



# Adsorption Capacity of Smectite Clay and Its Thermal and Chemical Modification for Two Anionic Dyes: Comparative Study

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**Abstract** The present research evaluates the influence of modification of smectite clay (BC) on its adsorption capacity of anionic dyes from aqueous solutions. Thermal (BC 250), acidic (BC H<sub>2</sub>SO<sub>4</sub>), and alkaline (BC NaOH) modification of clay was carried out. The clays were characterized by X-ray powder diffraction, energy-dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy. Adsorption of dyes was investigated by batch experiments at room temperature (23 ± 2 °C), a wide range of initial dye concentrations (1–1000 mg/dm<sup>3</sup>), and an adsorbent dose of 50 g. All modifications increased the clay's adsorption capacity for Reactive Red 198, in the order BC H<sub>2</sub>SO<sub>4</sub> > BC NaOH > BC 250 > BC; it was 10.32, 5.06, 3.32, and 2.92 mg/g, respectively. Acid and thermal modification of the clay increased its adsorption capacity for Acid Red 18, in the series BC H<sub>2</sub>SO<sub>4</sub> > BC 250 > BC > BC NaOH; it was 3.07, 2.66, 2.16, and 1.28 mg/g, respectively. The experimental data were analyzed by Freundlich, Langmuir, Dubinin–Radushkevich, and Sips isotherms, using nonlinear regression. The experimental data best fitted the Sips isotherm. Taking into account the structure of the adsorbent and adsorbates and the results obtained, it can be concluded that the dyes were probably bound through chemisorption, by forming hydrogen bonds between Si–OH and Al–OH groups in the clay and –NH, –NH<sub>2</sub>, and –OH groups in the dyes. From the

results obtained, it can be concluded that smectite clay is a promising material for dye adsorption.

**Keywords** Adsorption · Clay · Anionic dyes · Isotherms

## 1 Introduction

Water is a unique substance without which life on Earth could not exist. One of the most serious aquatic environment problems in modern society is pollution of water by synthetic dyes (Malakootian et al. 2015; Banaei et al. 2017; Kyziol-Komosinska et al. 2018). Synthetic dyes are widely used in dyeing processes, especially in textile dyeing, tanning, paper, cosmetics, food, iron, steel, and plastics, etc. (Özcan et al. 2005; Errais et al. 2010; Nejib et al. 2015; Adeyemo et al. 2017; Chaari et al. 2019). Due to their chemical structure, dyes belong to groups such as azo, anthraquinone, oxazine, acridine, formazan, phthalocyanine, thiazine, triphenylmethane, triarylmethane, nitroso, and nitro compounds, etc., and due to their application to reactive, acidic, cationic, direct, vat, disperse, solvent, and sulfur groups. Azo compounds are the largest group of organic-synthetic dyes; they consist of a diazotized amine coupled to an amine or a phenol and contain one or more azo (–N=N) linkages (Forgacs et al. 2004; Ventura-Camargo and Marin-Morales 2013; Hai et al. 2015; Malakootian et al. 2015; Chaari et al. 2019; Mishra and Maiti 2019; Mishra et al. 2020). Among the azo dyes, the most commonly used in the textile industry are reactive dyes. Due to their high water

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solubility and low degradability, reactive dyes are one of the most problematic pollutants found in wastewater from the textile industry. Reactive dyes are hydrophilic and therefore have little tendency to adsorption in biological biomass processing methods. Furthermore, these dyes have a high molecular weight, have aromatic rings, and are toxic to living organisms. Moreover, they are often stable, resistant to degradation, toxic, carcinogenic, and mutagenic. These dyes have a complex chemical structure, which can cause serious health problems such as allergies and dermatological diseases (Aksakal and Uzun 2010; Gao et al. 2013; Malakootian et al. 2015; Banaei et al. 2017). It is therefore necessary to effectively remove reactive dyes from wastewater before discharge into the sewerage system and the environment.

Many methods are known for removing dyes from wastewater from the textile industry, such as membrane filtration, ion exchange, electrochemical techniques, coagulation and flocculation, reverse osmosis, chemical oxidation, ozonation, biological treatment including activated sludge, and bacterial action (Robinson et al. 2001; Saffaj et al. 2004; Kim et al. 2005; Raghu et al. 2009; Szygula et al. 2009; Labanda et al. 2011; Gadekar and Ahamed 2015; Hassan and Carr 2018; Mishra and Maiti 2020). Among these methods, adsorption is one of the most effective for removing dyes from wastewater (Huang et al. 2007; Aguiar et al. 2017; Kausar et al. 2018). This method is characterized by high efficiency, simplicity of construction, ease of use, and flexibility, and—very importantly—compared to other methods is economical. The best known and most commonly used adsorbent is activated carbon, which has a high adsorption capacity. However, the main disadvantage of using activated carbon as a sorbent is its high cost (Jain et al. 2003; Kyziol-Komosinska et al. 2018). There is a need to search for alternative, relatively cheaper adsorbents that can be used to control water pollution. In recent years, many studies have been conducted on the adsorption capacity of materials in relation to organic pollutants, such as natural, waste, and synthetic materials (Tanyildizi 2011; Bharathi and Ramesh 2013; Vieira et al. 2014; Bello et al. 2015; Nejib et al. 2015; Amaral et al. 2016; Dotto et al. 2016; Mirzaei et al. 2016; Franciski et al. 2018; Dzieniszewska et al. 2019; Mishra et al. 2021). Among these, clay minerals deserve particular attention due to their easy availability, non-toxicity, large surface area, high swelling capacity, high cation capacity, and the presence of several types of active sites on the surface. The most commonly used

clay minerals are kaolinite, illite, and smectite (Errais et al. 2011; Errais et al. 2012; Santos and Boaventura 2016; Ngulube et al. 2017; Gamoudi and Srasra 2019).

The best known and most commonly used industrial clay minerals are smectites. They are defined as the group of phyllosilicates with a layer charge of between 0.4 and 1.2  $e^-$  per unit cell, arising from the non-equivalent substitution of central atoms in layers with lower valence cations (Madejova et al. 1998). The smectite group refers to a family of non-metallic clays primarily composed of hydrated sodium calcium aluminum silicate, a group of monoclinic clay-like minerals with the general formula  $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)4O_{10}(OH)_2 \cdot nH_2O$ , and chemically it is hydrated sodium calcium aluminum magnesium silicate hydroxide  $(Na, Ca)_x(Al, Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$  (Kausar et al. 2018). The 2:1 structure of smectites is formed by two tetrahedral sheets linked with an octahedral sheet. The tetrahedral sheets are built of  $T_2O_5$  units and as the central atom contain Si, Al, or Fe. In smectites' structure, there occur two types of octahedral sheet, i.e., the dioctahedral type, where two-thirds of the octahedral sites are occupied mainly by trivalent cations, e.g. Al(III) or Fe(III), and the trioctahedral type, with most of the sites occupied by divalent cations, e.g., Mg(II) (Tamayo et al. 2012). The negative surface layer charge, resulting from the isomorphous substitution of  $Mg^{2+}$  or  $Fe^{2+}$  for octahedral  $Al^{3+}$  or  $Fe^{3+}$  and  $Al^{3+}$  for tetrahedral  $Si^{4+}$ , causes binding of exchangeable cations to the interlayer sites. The charge of the smectite packet per unit cell is relatively small, which means that the cations are weakly bound in interpackage spaces and can be exchanged for other cations. This feature is extremely important because it allows for various structural modifications (Kyziol-Komosinska et al. 2010).

There have been numerous studies on the adsorption capacity of clays in relation to cationic dyes, especially methylene blue (Gürses et al. 2006; Nethaji et al. 2013; Santos and Boaventura 2016; Omer et al. 2018; Chaari et al. 2019). The novelty of these studies was the determination of the adsorption capacity of natural and thermally, acid- and alkaline-modified clay in relation to anionic dyes. The aim of this study was to determine the influence of clay modification on the adsorption capacity of anionic dyes from aqueous solutions. The adsorption studies were carried out on prepared model solutions of artificial anionic dyes and not on real wastewater samples. The use of distilled water eliminates any additional matrix effects and allows changes to

individual parameters and determination of their influence on the adsorption properties of the tested clay. In industrial wastewater, in addition to dye, there are also significant quantities of auxiliary substances, such as salts, which are present in wastewater in concentrations similar to those during application. Salts that can affect the adsorption capacity of fibers by changing their surface charge and changing the ionic nature, hydrophobicity, and solubility of the dye are often used in dyeing processes, which may have an adverse effect on test results. Their presence can have a negative impact on the results of laboratory tests.

Four isotherms of adsorption, i.e., Freundlich, Langmuir, Dubinin–Radushkevich, and Sips, were used to understand the nature of the adsorption process, and the estimation of parameters allowed determination of the maximum adsorption capacity and dye-binding mechanisms.

## 2 Materials and Methods

### 2.1 Preparation and Characterization of Clay

Smectite clay from the “Belchatow” lignite deposit (BC), obtained from the Belchatow Lignite Mine, Central Poland, was used for laboratory studies as an adsorbent (Fig. 1). The clay was dried at room temperature ( $25 \pm 2$  °C) and then ground to a fraction < 0.5 mm. Subsequently, modification of clay—thermal (BC 250), acidic (BC H<sub>2</sub>SO<sub>4</sub>), and alkaline (BC NaOH)—was carried out.

The thermal modification consisted of heating the clay samples in an oven at 250 °C for 5 h. The acid modification of clay was carried out accordance with Stoch et al. (1977), using a 16% H<sub>2</sub>SO<sub>4</sub> solution at 96 °C, for 8 h, with a solution to solid phase ratio of 5 : 1. After 2 h, the used acid was replaced by fresh acid to avoid the precipitation of CaSO<sub>4</sub>, MgSO<sub>4</sub>, and FeSO<sub>4</sub> salts. After cooling down, the samples were washed with distilled water until the reaction to SO<sub>4</sub><sup>2-</sup> ion disappeared; then the samples were centrifuged and then dried at 105 °C. The alkaline modification was performed using 5 M NaOH solution at 90 °C, for 8 h, with a solution to solid phase ratio of 5 : 1. Then the clay samples were washed with distilled water until they disappeared in the Na<sup>+</sup> ion solution and were dried at 105 °C (Öztop and Shahwan 2006).

The clay samples were characterized by X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (ED-XRF), and Fourier transform infrared spectroscopy (FT-IR).

Determination of mineral composition was carried out by XRD analysis using a Philips APD PW 3020 X’Pert diffractometer, which was equipped with a graphite monochromator using Cu-K $\alpha$  radiation. The XRD patterns were registered in the range of 2–73° 2 $\theta$ , with a step of 0.05° 2 $\theta$ .

The functional groups of clay were determined by infrared spectroscopy using a Fourier transform infrared spectrometer (Nicolet Magna FT-IR spectrometer).

The chemical composition of the clay was determined by X-ray fluorescence spectrometry (ED-XRF) using a Philips PW 1404 sequential spectrometer.

The specific surface area (SSA) was determined by the BET method from the nitrogen adsorption isotherms at 77 K and water adsorption isotherms at room temperature (Fisons, Sorptomatic 1990).

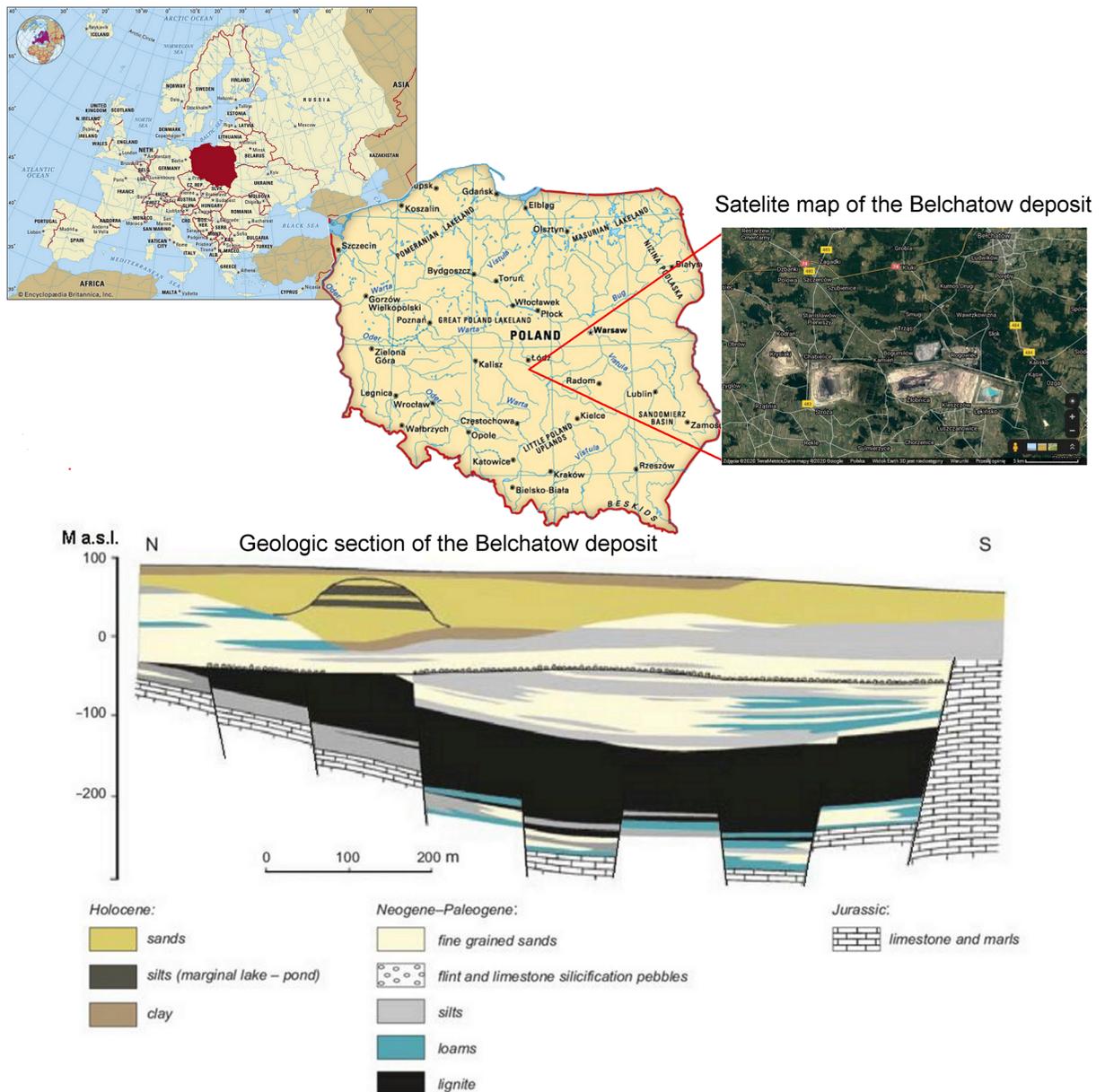
The porosity and pore size were determined by mercury porosimetry using a mercury intrusion porosimeter (Carlo Erba model 2000).

The pH values of the clays were measured in deionized water at a suspension ratio of 1 : 2.5, using a pH meter which is based on a combination pH electrode (glass membrane electrode and a reference electrode) (ERH-111 Hydromet, Poland).

The point of zero charge (pH<sub>PZC</sub>) of clay, defined as the pH at which the charge of the colloidal particles = 0, was determined with the method described by Calvete et al. (2009).

### 2.2 Characterization of Dyes

Reactive Red 198 (RR 198, CAS number: 145017-98-7, molecular formula: C<sub>27</sub>H<sub>18</sub>ClN<sub>7</sub>Na<sub>4</sub>O<sub>16</sub>S<sub>5</sub>) and Acid Red 18 (AR 18, CAS number: 2611-82-7, molecular formula: C<sub>20</sub>H<sub>11</sub>N<sub>2</sub>Na<sub>3</sub>O<sub>10</sub>S<sub>3</sub>) dyes were selected as a model of anionic dyes for the adsorption experiments; their chemical structures, properties, wavelengths at which the absorbance was measured ( $\lambda$ ), and the size of the dye molecule ( $d$ ) are shown in Fig. 2. Anionic dyes differ in the number of acceptors and donors: RR 198 has 3 donor groups and 22 acceptor groups, while AR 18 has 1 acceptor and 12 donors. The dyes are produced by Boruta Zachem-Kolor, Ltd. (Poland).

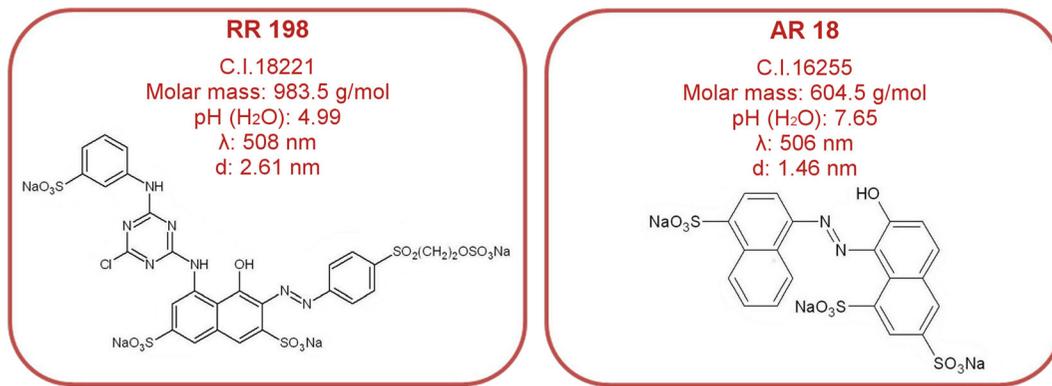


**Fig. 1** Location of the Belchatow brown coal deposit ([www.google.com/maps](http://www.google.com/maps)) and geologic section of the Belchatow deposit (based on Hycnar et al. 2018)

### 2.3 Adsorption Experiments

A batch experiment was carried out to measure the adsorption capacity of the natural and modified clay in relation to RR 198 and AR 18 dyes from aqueous solutions at room temperature ( $23 \pm 2$  °C). Clay was shaken with the aqueous solution of the dyes for 24 h. The initial concentrations of the dyes in aqueous solution were within a wide range of 1–1000 mg/

dm<sup>3</sup>, and the ratio of solution to solid phase was 20:1 (adsorbent dose 50 g). The initial ( $C_0$ ) and equilibrium ( $C_{eq}$ ) concentrations of RR 198 and AR 18 were determined using UV-vis spectrometry (Spectrometer Varian Cary 50 Scan UV-VIS) at wavelengths of  $\lambda = 508$  and 506 nm, respectively. In all solutions, pH values were measured by potentiometric method using a glass electrode pH meter (Elmetron ERH-111).



**Fig. 2** Characteristics of RR 198 and AR 18 dyes

The amount of dyes adsorbed ( $q$ ) by the used adsorbent was calculated with Eq. 1 and the removal efficiency (RE) was calculated from Eq. 2:

$$q = (C_0 - C_{eq}) \cdot \frac{V}{m} \quad (\text{mg/g}) \quad (1)$$

$$\text{RE} = \frac{C_0 - C_{eq}}{C_{eq}} \cdot 100\% (\%) \quad (2)$$

where  $C_0$  is the initial concentration of the dyes ( $\text{mg/dm}^3$ ),  $C_{eq}$  is the equilibrium concentration ( $\text{mg/dm}^3$ ),  $m$  is sorbent mass (g), and  $V$  is solution volume ( $\text{dm}^3$ ).

All experiments were performed in triplicate.

Before the laboratory studies on dye adsorption, the influence of the dye solution pH on absorbance was determined. Dye solutions with concentrations of 10 and  $50 \text{ mg/dm}^3$  were prepared. The pH of the dye solutions was adjusted to 4.0, 6.0, and 8.0 by adding 0.1 M HCl solution or 0.1 M NaOH solution. The effect of the pH of the RR 198 and AR 18 solutions on the absorbance was then analyzed using UV-vis spectrometry (Spectrometer Varian Cary 50 Scan UV-VIS). No change in absorbance was observed on changing the pH of the dye solutions (Fig. 3); therefore, the calibration curve for the tested anionic dyes was made at the natural pH of the dye solutions.

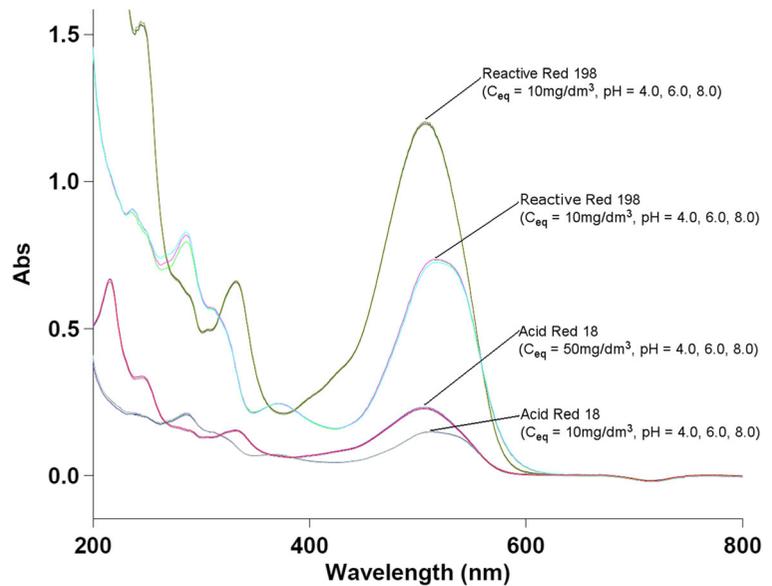
## 2.4 Adsorption Isotherm Models

To describe the adsorption behavior in different experimental conditions is to use mathematical models which are very useful, e.g., in process optimization, and provide a lot of valuable information about the adsorption process. In order to estimate

the maximum adsorption capacity of natural and modified clay and to determine the mechanisms of dye binding, four isotherm models were used, i.e., three 2-parameter models (Freundlich, Langmuir and Dubinin–Radushkevich isotherms) and one 3-parameter model (the Sips isotherm). The author's previous research (Pajak et al. 2019; Pajak and Dzieniszewska 2020) has shown that the nonlinear method is a better way to obtain the isotherm parameters and represent the most suitable isotherm. Also, other researchers (Kumar and Sivanesan 2005; Nebaghe et al. 2016; Yadav and Singh 2017; Jasper et al. 2020) have come to similar conclusions during their work. Therefore, the parameters in isothermal equations were estimated using a nonlinear regression method based on the Gauss–Newton method (Statistica software v. 9.0). A description of the four isotherm models and their equations is given in Online Resource 1 (Table 1).

Nonlinear regression, based on the classical least-squares method, was used to determine the values of parameters in the adsorption isotherms (Statistica v. 9.0–Gauss–Newton algorithm). In order to fit isotherm models to experimental results, three error functions, the sum of the squares of the errors (SSE), residual root mean square error (RMSE), and nonlinear chi-square test ( $\chi^2$ ), were used (additional data are given in Online Resource 2–Table 2). Error functions measure the differences between the experimental data and those calculated from mathematical models; lower values of error functions (SSE, RMSE, and  $\chi^2$ ) indicate the similarity of the values calculated based on models to those obtained experimentally and a good fit of the isotherm to the experimental data (Foo and Hameed 2010).

**Fig. 3** Effect of dye solution pH on absorbance



### 3 Results and Discussion

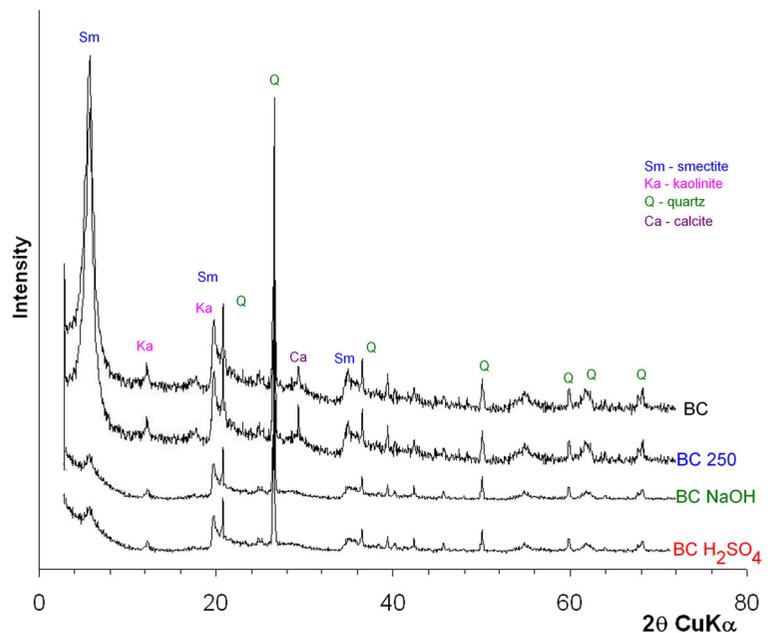
#### 3.1 Characterization of Natural and Modified Clays

On the basis of X-ray analysis of the clay samples, it was observed that the main mineral was Ca-smectite. The presence of other minerals, i.e., quartz, calcite, and kaolinite, was also determined (Fig. 4). The chemical composition reflected the mineral composition of clay. The studied clay contained SiO<sub>2</sub> (55.81%), Al<sub>2</sub>O<sub>3</sub>

(15.25%), Fe<sub>2</sub>O<sub>3</sub> (6.45%), CaO (2.82%), MgO (1.40%), Na<sub>2</sub>O (0.42%), and K<sub>2</sub>O (0.70%). In addition, to better present the changes occurring during modification, the ratio of silica to alumina was calculated (Table 1).

On the basis of the infrared spectrum analysis, it was observed that the main functional groups of the clay surface were dissociated silanol groups (–Si–O) in tetrahedral sheets; aluminol groups (–Al<sub>2</sub>–OH) in octahedral sheets; –AlFe–OH groups, reflecting the partial

**Fig. 4** XRD patterns of natural (BC) and thermally (BC 250), alkaline (BC NaOH)- and acid (BC H<sub>2</sub>SO<sub>4</sub>)-modified clay



**Table 1** Physicochemical properties and chemical composition (%) of natural and modified clay

	BC	BC 250	BC H <sub>2</sub> SO <sub>4</sub>	BC NaOH
SiO <sub>2</sub>	55.81	56.65	92.11	32.11
Al <sub>2</sub> O <sub>3</sub>	15.25	16.57	5.34	40.17
Fe <sub>2</sub> O <sub>3</sub>	6.45	7.65	0.3400	1.11
CaO	2.82	3.23	0.5600	2.23
MgO	1.74	2.32	0.6700	2.94
Na <sub>2</sub> O	0.04200	1.11	0.01001	20.63
K <sub>2</sub> O	0.5700	3.32	0.2100	0.7800
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	3.66	3.42	17.25	0.8200
SSA (m <sup>2</sup> /g)	141.80	150.20	143.20	214.10
Porosity (%)	6.82	11.13	42.68	53.34
Average pore diameter (μm)	0.01860	0.03220	2.11	0.6362
pH	7.95	7.83	3.39	10.28
pH <sub>PZC</sub>	7.42	7.20	3.22	9.66

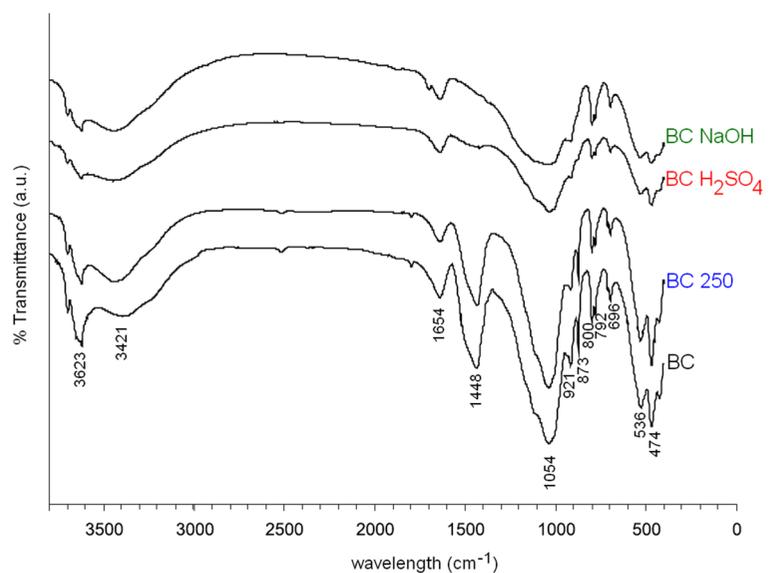
substitution of the octahedral Al by Fe; –OH groups, originating from the smectite and kaolinite minerals; and –H–O–H molecules of water adsorbed in the smectite minerals (Fig. 5).

The total SSA of the BC was 141.80 m<sup>2</sup>/g, the porosity was 6.82%, the average pore diameter was 0.01860 μm, and the pH value for natural clay was 7.95, while the point of zero charge was 7.42 (Table 1).

Thermal modification of clay caused dehydration of smectite structures; moreover, only slight changes in the

diffraction pattern were observed (Fig. 4), consisting in a shift of the peaks corresponding to the structure of smectite towards higher values of 2θ. Structural changes caused by smectite dehydration can also be observed in the FT-IR spectra (Fig. 5) of the tested samples. The removal of water molecules as a result of heating the sample to 250 °C is reflected in the FT-IR spectra of BC clay as a reduction in the intensity of IR bands located at 3623 and 1654 cm<sup>-1</sup>, coming from –OH and –H–O–H groups. Slight changes were found in the chemical composition of BC 250, which mainly resulted from dehydration and dehydroxylation of hydrated minerals. Furthermore, thermal modification resulted in a 6.50% increase in the silica-to-alumina ratio. SSA increased by almost 6%. The elimination of water molecules contributed to a significant increase in porosity (63%), as well as an almost twofold increase in the average pore diameter. The values of pH and pH<sub>PZC</sub> decreased slightly, from 7.95 to 7.83 and from 7.42 to 7.20, respectively (Table 1).

Based on the clay diffraction pattern analysis, it was observed that acid modification resulted in decrease and disappearance of the basic smectite peaks, as well as disappearance of the calcite peak (Fig. 4). On the basis of X-ray analysis of the clay sample, it was observed that acid modification caused a reduction in intensity and smoothing of the main smectite peaks, while the peaks attributed to kaolinite remained unchanged and the calcite peak disappeared. During modification of the clay samples with sulfuric acid, protons penetrated the

**Fig. 5** FT-IR spectra of natural (BC) and thermally (BC 250), alkaline (BC NaOH)- and acid (BC H<sub>2</sub>SO<sub>4</sub>)-modified clay samples

clay mineral layer and attacked the structural –OH groups. As a result of dehydroxylation, the octahedral layer was destroyed, which was also reflected in the FT-IR spectra (Fig. 5). Destruction of the octahedral smectite sheets was additionally confirmed by complete disappearance of the peak intensity of the characteristic band at  $873\text{ cm}^{-1}$ , coming from –AlFe–OH groups, as well as a decrease in intensity at  $921$  and  $536\text{ cm}^{-1}$ , coming from –Al<sub>2</sub>–OH and –AlFe–OH groups, respectively. Moreover, a decrease in the intensity of the vibrations centered at  $1054$  and  $474\text{ cm}^{-1}$  was observed, coming from –Si–O groups, related to degradation of the tetrahedral layers. Furthermore, the  $1448\text{ cm}^{-1}$  peak from calcite disappeared as a result of chemical reactions:  $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{CO}_2 + \text{H}_2\text{O}$ .

The exchange of spent sulfuric acid during modification prevented the precipitation of  $\text{CaSO}_4$ . As a result of acid leaching and dissolution of the octahedral layers, there was a significant increase in  $\text{SiO}_2$  content (65%), as well as a decrease in  $\text{Al}_2\text{O}_3$  by 65%, thus contributing to a 4.7-fold increase in the silica to alumina ratio to 17.25. The remaining oxide content as a result of acid modification also decreased significantly ( $\text{Fe}_2\text{O}_3$  decreased by 95%,  $\text{CaO}$  by 80%,  $\text{MgO}$  by 61.50%,  $\text{Na}_2\text{O}$  by 76%, and  $\text{K}_2\text{O}$  decreased by 63%) (Table 1). This modification resulted in a slight increase (about 1%) in the SSA. In turn, the porosity increased 6.3-fold to 42.68%, while the average pore diameter increased over 100 times to  $2.11\text{ }\mu\text{m}$ . Saturation of the sorption complex with  $\text{H}^+$  ions caused a noticeable decrease in pH to 3.39, as well as in  $\text{pH}_{\text{PZC}}$  to 3.22. Similar observations were made by other researchers (Akpomie and Dawodu 2016) who conducted studies on sorption of heavy metals using modified montmorillonite. They observed that the acid modification of montmorillonite also caused an increase in porosity and decrease in pH and  $\text{pH}_{\text{PZC}}$ . Chaari et al. (2008), during laboratory studies on the removal of lead from aqueous solutions by smectitic clay, also observed that modification with  $\text{H}_2\text{SO}_4$  acid improved the physicochemical properties of smectite clay compared to natural clay.

On the basis of diffractogram analysis, it was observed that alkaline modification of clay resulted in decrease and disappearance of basic smectite peaks as well as calcite peaks (Fig. 4). This is also confirmed by the FT-IR spectra (Fig. 5), where a decrease in intensity at  $1054$  and  $476\text{ cm}^{-1}$ , coming from vibrations of –Si–O groups in the tetrahedral layer, was observed. Furthermore, the  $1448\text{ cm}^{-1}$  peak from calcite disappeared as a

result of chemical reactions:  $\text{CaCO}_3 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{CaO}\downarrow + \text{H}_2\text{O}$ .

The modification using NaOH resulted in a significant, almost 500-fold, increase in  $\text{Na}_2\text{O}$  content. In addition, dissolution of the tetrahedral layers and free silica resulted in an increase in  $\text{Al}_2\text{O}_3$  content of about 164% and a decrease in  $\text{SiO}_2$  by 42.50%, thus contributing to a 4.5-fold decrease in the silica to alumina ratio to 0.82. The content of  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  oxides decreased by 83% and 21%, respectively, while that of  $\text{MgO}$  and  $\text{K}_2\text{O}$  oxides increased by 69% and 37%, respectively. Moreover, there was a significant increase in the surface area (51%) and a 7.8-fold increase in porosity, as well as a 34-fold increase in the mean average pore diameter to  $0.6362\text{ }\mu\text{m}$ . This modification also affected the pH and  $\text{pH}_{\text{PZC}}$  values, which increased to 10.28 and 9.66, respectively (Table 1). Soni et al. (2018) during their study found that the alkaline modification of clay also significantly increased the SSA and porosity of the studied clay, and also increased the pH and  $\text{pH}_{\text{PZC}}$  values.

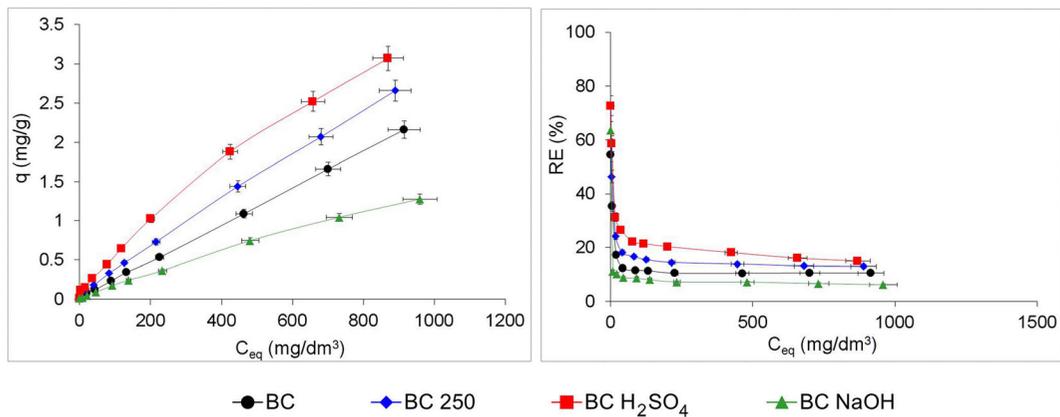
### 3.2 Adsorption of RR 198 and AR 18 Dyes onto Natural and Modified Clay

The adsorption capacity ( $q$ ) was plotted as a function of the equilibrium concentration ( $C_{\text{eq}}$ ), and removal efficiency (RE)—which shows the percentage of RR 198 and AR 18 dyes adsorbed from aqueous solutions—as a function of initial concentration ( $C_0$ ) (Figs. 6 and 7).

It was observed that the adsorption capacity of clay depended on the initial concentration of dye in the solution, the type of dye, and the kind of clay modification.

The results show that all the modifications of the clay increased its adsorption capacity in relation to the reactive dyes (Fig. 6). At the maximum initial concentration of  $1000\text{ mg/dm}^3$ ,  $2.91\text{ mg/g}$  (RE 14.78%) of RR 198 dye was bound by BC; 16.79% more RR 198 dye was bound by BC 250 than by BC, i.e., a maximum of  $3.32\text{ mg/g}$  (RE 16.79%); and 73.20% more of the dye was removed by BC  $\text{H}_2\text{SO}_4$  than by BC, i.e.,  $5.06\text{ mg/g}$  at the maximum initial concentration (RE 25.22%). The largest amount of RR 198 dye was removed by BC  $\text{H}_2\text{SO}_4$ ,  $10.32\text{ mg/g}$  at a maximum initial dye concentration of  $1000\text{ mg/dm}^3$  (RE 51.40%). BC  $\text{H}_2\text{SO}_4$  bound 253% more of the reactive dye than BC.

Smaller amounts of AR 18 dye than RR 198 dye were removed by both natural and modified clay:  $2.16\text{ mg/g}$  (RE 10.56%) of AR 18 dye was bound at a



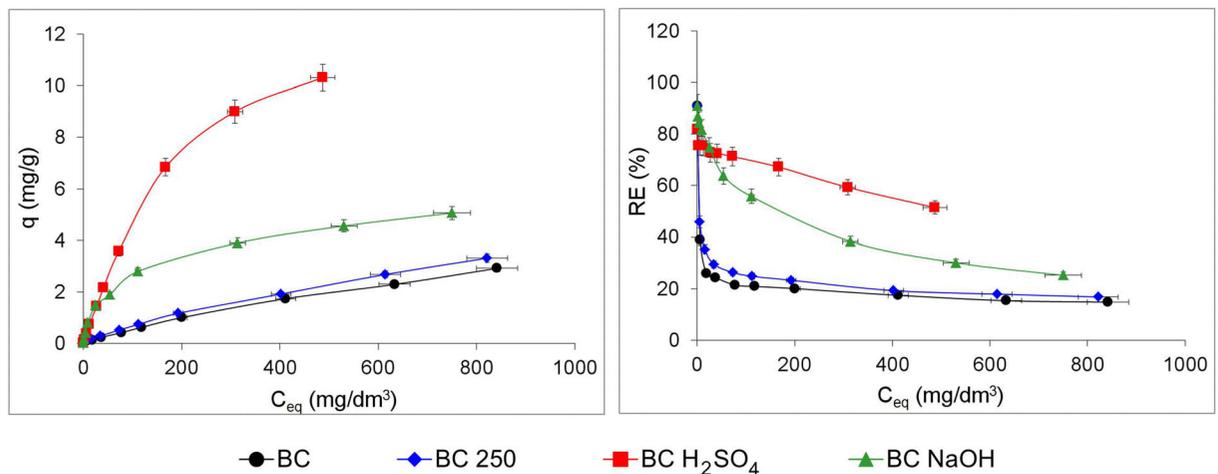
**Fig. 6** Equilibrium adsorption isotherms and removal efficiency of RR 198 onto natural and modified clays

maximum initial concentration of 1000 mg/dm<sup>3</sup>; 23.15% more of this dye was bound by BC 250 than by BC, i.e., a maximum of 2.66 mg/g (RE 13%). As observed for RR 198, the largest amounts of AR 18 dye were removed by BC H<sub>2</sub>SO<sub>4</sub>; 42.13% more of the dye was bound by BC H<sub>2</sub>SO<sub>4</sub> than by BC, i.e., a maximum of 3.07 mg/g (RE 15.01%). In contrast, BC NaOH bound 40.74% less AR 18 dye, i.e., a maximum of 1.28 mg/g (RE 6.24%) (Fig. 7).

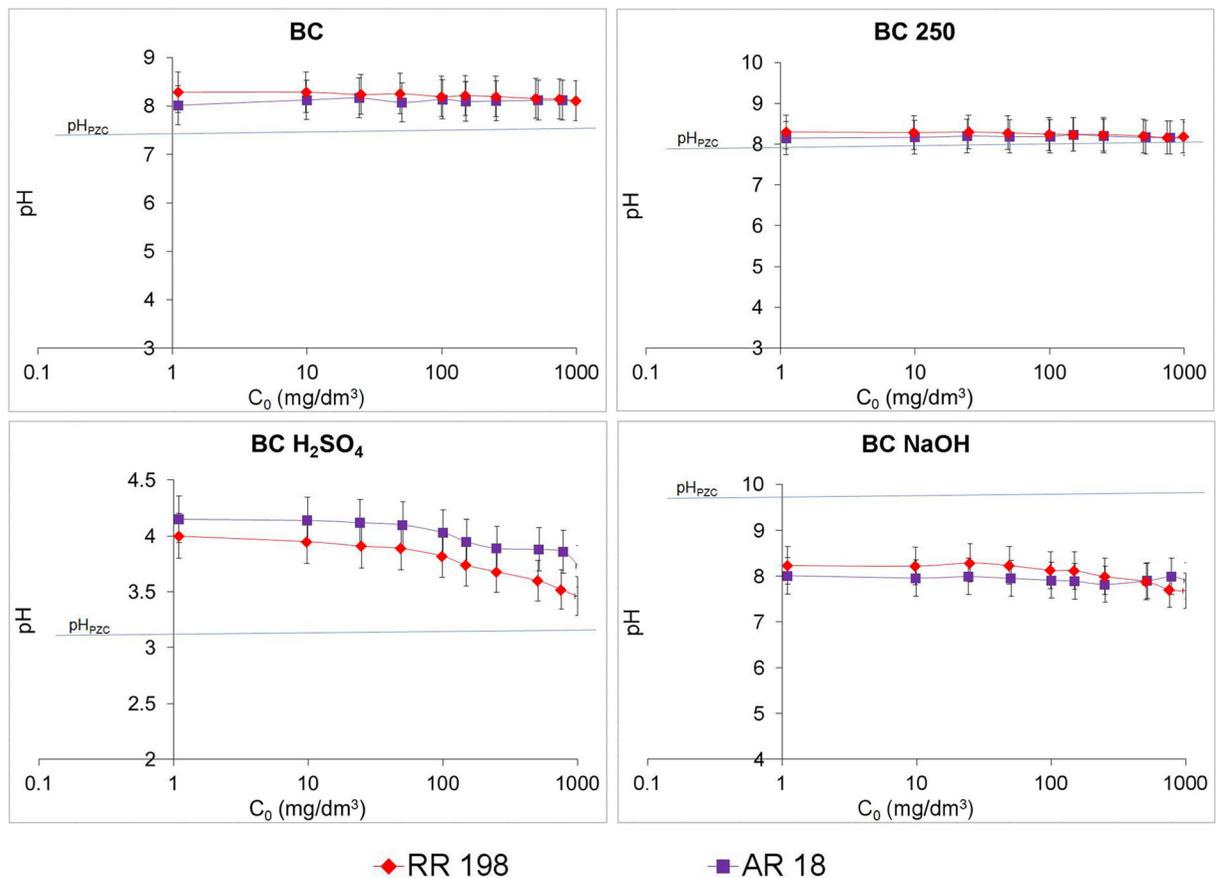
Dependence of the pH values of the equilibrium solutions and the type of adsorbent modification used was observed (Fig. 8). The adsorption of RR 198 and AR 18 from aqueous solutions onto BC occurred at pH in the range of 8.11–8.29 and 8.02–8.17, respectively, i.e., at a pH close that of the BC. Adsorption of dyes onto BC 250 was carried out at similar pH values, i.e., for dye RR 198 in the range of 8.19–8.30 and for dye AR 18 in the range of 8.13–8.24. Adsorption of the dyes

by BC H<sub>2</sub>SO<sub>4</sub> was carried out at pH in the range of 3.46–3.95 for dye RR 198 and 3.75–4.15 for AR 18. These values were also close to the pH values of the clay after modification with acid H<sub>2</sub>SO<sub>4</sub>. However, the process of adsorption of RR 198 and AR 18 onto clay modified with NaOH solution was carried out at pH values in the range of 7.68–8.23 and 7.89–8.01, respectively.

It was observed that the adsorption of RR 198 and AR 18 dyes onto BC, BC 250, and BC H<sub>2</sub>SO<sub>4</sub> occurred at a pH higher than the adsorbent’s point of zero charge (Fig. 8), which means that the surface of the clay during adsorption of the dyes was negatively charged, according to the reaction:  $AOH \leftrightarrow AO^- + H^+$  (where A is Si or Al). RR 198 and AR 18 are anionic dyes and cannot be bound due to electrostatic interactions in these cases. To explain the mechanisms of adsorption, it is necessary to take into account the surface structure of the adsorbent



**Fig. 7** Equilibrium adsorption isotherms and removal efficiency of AR 18 onto natural and modified clays



**Fig. 8** pH values in equilibrium solutions for RR 198 and AR 18

with various functional groups, and the structure of the dyes, and the amount of hydrogen atom donors and hydrogen atom acceptors they have should also be considered. On the surface of the adsorbents, depending on the type of clay (natural or modified), there are areas rich in silica or alumina with  $-OH$  and  $-OH_2^+$  groups and oxygen bridges depending on the pH of the solution. Taking into account the structure of the dyes RR 198 and AR 18 as well as the structure of BC, BC 250, and BC H<sub>2</sub>SO<sub>4</sub>, it can be concluded that the dyes were probably bound through chemisorption by forming hydrogen bonds between the  $-Si-OH$  and  $-Al-OH$  groups in the clay and the  $-NH$ ,  $-NH_2$ , and  $-OH$  groups in the dyes. Moreover, it was observed that with an increase in the number of donor groups, e.g.,  $-OH$ ,  $=NH$ , and  $-NH_2$  in the dye molecule, the amount of dye bound by clay increased.

In turn, the adsorption of anionic dyes onto BC NaOH occurred at a pH below the adsorbent's point of zero charge, which means that the surface of the clay

during adsorption of the dyes was positively charged, according to the reaction:  $AOH_2^+ \leftrightarrow AOH + H^+$  (where A is Si or Al), which may suggest the possibility of electrostatic interactions. However, taking into account the fact that the smallest quantities of both anionic dyes were removed by BC NaOH, it can be assumed that these interactions had a negligible effect on the amount of dye bound. These results are consistent with other studies showing that the structure of anionic dyes and structure of adsorbents rich in silica and aluminum oxides play a significant role in adsorption of anionic dyes and in determining the binding mechanism of anionic dyes. Wawrzakiewicz et al. (2015) in their work on adsorption of acid, reactive, and direct dyes from aqueous solutions and wastewater using mixed silica-alumina oxide came to a similar conclusion. Similar observations were made by Anbia and Salehi (2012) during their research on the removal of acid dyes from aqueous media by adsorption onto amino-functionalized nanoporous silica, as well as by Krysztafkiewicz et al.

(2002) in their studies on the adsorption of dyes onto a silica surface.

The highest maximum adsorption capacity of the natural and modified clay in relation to RR 18 and AR 198 from aqueous solution is shown in Fig. 9.

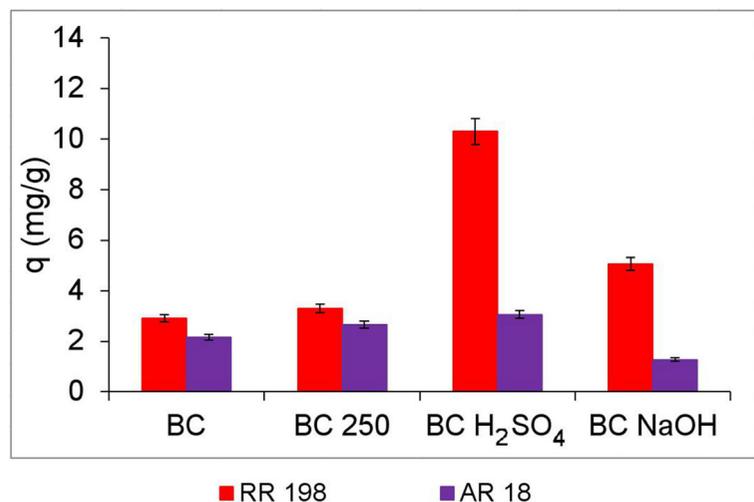
According to the results obtained, it was observed that RR 198 dye was bound in noticeably larger amounts than AR 18 dye, i.e., 6.02%, 24.81%, 236.16%, and 295.31% larger by BC, BC 250, BC H<sub>2</sub>SO<sub>4</sub>, and BC NaOH, respectively. In addition, it is seen that acid activation significantly increased the adsorption capacity for the anionic dyes tested. Significant differences in the amount of anionic dyes bound to the tested adsorbents most likely result from the dye structure and the difference between the hydrogen atom donors and the hydrogen atoms acceptors in the dyes, as well as from the surface structure of the adsorbent with different functional groups, which differ depending on the modification applied. Moreover, it has been observed that there is a relationship between maximum adsorption capacity and average pore diameter. As the pore size increases, depending on the clay modification used, the maximum adsorption capacity of both anionic dyes increases. Gil et al. (2013), during studies on adsorption of methylene blue on thermally and acid-activated clay minerals, found that the acid activation of clay, such as montmorillonite, significantly increases the adsorption capacity for anionic dye. Similar results were obtained by Akpomie et al. (2017) who carried out adsorption studies of anionic dye onto acid-activated montmorillonite.

### 3.3 Adsorption Isotherms

The parameters estimated from the Freundlich, Langmuir, Dubinin–Radushkevich, and Sips models using nonlinear regression analysis, the determination coefficient ( $R^2$ ), and the error functions (SSE, RMSE, and  $\chi^2$ ) are presented in Table 2. On the basis of the determination coefficient ( $R^2 < 0.9000$ ) and the lowest values of the error function, it can be seen that the models of isotherms used, i.e., Freundlich, Langmuir, Dubinin–Radushkevich, and Sips, demonstrated good quality of fitting of the isotherm equations to the experimental data.

The values of the parameter  $1/n_F$  estimated from the Freundlich isotherm for all clay–dye systems, except in one case, were lower than 1. If the value of  $1/n_F$  is smaller than 1, reflecting favorable adsorption, then the sorption capacity increases and new adsorption sites occur (Özcan et al. 2004). Bendaho et al. (2017), in research on the adsorption of acid dye onto activated clay, obtained similar results; namely, on the basis of the value of the parameter  $1/n_F$ , they found that the adsorption of methyl orange onto clay also has a favorable nature, as did Arellano-Cárdenas et al. (2013) who carried out adsorption studies of malachite green onto organically modified clay. The value of the parameter  $1/n_F$  for adsorption of AR 18 dye onto alkaline-modified clay was above 1, which indicates the unfavorable nature of the adsorption process, which also resulted in the lowest adsorption capacity of the alkaline-modified clay in relation to this dye (Fig. 7). Similar results were obtained by Özcan et al. (2004) who carried out

**Fig. 9** Comparison of maximum adsorption capacities of natural and modified clay for anionic dyes



**Table 2** Isotherm parameters and error functions data

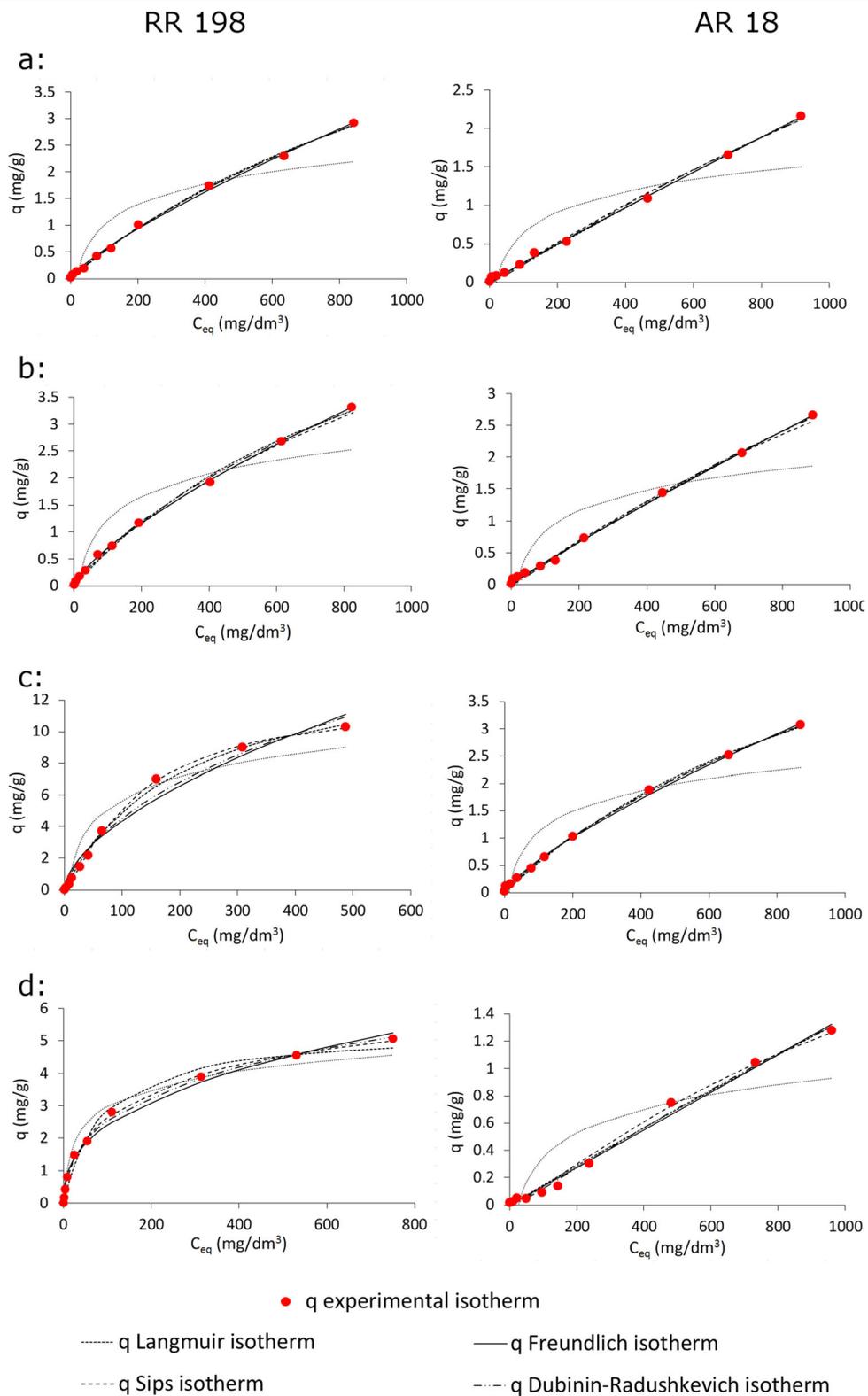
	AR 18				RR 198			
	BC	BC 250	BC H <sub>2</sub> SO <sub>4</sub>	BC NaOH	BC	BC 250	BC H <sub>2</sub> SO <sub>4</sub>	BC NaOH
Freundlich isotherm								
$1/n_F$	0.7919	0.7365	0.5879	0.3895	0.9576	0.9246	0.7591	1.01
$K_F$ (mg/g(L/mg) <sup>1/n<sub>F</sub></sup> )	0.01413	0.02363	0.2922	0.3981	0.003130	0.004993	0.01823	0.001338
$R^2$	0.9978	0.9995	0.9717	0.9892	0.9984	0.9982	0.9985	0.9912
SSE	0.02150	0.006120	3.85	0.3418	0.007923	0.01452	0.01601	0.01774
RMSE	0.04637	0.02474	0.6208	0.1849	0.02815	0.03810	0.04001	0.04212
$\chi^2$	0.1763	0.06685	1.62	0.4650	0.2347	0.3728	0.09704	0.4161
Langmuir isotherm								
$q_{exp}$ (mg/g)	2.92	3.32	10.32	5.06	2.16	2.66	3.07	1.28
$q_{max}$ (mg/g)	7.79	7.47	14.79	5.35	45.02	20.30	7.36	20.59
$K_L$ (L/mg)	0.0006944	0.0009353	0.005006	0.01115	0.00005480	0.0001688	0.0008107	0.00007072
$R_L$	0.9980	0.9969	0.9509	0.9466	0.9999	0.9995	0.9975	0.9999
$R^2$	0.9982	0.9960	0.9962	0.9863	0.9981	0.9981	0.9984	0.9916
SSE	0.01722	0.04881	0.5095	0.4309	0.009569	0.01531	0.01673	0.01692
RMSE	0.04150	0.06987	0.2257	0.2076	0.03093	0.03913	0.04090	0.04114
$\chi^2$	0.7804	0.7048	0.2366	0.6550	0.3201	0.5896	0.5011	0.3893
Dubinin–Radushkevich isotherm								
$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	0.008141	0.007485	0.005437	0.003552	0.01086	0.01042	0.008338	0.01152
$q_D$ (mmol/g)	0.00003441	0.00003235	0.00007503	0.00001579	0.00005612	0.00006387	0.00004408	0.00003943
$E$ (kJ/mol)	7.94	8.17	9.59	11.86	6.79	6.93	7.74	6.59
$R^2$	0.9984	0.9981	0.9828	0.9972	0.9959	0.9971	0.9986	0.9944
SSE	0.01498	0.02262	2.34	0.08931	0.02077	0.02289	0.01539	0.01116
RMSE	0.03870	0.04756	0.4840	0.09450	0.04557	0.04785	0.03924	0.03341
$\chi^2$	4.29	1.66	0.8921	0.1398	2.48	5.10	0.8383	11.36
Sips isotherm								
$q_{max}$ (mg/g)	11.38	14.77	12.13	7.83	10.95	11.08	13.19	2.84
$K_S$ ((L/mg) <sup>1/n<sub>S</sub></sup> )	0.0007054	0.001019	0.002177	0.02796	0.0002092	0.0003094	0.0008423	0.0001753
$1/n_S$	0.9174	0.8359	1.26	0.6266	1.03	1.01	0.8698	1.23
$R^2$	0.9984	0.9992	0.9992	0.9984	0.9991	0.9986	0.9991	0.9977
SSE	0.01486	0.02206	0.1024	0.04901	0.01647	0.02452	0.01014	0.01173
RMSE	0.03855	0.04696	0.1012	0.07001	0.04058	0.04951	0.03184	0.03426
$\chi^2$	0.01697	0.02073	0.06286	0.02711	0.03837	0.06979	0.009294	0.04748

adsorption studies of Acid Blue 193 from aqueous solutions onto bentonites.

A higher intensity was observed for the adsorption of RR 198 dye ( $K_F$ ) onto BC H<sub>2</sub>SO<sub>4</sub> and BC NaOH, which is reflected in the experimental results obtained shown in Fig. 10.

Useful information, such as the maximum adsorption capacity ( $q_{max}$ ) and isothermal constant ( $K_L$ ), which is associated with binding site affinity and binding energy,

is provided by the Langmuir isotherm. The values of the  $q_{max}$  parameter for all investigated dye–adsorbent systems were greater than the experimental values, which may indicate incomplete covering of the monolayer. The calculated value of the  $K_L$  parameter, related to the adsorption energy of the dyes, was in the range of 0.01115–0.0006944 and 0.0001688–0.00005480 dm<sup>3</sup>/mg for RR 198 and AR 18, respectively. This indicates a higher affinity of RR 198 to the surface of natural and



**Fig. 10** Comparison of experimental data with the adsorption isotherms of RR 198 and AR 18 onto natural and modified clay ((a) BC, (b) BC 250, (c) BC H<sub>2</sub>SO<sub>4</sub>, (d) BC NaOH)

modified clays and a low energy of dye binding by clays. These assumptions were confirmed by the studies of other researchers, e.g., in tests on the adsorption of acid dyes from aqueous media onto amino-functionalized nanoporous silica carried out by Anbia and Salehi (2012), as well as by the studies carried out by Wawrzekiewicz et al. (2015) on the adsorption of acid, reactive, and direct dyes from aqueous solutions and wastewater onto mixed silica–alumina oxide. The Langmuir constant ( $K_L$ ) was lowest for the adsorption of AR 18 dye onto BC NaOH, indicating lower affinity of the dye for the BC NaOH surface. The calculated parameter values are reflected in the experimental results presented in Fig. 6. Moreover, the values of the parameter  $R_L$  were below 1, indicating that the adsorption process is favorable for all dye–clay systems. Values of the parameter  $R_L$  less than 1 were also obtained by Gamoudi and Srasra (2019) studying the adsorption of organic dyes by modified clay, as well as by Chang et al. (2016) investigating the adsorption of methylene blue onto  $Fe_3O_4$ /activated montmorillonite nanocomposite.

The values of the parameter  $E$ , which were calculated from the Dubinin–Radushkevich equation, were above 8 kJ/mol for the adsorption of RR 198 dye onto BC 250, BC  $H_2SO_4$ , and BC NaOH, indicating that the adsorption is a chemical process. For the adsorption of RR 198 onto BC, as well as the adsorption of AR 18 onto BC and modified clay, the values of the parameter  $E$  were below 8 kJ/mol, indicating the physical nature of the process. Genc and Oguz (2010) obtained similar results during sorption studies of acid dyes from aqueous solution using non-ground ash and slag. They noticed that the magnitude of the constant in the Dubinin–Radushkevich isotherm ( $E$ ) was very small, indicating that the adsorption energy is very low. Values of the parameter  $E$  less than 8 kJ/mol were also obtained by Chicinas et al. (2018) during research on the ability of a montmorillonitic clay to interact with cationic and anionic dyes in aqueous solutions.

When the  $1/n_S$  parameter estimated from the Sips model, representing surface inhomogeneity, deviates from unity, then it indicates a heterogeneous surface. Moreover, the values of the  $1/n_S$  parameter for all tested adsorbent–adsorbate systems were higher than the values of the  $1/n_F$  parameter, calculated from the Freundlich isotherm, which additionally suggests the heterogeneity of the surface of the adsorbent. Hokkanen et al. (2018), as well as Dzieniszewska et al. (2019) and Saruchi Kumar (2019), presented similar assumptions in

their research. As it is known, the Sips isotherm is a combination of the Langmuir and Freundlich equations, so it can be concluded that the mechanism of binding anionic dyes by natural and modified clay does not follow ideal monolayer adsorption. Therefore, it should be assumed that the binding mechanism of the tested dyes is more complex. Moreover, the adsorption capacity calculated from the Sips equation is more realistic than that calculated from Freundlich or Langmuir equations and indicates that different adsorption centers participate in dye uptake.

On the basis of the parameters estimated using non-linear regression, the theoretical isotherms were plotted and are presented together with the experimental data in Fig. 8. It was found that the Sips isotherm best describes the experimental data over the whole range of the initial concentrations of both anionic dyes. Also, the values of the determination coefficient  $R^2$  and analysis of the error functions SSE, RMSE, and  $\chi^2$  (Table 2) indicate that the applied three-parameter Sips isotherm is the model which best fits the adsorption process, among the five isothermal models used.

#### 4 Conclusions

The present research shows that smectite clay from the lignite deposit “Belchatow” (BC), obtained from the Belchatow Brown Coal Mine in Central Poland, can be used as a cheap, effective, and easily available alternative to expensive commercial activated carbon to remove acid dyes from an aqueous solution. Moreover, it was found that modifications of the clay (i.e., thermal, acidic, and alkaline) influenced its physicochemical properties, chemical composition, and, what is more, its adsorption capacity in relation to two anionic dyes. Thermal modification mainly influenced the increase in total SSA and porosity, while the chemical modifications influenced the changes in total SSA and porosity, as well as in the chemical composition, which was reflected in changes of pH and  $pH_{PZC}$ . It was observed that the dye RR 198 was bound in noticeably larger amounts than the dye AR 18, by both natural clay and modified clay, i.e., 6.02%, 24.81%, 236.2%, and 295.3% more onto BC, BC 250, BC  $H_2SO_4$ , and BC NaOH, respectively. Moreover, all modifications applied to the clay increased its adsorption capacity in relation to RR 198, while the acidic and thermal modification of clay increased its adsorption capacity in

relation to AR 18. The highest amounts of both anionic dyes were removed by BC H<sub>2</sub>SO<sub>4</sub>, i.e., a maximum of 10.32 and 3.07 mg/g for RR 198 and AR 18, respectively. Taking into account the values of the determination coefficient and the lowest values of the error function, it was found that the best quality of the isotherm equation fit to the experimental data was demonstrated by the Sips isotherm model over the whole range of the initial concentrations of both anionic dyes. Based on the structure of the dyes RR 198 and AR 18, the number of donor groups, e.g., –OH, =NH and –NH<sub>2</sub> in the dye molecules, and the structure of BC, BC 250, and BC H<sub>2</sub>SO<sub>4</sub>, it can be assumed that the dyes were most likely bound by chemisorption by forming hydrogen bonds between the –Si–OH and –Al–OH groups in the clay and the –NH, –NH<sub>2</sub>, and –OH groups in the dyes. However, taking into account the calculated parameters of adsorption isotherms and fitting of isothermal models, it should be assumed that the binding mechanism of the tested dyes is a more complex process. The research results obtained here suggest the direction of using smectite clay as an effective adsorbent for treatment of wastewater from the textile industry.

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