced Chi-Sqr	k_{d2} (mg/g·min ^{1/2})	c_2 (mg/g)	R_2^2	Reduced Chi-Sqr
Chloroxylenol	1.22	0.81	0.8963	0.270	0.02	4.24	0.8767	0.160
Chlorophene	5.49	1.43	0.9367	3.020	0.11	16.44	0.9161	0.128

Table 8
Langmuir (one-center) equations parameters and correlation coefficients R^2 and reduced Chi-Sqr for the adsorption of chloroxylenol and chlorophene on HC2-24 adsorbent

Isotherm	Parameters	Adsorbate	
		Chloroxylenol	Chlorophene
Langmuir (one-center)	K_L (dm ³ /mg)	0.51	0.80
	q_m (mg/g)	14.84	71.43
	R^2	0.999	0.996
	Reduced Chi-Sqr	2.451	2.31

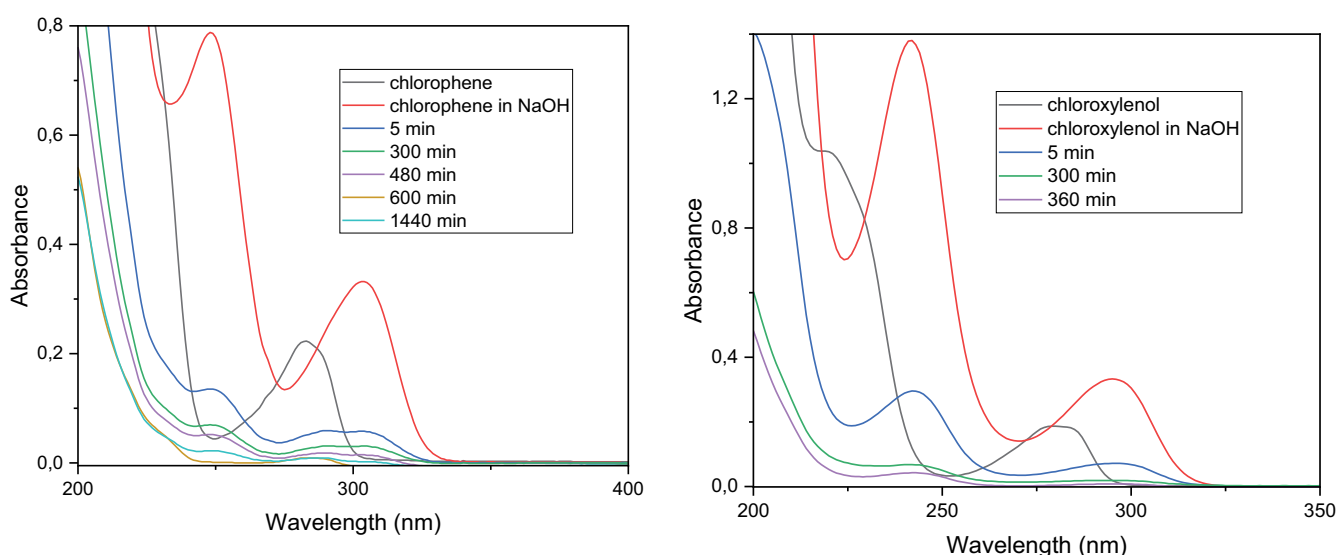


Fig. 9. Absorption spectra of chloroxylenol and chlorophene solution measured before and after various times of contact with HC2-24 adsorbent.

on the HC2-24 composite. Adsorption kinetics for both adsorbates on the HC2-24 composite can be described with the pseudo-second-order kinetic model. The Weber–Morris analysis confirmed multi-stage adsorption process, which proceeded in accordance with the Langmuir adsorption model. The comparison of pseudo-second-order rate constants and adsorption constants for both adsorbates show that chlorophene is a more efficient adsorbing material than chloroxylenol with respect to aqueous solutions on the HC2-24 composite. The maximum adsorption capacity of HC2-24 composite according to Langmuir isotherm was 14.48 for chloroxylenol and 71.43 mg/g for chlorophene. The value of $\log K_{ow}$ was equal 3.27 for chloroxylenol and 4.47 for chlorophene. It can be seen that the higher value of

the $\log K_{ow}$ the higher adsorption capacity. The adsorption mechanism can occur by electrostatic interactions between the ionized forms of the adsorbate molecules and the surface of the adsorbent.

Carbon materials have been widely applied as adsorbents, but some disadvantages restrict their feasible applications in practice, such as high costs or complex preparation process. Halloysite is a low-cost and environmentally-friendly nanomaterial which can be combined with different carbon precursors to obtain new adsorbent classes. It has been shown that using corrugated cardboard as carbon precursor during synthesis of new carbon-halloysite nanocomposites can give new materials showing interesting physicochemical and adsorptive properties.

Although the obtained materials show rather low specific surface area as compared to carbonaceous adsorbents, they exhibit basic surface character.

Therefore, they can function as attractive adsorbents for removing pollutants with acidic character, including phenol derivatives. This means that the newly synthesized nanocomposites have great potential for industrial removal applications.

Acknowledgements

Publication was financed within the framework of the Ministry of Science and Higher Education research project SMGR RN.20.271.665.

Laura Frydel acknowledges financial support through the project “AKCELERATOR ROZWOJU Uniwersytetu Jana Kochanowskiego w Kielcach” (Development Accelerator of the Jan Kochanowski University of Kielce), co-financed by the European Union under the European Social Fund, with no. POWR.03.05.00-00-Z212/18.

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