Zeolite properties improvement by chitosan modification—Sorption studies

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\textbf{A B S T R A C T}

In the paper the potential of chitosan modified zeolite (NaP1CS) as a cheap adsorbent for methylene blue (MB) removal from aqueous solutions was determined. Fourier transform infrared spectroscopy analyses, nitrogen adsorption/desorption isotherms and scanning electron microscopy were applied to characterize the adsorbent. Batch adsorption studies were carried out to examine effects of various factors such as pH, contact time, initial MB and Cu(II) concentrations, temperature influence on the sorption process. The impact of different ways of zeolites modification with chitosan on sorption capacity and the comparison of adsorption of unmodified zeolite and fly ash are presented. The effect of different metal ions such as Cu(II), Zn(II), Mn(II), Fe(III) and also that of foreign ions on the MB sorption were also studied. The pseudo-first order, pseudo-second order and intraparticle diffusion models were fitted to the kinetic data. The best fit was achieved with both the pseudo-second order and intraparticle diffusion models. The experimental equilibrium data were evaluated by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The calculated thermodynamic parameters indicated a spontaneous and endothermic sorption process. Desorption studies were carried out with different desorbing agents. HCl proved to be the most effective desorption agent for MB and Cu(II).

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\textbf{Introduction}

Every year more than $7 \times 10^{-3}$ tonnes and 100,000 kinds of dyes are produced. In practice, the concentrations lower than 1 mg dm$^{-3}$ of dyes can give undesirable color to water [1]. Methylene blue is a basic dye which belongs to the widely applied main group of dyes. It is used in industry for dyeing cotton, silk and wood [2]. In water it exists as a cation. Investigations on sorption of methylene blue were carried out by many scientists [3–9]. Generally, most of the dyes used in printing and paper industries cause major environmental problems. They are toxic for both humans and animals, and can cause cancer, besides they are non-biodegradable and stable in the environment. These colorful effluents with different temperatures, pH values, high chemical oxygen demand cause disorder of photosynthesis reducing light permeability. Therefore the removal of synthetic dyes in recent decades has become a global problem [10–14]. Furthermore, during the printing and dyeing processes, copper salts are widely used as additives to optimize various properties of the printing and dyeing products. Copper has attracted much attention because of its harmful effects on humans. Large doses of copper can cause high blood pressure, anemia, widespread capillary damage and permanent damage in the liver and kidney [15,16]. Therefore these two components are present together in the aqueous media. It is important to find a suitable method for simultaneous removal of dyes and heavy metals from wastewaters.

The widely applied method for purification of waters is adsorption on solid sorbents like ion exchange resins [17], active carbon [18], natural and synthetic zeolites and fly ashes [19–21]. A promising area of zeolite synthesis is possibility of reusing solid wastes from power plants. Low cost of raw materials makes them an alternative to traditional sorbents like active carbon [22]. In many papers zeolites showed perfect sorption efficiency for heavy metals [19,23–26], phosphates [27], ammonium [28–30], land-based petroleum spills [31] or BTX [32]. Dyes were also investigated but not so extensively [32]. Negative charges in the porous crystal structure of zeolites make them suitable for adsorbing cationic dyes like methylene blue. However, cheap sorbents such as fly ash or zeolites are very often characterized by insufficient sorption.
capacities, so new methods of chitosan modification are searched for to increase them to make sorption most efficient.

Many methods for improving sorption capacity of zeolites are known. The first example is the modification of zeolites by quaternary ammonium salts. As follows from the paper by Muir and Bajda [33] the more effective the modification, the longer the carbon chain of the surfactant is. Modification of the surfactants has also proved effective in the adsorption of dyes [1]. Motlagh Bahadory Esfahani and Faghhiian [34] have proposed the modification by ethylenediamine and monoethanolamine for Pb(II) adsorption. There are also known works on sorption of dyes and heavy metal ions on chitosan modified zeolites [35–37]. Khanday et al. used oil palm ash for preparing zeolite A and then modified it by chitosan in order to remove methylene blue and acid blue 29 from wastewaters [38]. However, these processes are not carried out in a multicomponent system but only in a one-component system. To this aim different kinds of zeolites can be applied [39,40].

Kyzas and Bikiaris presented an overview of modified chitosan adsorbents application [41]. Generally, chitosan is well investigated in order to improve the sorption capacity of many materials like magnetic Fe3O4 nanoparticles [42], active carbon [43] and for preparing new types of compounds. Magnetic chitosan with graphene oxide was prepared in order to remove cationic and anionic dyes. Maximum removal efficiency was found to be 89.9% for the cationic dye methyl violet and 69.5% for the anionic dye Alizarin yellow [44]. Karaer and Kaya studied adsorption of methylene blue and reactive blue 4 on the magnetic chitosan/active charcoal composite. The adsorption percentage is dependent on temperature, for reactive blue 4 it decreases from 75% to 47%, whereas for methylene blue it rises from 65% to 95% in the increasing temperature range from 25 to 45 °C, respectively [43]. Methylene blue removal was also studied by Cho et al. on the magnetic chitosan composite which was prepared by entrapping crosslinked chitosan and nano-magnette on the clay surface [45].

In this study zeolite NaP1 which is characterized by two types of channel size and has a potential of sorption in water purification, was modified by CS to obtain an effective sorbent for metal ions sorption in the presence of methylene blue (MB).

Chitosan (CS) as a natural polymer is produced from deacetylation of chitin, extracted from the shells of crustaceans, skin fungal cell walls and insects. It is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity as well as sorption properties. Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites [46]. Amino groups of chitosan can be protonated after strong anionic dyes adsorption by electrostatic attractions in the acidic media. Due to its large size, chitosan possesses negative charges only on the outside surface. Negative interior charges are even accessible to inorganic cationic pollutants [47].

A new type of inorganic–organic hybrid material based on the modified zeolite by chitosan (NaP1CS) was investigated by terms of its efficiency to remove MB and Cu(II) ions from wastewaters. For comparison different types of chitosan (low, medium and high molecular weight) were used and two different methods of modification were applied. The first one using glutaraldehyde and the second one epichlorohydrin and then they compared with raw fly ash. Simultaneous removal of both MB and heavy metal ions such as Cu(II), Fe(III), Mn(II), Zn(II) was also studied.

## Experimental

### Preparation of adsorbents

Coal fly ash (FA) was obtained from the Power Plant in Koziencie, Poland. The coal fly ash was converted into zeolite (NaP1) in the the sub-pilot scale process. Thus, there were applied the following conditions: 20 kg of fly ash, 12 kg of NaOH, 90 dm³ of water, the reaction temperature: 353 K and the reaction time: 36 h which were described in papers [48,49]. Chitosan (deacetylation degree of chitosan flakes >75%, flakes) was obtained from Sigma Aldrich.

For the modification of NaP1 by chitosan, a chitosan solution was at first prepared by dissolving 2 g of chitosan in 0.2 dm³ of 1% glycolic acid. The solution was being stirred using a magnetic stirrer for 24 h at 1000 rpm at room temperature to complete dissolution. Then 16 g of zeolite was added into the solution of chitosan and mixed for next 6 h under the same conditions. After this 1 M NaOH was added dropwise to the mixture to obtain pH 9. Subsequently, the solution was washed with distilled water to obtain neutral pH and then it was filtered. The obtained material (NaP1CS) was dried and ground in the mill.

Moreover, in order to compare the sorption capacity of the resulting modified zeolite NaP1CS, modifications were performed using three different kinds of chitosan: high molecular weight (CS H), medium molecular weight (CS M) and low molecular weight (CS L). Likewise, there were also applied two other methods of modifying zeolite with glutaraldehyde (NaP1CS GLU) and epichlorohydrin (NaP1CS EPI).

### Preparation of adsorbates

A typical basic, cationic dye, methylene blue (MB) was chosen because of its extensive applications. Its characteristics and structure are presented in Table 1.

A stock solution of 1000 mg dm⁻³ MB was prepared by diluting methylene blue (Chempur, Poland). The adsorption was performed by batch experiments. Before the measurement, a calibration curve was made up using the known concentrations of MB. The determination of dye concentration was made by means of the spectrophotometer Cary 60 (Agilent Technologies) by measuring absorbance at λmax = 665 nm. Fig. 1 shows the evolution of absorbance vs. the concentration of MB.

The Cu(II) metal ions stock solution was prepared using CuCl2·2H2O (Avantor Performance Materials Poland S.A.) in distilled water. In order to obtain appropriate concentrations, the stock solution was diluted. The Cu(II) concentrations in solution were measured by an atomic adsorption spectrometer Spectr AA 240 FS (Varian, Australia). The appliance is equipped

### Table 1

<table>
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<th>Parameter</th>
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<tr>
<td>Molecular formula</td>
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<tr>
<td>Molecular weight, g/mol</td>
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with a deuterium, cathode lamp for Cu. The Cu(II) detection occurs at 324.7 nm.

The stock solutions of Cu(II), Zn(II) Mn(II), Fe(III) and MB were prepared using CuCl2·2H2O, ZnCl2, MnCl2·4H2O, FeCl3·6H2O and methylene blue (Avantor Performance Materials Poland S.A.). The concentrations of the above-mentioned components were measured by the inductively coupled plasma optical emission spectrometry (ICP-OES).

**Characterization of adsorbents**

In order to examine the structure of adsorbents (NaP1, NaP1CS) the following analyses were made: Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption/desorption isotherm analysis and scanning electron microscopy (SEM).

**Batch adsorption studies**

To study the effect of pH on adsorption, the samples of dye solution were adjusted to reach the initial pH ranging from 2 to 9 by adding 1 M NaOH or 1 M HCl. The pH meter pHM82 (Radiometer, Copenhagen) was used to measure the solution pH.

The adsorption process was performed by the batch experiments in 0.1 dm³ conical flasks. 0.1 g of the adsorbent NaP1 or NaP1CS with 0.02 dm³ of MB and/or Cu(II) ions solution was studied. The initial concentration of MB and Cu(II) ranged from 50 to 100 mg dm⁻³. The samples were shaken on the mechanical shaker 358A (Elpin Plus, Poland) at amplitude 7, 180 rpm, at room temperature for a specified time from 1 to 240 min. The batch experiments were also performed with simultaneous adsorption of MB and Cu(II) at different initial concentrations.

Apart from the addition of MB and Cu(II) there was also tested the simultaneous sorption of other metal ions like Cu(II), Zn(II), Mn(II), Fe(III) and MB.

In order to investigate the influence of foreign ions on MB and Cu(II) adsorption, it was studied in the presence of nitrate (NO₃⁻), chloride (Cl⁻) and sulfate (SO₄²⁻) ions. The solutions containing foreign ions at the concentration 1000 mg dm⁻³ with the appropriate MB and Cu(II) concentrations were prepared. The interfering ions effect was examined using 0.02 dm³ of solution with 0.1 g of sorbent by means of the mechanical shaker for 120 min at room temperature and amplitude 7. The concentrations of NO₃⁻, Cl⁻ and SO₄²⁻ ions were measured by the ion chromatography method using Vario 940 Professional IC (Metrohm).

The uptake of dye and heavy metal ions [mg g⁻¹] was calculated using the equation:

\[
q_t = \frac{(c_0 - c_t)V}{m}
\]

where: \(c_0\) — the initial concentration of the solution [mg dm⁻³], \(c_t\) — the solution concentration after time \(t\) [min], \(V\) — the volume of the solution [dm³], \(m\) — the dry weight of the adsorbent [g].

The sorption percentage \(\%S\) [%]:

\[
\%S = \frac{(c_0 - c_t)100}{c_0}
\]

where: \(c_0\) — the initial concentration of the solution [mg dm⁻³], \(c_t\) — the solution concentration after time \(t\) [min].

The mechanism of adsorption of MB and Cu(II) on NaP1 and NaP1CS was investigated using the pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion models (IPD). The appropriate equations are given below:

\[
\log(q_1 - q_t) = \log(q_1) - k_1t/2.303
\]

\[
t/q_t = 1/k_2q_t^2 + t/q^2
\]

\[
q_t = k_t^{1/2} + C
\]

where: \(t\) — the contact time [min], \(k_1\) — the rate constant of the pseudo-first order model, \(k_2\) — the adsorption rate constant [g mg⁻¹ min⁻¹], and \(q_t\) and \(q_0\), \(q_x\) — the adsorption capacities of adsorbate at time \(t\) and at equilibrium [mg g⁻¹], respectively, \(k_2\) — the diffusion rate constant [mg (g min⁰⁵)]⁻¹, \(C\) — the intercept which reflects the boundary layer effect [–].

\(q_e\) and \(k_2\) values were estimated experimentally from the intercept and slope of a plot of \(t/q_t\) vs. \(t\).

**Equilibrium and thermodynamic analysis**

The experimental results are also presented in the form of the Langmuir [53], Freundlich [54], Temkin [55] and Dubinin–Radushkevich (D–R) [56] isotherms.

The Langmuir isotherm is presented using the following equation:

\[
q_e = q_mK_LC_e/1 + K_LC_e
\]

where: \(K_L\) — the Langmuir adsorption constant [dm³ mg⁻¹], \(C_e\) — the equilibrium concentration of adsorbate in the liquid phase [mg dm⁻³], \(q_m\) — the maximum adsorption capacity [mg g⁻¹] to form a complete monolayer coverage.

The Freundlich isotherm is presented using the following equation:

\[
q_e = K_FC_e^{1/n}
\]

where: \(K_F\) — the Freundlich constant [mg g⁻¹] [dm³ mg⁻¹]¹/n, \(n\) — the Freundlich isotherm parameter.

The Temkin isotherm is presented using the following equation:

\[
q_e = RT/b_f\ln(a_fC_e)
\]

where: \(b_f\) — the Temkin constant related to the heat of sorption [kJ mol⁻¹], \(a_f\) — the equilibrium binding constant corresponding to the maximum binding energy [dm³ g⁻¹], \(R\) — the gas constant \([8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}]\).

The Dubinin–Radushkevich isotherm is presented using the following equation:

\[
q_e = X_m e^{-b_d\theta}
\]
where \( X_m \)—the theoretical saturation capacity [mg g\(^{-1}\)], \( K_{ob} \)—the constant related to the mean free energy of adsorption [mol\(^2\) kJ\(^{-2}\)], e—the mean energy of adsorption [kJ mol\(^{-1}\)].

The thermodynamic parameters associated with the process of adsorption are: \( \Delta G^\circ \) free energy change [kJ mol\(^{-1}\)], \( \Delta S^\circ \) entropy change [J K\(^{-1}\) mol\(^{-1}\)], \( \Delta H^\circ \) enthalpy change [kJ mol\(^{-1}\)] and they are considered in the equations presented below:

\[
\ln K_c = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

\( \Delta G^\circ = -RT\ln K_c \) (11)

where \( R \)—the gas constant [8.314 J K\(^{-1}\) mol\(^{-1}\)], \( T \)—the temperature [K] and \( K_c \) —the equilibrium constant.

Desorption studies

The studies of MB and Cu(II) release from sorbents are important for reusing this material in the process of sorption and wastewater treatment. For the desorption studies, NaP1 and NaP1CS after the sorption of MB and Cu(II) were used. The MB and Cu(II) concentrations in the solution were determined to calculate those of dye and Cu(II) in the filtrate. Afterwards the MB and Cu(II) loaded adsorbent was dried and the process of desorption was conducted in conical flasks on a mechanical shaker at 180 rpm and amplitude 7 for 240 min. In this process the solvents: 99.8% CH\(_3\)OH, 1 M NaCl, 1 M CH\(_3\)COOH, 96% C\(_2\)H\(_5\)OH, 1 M HCl, 1 M NaOH, H\(_2\)O were used.

Results and discussion

Characteristics of sorbents

Fig. S1(a and b) shows the FTIR spectra of NaP1 and NaP1CS before and after MB sorption in the range of the spectra absorbance 2000–600 cm\(^{-1}\) indicating only the most important bands. Besides those shown in the figures, the broad bands at 3418 cm\(^{-1}\) for NaP1 and 3390 cm\(^{-1}\) for NaP1CS contribute to the stretching vibrations of the O—H groups. After the MB sorption new bands appear at 2894 cm\(^{-1}\) and 2893 cm\(^{-1}\) for NaP1 and NaP1CS, respectively. Stretching vibrations derived from N—H and C—H in —CH\(_2\) as well as CH\(_3\) can be observed. The band 1640 cm\(^{-1}\) is characteristic only of NaP1CS. After the MB sorption its intensity increased which can be attributed to the N—H band indicating the presence of CS. Compared with the spectra before the MB sorption, three peaks at 1491 cm\(^{-1}\), 1394 cm\(^{-1}\) and 1342 cm\(^{-1}\) for NaP1 and three peaks at 1490 cm\(^{-1}\), 1392 cm\(^{-1}\) and 1345 cm\(^{-1}\) are shown in the spectra of MB adsorbed onto the zeolites NaP1 and NaP1CS. The above indicates the presence of C—S\(^\circ\), the C—N stretching vibrations and the CH\(_3\) group vibrations, respectively [12]. This proves that the adsorption of MB occurred. Moreover, the bands at 740 cm\(^{-1}\) and 734 cm\(^{-1}\) were shifted to 725 cm\(^{-1}\) and 734 cm\(^{-1}\), for NaP1 and NaP1CS after the MB sorption, respectively.

Textural characteristics of the zeolite surface were made using the nitrogen adsorption/desorption isotherms at a liquid nitrogen temperature 77.3 K using the sorption analyzer ASAP 2420 M (Micromeritics). Thus the most important textural properties were determined. The nitrogen adsorption/desorption isotherms are shown in Fig. S2. The obtained isotherm could be classified as the type-IV isotherm and the H2/H3 hysteresis loop according to the IUPAC classification. The IV type is characterized by the hysteresis loop and the desirable adsorption proceeds at the high pressure p/p\(_0\). This can be found in the case of porous adsorbents. The loop H2/H3 would indicate the presence of mesopores. The Brunauer—Emmett—Teller (BET) method was used to calculate the specific surface area of NaP1 and NaP1CS microparticles. The average BET specific surface area (S\(_{BET}\)) for NaP1 was equal to 98.49 m\(^2\) g\(^{-1}\). The total pore volume was 0.3018 cm\(^3\) g\(^{-1}\) and the micropore volume 0.0061 cm\(^3\) g\(^{-1}\). The desorption average pore width was 113.8 Å obtained based on the Barrett, Joyner and Halenda model (BJH). This can be compared with NaP1CS where the average BET specific surface area (S\(_{BET}\)) is 53.54 m\(^2\) g\(^{-1}\). The total volume of pores was 0.1336 cm\(^3\) g\(^{-1}\) and the micropore volume 0.0045 cm\(^3\) g\(^{-1}\). The desorption average pore width was 111.7 Å. These results indicate the modification process.

Morphological analyses of NaP1 and NaP1CS after the MB sorption were carried out using SEM (FEI Quanta 3D FEG) and the results are shown in Fig. S3. Typically the fly ash particles have a spherical shape and smooth surface. After transformation to zeolite, the surface became rugged, which indicates appearance of zeolite crystal clusters. The obtained images of NaP1 and NaP1CS after the MB sorption show irregular and cracked surfaces which indicates that the layer structure is filled with MB molecules.

As follows from the studies the hydroxyl groups of CS can react with the silanol and alumina groups of NaP1 with the hydrogen bonds formation and/or can get into the condensation reaction. Moreover, the amino groups of CS promote their hydrolysis and condensation. The reaction of the silanol and alumina groups with the carbonyl groups of CS can lead to formation of Si—O—C bonds:
Effect of initial solution pH

One of the decisive factors of the sorption process is the initial pH of the solution. Therefore the absorption process of MB and Cu(II) was studied, depending on the initial pH of the solution. The kinetics of the process are shown in Figs. 2 (a and b) and 3 (a and b).

As in Refs. [57,58] it was found that MB sorption capacity increases with the increasing pH of the solution. During the MB sorption there takes place the following process that is the electrostatic interactions between the cationic molecules of MB and CS molecules. This effect is evident when pH changes from 3 to 5 when great improvement in adsorption is observed. This process can be presented schematically as follows:

The same results were obtained in this paper although in the case of Cu(II), the trend is reversed, with the increasing pH q decreases. In the lower range of pH, the zeolite surface has positive charge. With the increasing solution pH, the sorption capacity increased due to the weaker forces of repulsion between the adsorbent and MB. Dependence of pH could be also explained from the zero charge (pH\textsubscript{pzc}). This parameter indicates positive or negative adsorbent surface charge. In the case of NaP1 the value was found to be about 9.0. Therefore the adsorbent surface has negative charge at pH > 9 and positive charge at pH < 9. Thus favorable pH for adsorption of cationic dyes such as MB will be greater than pH 9.

Moreover, the effect of pH on MB and Cu(II) with several modifications of zeolite with chitosan: NaP1CS H, NaP1CS M, NaP1CS L and two other modifications NaP1CS GLU and NaP1CS EPI on NaP1 and NaP1CS was studied as shown in Fig. 4(a and b). Besides, the raw fly ashes FA 1000, FA 5000 and NaP1 were also examined to determine the pH effect (Fig. 5(a and b)). The obtained capacities show that the highest values for Cu(II) were at pH 3 (e.g. NaP1CS—8.98 mg g\textsuperscript{-1}).

All types of modified zeolites show the same dependence but differences were not significant (from 8.64 to 8.98 mg g\textsuperscript{-1}). The inverse dependence was obtained for MB (e.g. NaP1CS—9.92 mg g\textsuperscript{-1}), the best pH was equal to 9. It can be also concluded that NaP1 is characterized by a greater value of q, compared to FA 1000 and FA 5000 for both MB and Cu(II). However, for simultaneous removal of MB and Cu(II) pH 5.0 was the most efficient.

Removal of MB as well as Cu(II), Fe(III), Mn(II), Zn(II) was also conducted. In this experiment NaP1CS was used as the adsorbent for comparison of modified fly ash with 1000 FA + CS. The obtained values of sorption capacity for NaP1CS are significantly higher than those for 1000 FA. For MB, Cu(II), Fe(III), Mn(II), Zn(II) on NaP1CS they were 9.34, 4.33, 3.41, 3.80, 5.5 mg g\textsuperscript{-1}, respectively. Whereas for 1000 FA these values were 1.41, 0.17, 1.38, 0.03 and 0.10 mg g\textsuperscript{-1}, respectively. Fig. S4(a and b) shows the above results.

Effects of initial concentrations of MB and Cu(II) and phase contact time

The simultaneous sorption process of MB and Cu(II) was studied at phase contact times (1–240 min), at two different initial concentrations of MB and Cu(II) (50 mg dm\textsuperscript{-3} and 50 mg dm\textsuperscript{-3} as well as 100 mg dm\textsuperscript{-3} and 100 mg dm\textsuperscript{-3}) at room temperature and pH 5, respectively (Fig. 6(a and b)).

It was found that the sorption capacity increases with the increasing initial concentration of the solution and the phase contact time. It was observed that for MB the equilibrium was achieved at 9.86 mg g\textsuperscript{-1}, 19.28 mg g\textsuperscript{-1} at the concentrations 50 and 100 mg dm\textsuperscript{-3} for NaP1 as well as 3.10 mg g\textsuperscript{-1}, 15.56 mg g\textsuperscript{-1} for NaP1CS, respectively. In the case of Cu(II) the plateau was established at 8.18 mg g\textsuperscript{-1} and 19.92 mg g\textsuperscript{-1} at the same
concentrations as for MB on NaP1 and 8.19 mg g\(^{-1}\) and 19.57 mg g\(^{-1}\) for NaP1CS. The equilibrium time was achieved after 60 min for each component. Furthermore, the MB and Cu(II) sorption curves are similar. In the initial stage, a rapid increase in the sorption capacity was observed, followed by a balance between the sorbent and adsorbate.

**Effect of foreign ions**

In order to study the selectivity of NaP1 and NaP1CS toward MB and Cu(II) ions, the adsorption of MB and Cu(II) ions was performed at appropriate concentrations and in the presence of foreign ions. The results are shown in Fig. 7(a and b). The presence of accompanying ions such as Cl\(^-\), NO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) increases the sorption capacity of NaP1 and NaP1CS for both MB and Cu(II). However with the addition of foreign ions (9.97 mg g\(^{-1}\)) and without (9.43 mg g\(^{-1}\)) the difference in sorption capacity is not significant.

**Kinetic models**

Under the optimum operating conditions, the kinetics of MB and Cu(II) removal were determined by means of kinetic models. The results show that the pseudo-second order kinetic model describes better the adsorption process than the pseudo-first order kinetic model. This is evidenced by the experimental data based on the \(R^2\) values. It is higher than 0.999 for both MB and Cu(II). This is consistent with the literature data showing that in the process of adsorption of heavy metal ions and dyes the kinetic pseudo-second order equation describes the phenomena best [59]. The adsorption capacity \(q_e\) and the adsorption rate constant \(k_2\) were established from the slope and intercept of the plot of \(q_t\) vs. \(t\). All obtained parameters are presented in Tables 2 and 3. The experimental values of \(q_t\) retrieved from the pseudo-second order were close to the theoretical ones. The adsorption rate decreased with the increase of the phase contact time as indicated by the low values of rate constant \(k_2\).

The experimental data were also fitted to the intraparticle diffusion model, so-called the Weber–Morris [60,61] plot of \(q_t\) vs. \(t^{1/2}\). The sorption process was controlled by intraparticle diffusion when the plots were a straight line but when the data proved multi-linear plots, the sorption process was influenced by two or more steps. The first stage of adsorption can be explained by the fact that the external resistance to mass transfer surrounding the particles is important in the early stages of adsorption. The second stage is linear and adsorption is controlled by the intraparticle diffusion. As follows from Tables 2 and 3, the values of \(R^2\) range from 0.729 to 0.983 for MB and from 0.832 to 1.0 for Cu(II). The value of the intercept \(C\) provides information about the thickness of the boundary layer. The greater the value of \(C\), the greater the effect of the boundary layer on the adsorption process. The
intraparticle diffusion plots show three-linear portions. Therefore there are two or more steps affected by the adsorption process. Tables 2 and 3, show that the order of adsorption rate decreases according to the three stages $k_1 > k_2 > k_3$.

At first, it was the instantaneous diffusion period $k_1$, where MB and Cu(II) were adsorbed by the outside surface of NaP1 and NaP1CS. Then the value of $k_2$ decreased which means that the exterior surface reached saturation, MB and Cu(II) diffused into the pores of NaP1 and NaP1CS. During the third stage the equilibrium was reached and the intraparticle diffusion rate $k_3$ slowed down. The intraparticle diffusion cannot be accepted as the only rate controlling step for the adsorption of MB and Cu(II) on NaP1 and NaP1CS as it results from the non-linearity of the plots. Thus, the whole process of adsorption can be controlled by more than one step.

**Adsorption isotherms**

The experimental results were fitted using the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The Langmuir isotherm is described as homogeneous within the adsorbent surface because once a molecule occupies a site, no adsorption can take place at that site. Therefore the adsorption process is monolayer in nature. The Freundlich isotherm model shows that the adsorption process proceeds on the heterogeneous surface. Its mechanism is multilayer [62,63]. The third model is the Temkin isotherm which assumes interactions between the adsorbents and adsorbates. They cause the linear decrease of the adsorption heat of the molecules in the layer with coverage [64]. Finally, the Dubinin–Radushkevich model is useful to determine the adsorption type and it describes absorption in the micropores [65]. The experimental results are shown in Tables 4 and 5.

**Table 2**

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<td>0.999</td>
</tr>
<tr>
<td>$h$</td>
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<tr>
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</tr>
<tr>
<td>$R^2_3$</td>
<td>0.729</td>
<td>0.846</td>
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It was found that the Langmuir model fits the best, with the highest determination coefficient values $R^2$ (0.978–0.996) for both MB and Cu(II) when compared it with the Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The value of $R_e$ indicates the nature of the adsorption process. If the value of $R_e = 1$ the process is linear, if $R_e > 1$ the process is unfavorable and if $0 < R_e < 1$ it is favorable. In this study the obtained values $R_e$ related to MB and Cu(II) were 0.172–0.395 so the adsorption process is favorable.

The Temkin isotherm parameters $A$, $B$ and $R^2$ are also presented in Tables 4 and 5. These constants $A$ (gd$^{-1}$m$^{-2}$) and $B$ (m$^2$mol$^{-1}$) are associated with the adsorption potential and the heat of adsorption, respectively. The parameter $B$ for both MB and Cu(II) increases with the temperature. The data of $R^2$ obtained from the Temkin model indicate that for MB the values of $R^2$ range from 0.871 to 0.932. The highest value of $R^2$ for Cu(II) adsorption is 0.985 at 313 K, so these results show that this isotherm is suitable for description of the isotherm of Cu(II) adsorption on NaP1CS.

The values of $R^2$ in the Dubinin–Radushkevich isotherm from Tables 4 and 5 prove to be higher for Cu(II) than MB. NaP1CS exhibits higher adsorption capacity for Cu(II) than for MB. This means that the Dubinin–Radushkevich isotherm gives a very good fit for Cu(II) adsorption. Furthermore, it is reported that when the value of $E$ is below 8 kJ/mol, the adsorption process can be defined as the physical one. However, if the value of $E$ is in the range of $>$8 kJ/mol, this is the chemical adsorption. It follows from Tables 4 and 5 that the obtained values of $E$ are in the range 14.721–32.113 which indicates chemical adsorption.

### Thermodynamic analysis

The values of $\Delta G^\circ$ were calculated from Eq. (11) and $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of the plot of ln $K_e$ vs. $T^{-1}$. The value of $\Delta H^\circ$ is very useful for determining the type of adsorption. Physisorption is generally below 20 kJ mol$^{-1}$, in the range 20–80 kJ mol$^{-1}$ the physisorption together with chemisorption occurs and in the range 80–400 kJ mol$^{-1}$ chemisorption takes place [66]. All set parameters are shown in Table 6.

In this case the values for MB and Cu(II) are 13.32 kJ mol$^{-1}$ and 26.59 kJ mol$^{-1}$, respectively. This denotes a physical adsorption process. The positive value of $\Delta H^\circ$ for the adsorption process of MB and Cu(II) on NaP1CS shows that the adsorption was an endothermic process with random characteristics.

Calculations of $\Delta G^\circ$ indicate that the adsorption process is spontaneous due to the negative values of this parameter for both MB and Cu(II) at all temperatures. Increase in temperature and decrease in the values of free energy change indicate that the adsorption process is more favorable at higher temperatures [67]. The entropy change $\Delta S^\circ$ was 29.91 J mol$^{-1}$ K$^{-1}$ for MB and 89.6 J mol$^{-1}$ K$^{-1}$ for Cu(II). The positive value of this parameter indicates an increase in randomness at the solid/solution interface during the adsorption process. This value also indicates whether the mechanism of adsorption is associative or dissociative. If the value is greater than $–10$ J mol$^{-1}$ K$^{-1}$, the process of adsorption is in the dissociative form. The obtained values of $\Delta S^\circ$ for MB and Cu(II) indicate the associative mechanism of adsorption.
agents such as initial pH, contact time, initial MB and Cu(II) concentrations, temperature and the presence of foreign ions such as nitrate, chloride, and sulfate. The experimental data for MB and Cu(II) are consistent with the pseudo-second-order kinetic model and show the presence of intraparticle diffusion mechanism. Of the adsorption isotherm models tested, the Langmuir one gave the best fit to the experimental data for both MB and Cu(II). The thermodynamic studies showed an endothermic process with the increasing qe of both MB and Cu(II) with temperature. The obtained values of ΔS° for MB point out to the associative mechanism of adsorption.

Acknowledgment

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References
