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ORIGINAL CONTRIBUTION

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Thermo-XRD-analysis and peptization study of the adsorption of alizarinate by Co-, Ni-, and Cu-montmorillonite

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Abstract The adsorption of the monovalent anionic dye alizarinate onto Co-, Ni- and Cu-montmorillonite was carried out by adding the dye into aqueous clay suspensions. During the loading of the clay suspension by alizarinate, only some of the added organic anion is adsorbed by the clay forming *d*-coordination chelate complexes on the clay surface. Maximum adsorption of Co-, Ni- and Cu-clay were 13, 13 and 25 mmol dye per 100 g clay. Since the capacity of the clay for these transition metal cations is 38 mmol per 100 g clay, these saturations indicate that only part of the transition metal cations form positively charged *d*-coordination chelate complexes with metal:ligand ratio of 1. The complex cations can be located inside the interlayer spaces or on the broken bonds surfaces. Thermo-XRD-analysis and peptization studies of the solids and the clay water systems respectively were used here to identify the sorption sites. The Co and Ni complexes were obtained on the broken bonds surfaces whereas the Cu complexes were obtained in the interlayer space. Co^{2+}, Ni^{2+} and Cu^{2+} were extracted from the clay into suspensions containing excess alizarinate.

Keywords Alizarinate adsorption · Co-alizarinate complex · Cu-alizarinate complex · Montmorillonite · Ni-alizarinate complex · Peptization · Thermo-XRD-analysis

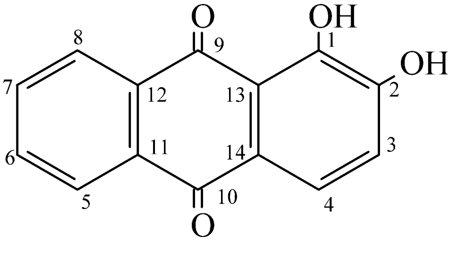
Introduction

The present paper is part of our study on the adsorption of organic anions by clay minerals, which has been performed in our laboratory for several years [1]. The principal adsorption sites for anions are the broken bonds, at the edges of the clay platelets [2]. Anions of strong acids are nonspecifically adsorbed onto the broken bonds surfaces of layer clay minerals by Coulombic interactions. The adsorption capacity depends on the pH of the system; it decreases with the rise in pH. Anions of weak acids are specifically adsorbed onto the broken bonds surfaces of layer clay minerals by partial covalent interactions [3]. It may result from exchange with surface ligands followed by the formation of localized bonds. The adsorption capacity depends on the pH, showing a correlation between the pK of the acid and the pH of maximum sorption [4]. When the organic anions are large, van der Waals interactions between adjacent adsorbed species may contribute to the adsorption. In addition, they break the water structure in the vicinity of the clay surface and thereby increase the role of hydrophobic adsorption [5]. On the basis of the knowledge of the adsorption mechanism of inorganic anions, Yariv [1] suggested six different mechanisms for the adsorption of organic anions: (1) adsorption by the mechanism of nonspecific anion exchange followed by van der Waals interactions; (2) adsorption by the mechanism of nonspecific anion exchange followed by the formation of hydrogen bonds between the anion and Brønsted acid surface groups; (3) replacement of exposed OH groups; (4) coordination with nonhydrated polyvalent cations (mainly of transition metals) at the edges of surface groups, which are strong Lewis acid sites; (5) sorption on oligomeric hydroxy cations sorbed earlier on the broken-bonds surface; and (6) sorption on bi- or polydentate organic cations sorbed earlier on the broken-bonds surface, and bridging between a negative site on the broken bonds, and the adsorbed organic anionic species.

Adsorption of anions into the interlayer space seems to be more complicated [6]. Negatively charged oxygen planes border the interlayer space, and, consequently negatively charged species should be repelled from this space. Anions are adsorbed from aqueous solutions by smectites only if they can form positively charged coordination species. For example, the reaction between the anionic herbicide glyphosate, known commercially as Roundup, $[CO_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}PO_3H]^{2-}$, which is adsorbed by Al-montmorillonite by forming a cationic chelate complex in the interlayer space [7].

In a previous publication the adsorption of the monovalent anionic species alizarinate by Al- and Na-montmorillonite was investigated [8]. By thermo-XRD-analysis and peptization we showed that on Al-montmorillonite the alizarinate was adsorbed into the interlayer space and onto the broken-bonds surface whereas on Na-montmorillonite it was adsorbed onto the broken–bonds surface. By visible-spectroscopy study of the alizarinate-montmorillonite complexes we concluded that in Al-montmorillonite alizarinate formed a coordination complex with exchangeable Al^{3+}. In Na-montmorillonite it formed bonds with Al exposed on the broken-bonds sites.

Alizarin (1,2-dihydroxyanthraquinone, Scheme 1) is a di-basic acid. The corresponding pK values in aqueous solution are equal to 5.98 ± 0.05 and 9.88 ± 0.05, respectively [9]. Fully protonated alizarin is insoluble in water. At pH between 6.8 and 10.1 most alizarin occurs as a red monovalent anion and is soluble. As an analytical reagent, it is used for the determination of several transition metallic cations, such as Co^{2+}, Ni^{2+} and Cu^{2+}, by forming colored lake complexes [9, 10, 11, 12, 13, 14]. The present paper describes the study of the adsorption of monovalent alizarinate anion by Co-, Ni- and Cu-montmorillonite. The amounts of adsorbed dye were determined from the spectra of the supernatants. We also describe thermo-XRD-analyses of the solid organo-clay complexes. This study should give information on whether the alizarinate is adsorbed into the interlayer space. The colloid properties of clay systems depend very much on the adsorption of organic species onto the broken-bonds surface. It is therefore expected that the adsorption of alizarinate onto the broken-bonds surface will have an effect on the peptization of the clay. In the present paper we describe the effect of the exchangeable metallic cation and of the amount of adsorbed alizarinate on the peptization of the clay. The peptization was determined by the chemical analysis of the elements Si, Al and Mg in the supernatants of the clay-dye suspensions obtained after similar centrifugation conditions (standard centrifugation).



Scheme 1

Experimental

Materials

Montmorillonite used in the present study (Wyoming bentonite supplied by Words, Natural Establishment, Inc), the determination of its exchangeable cations and its purification were previously described [15]. Alizarin was supplied by Sigma and was used as received. According to specification tests of the manufacturer there was 1% sulfated ash. Thin-layer chromatography and pH transition showed purity corresponds to standards.

Methods

Co-, Ni- and Cu-montmorillonite were prepared by suspending 2 g of the purified Na-clay for 24 h in 40 mL of 0.1 mol/l of the nitrate salts. The monoionic clays were washed four times in 200 mL of distilled water and separated by centrifugation (4000 rpm for 15 min). Suspensions of 1.0% monoionic clay were used as stock solutions.

Aqueous NaH-alizarinate stock solution was prepared from neat alizarin dissolved in 0.001 mol/l NaOH solution with a final pH of 9.2 ± 0.2 [8]. A 5×10^{-4} mol/l alizarinate solution was used as a stock solution. A fresh solution was prepared every four weeks.

The preparation of the aqueous clay suspensions, the treatment in an ultrasonic bath and the loading of the suspension by the required amount of NaH-alizarinate were previously described [8].

Thermo-X-ray diffraction analysis Samples for XRD were prepared as follows: 12 mL suspensions of 0.1% (final concentration) of Co- Ni- and Cu-montmorillonite, unloaded or loaded with NaH-alizarinate solution (5, 10, 20, 50 and 75 mmol alizarinate per 100 g clay, the latter only in the case of Cu-montmorillonite) were left for 48 h in measuring cylindrical tubes. After the sedimentation of the clay to a volume of about 1.0 mL, the upper 11.0 mL water, which contained most of the excess non-adsorbed dye, was decanted. The 1.0 mL concentrated clay suspensions were air dried on microscope glasses. The XRD measurements of the dried samples were made at room temperature and in air atmosphere. Samples were diffracted before any thermal treatment and after heating them at 120, 250 and 360 °C for 3 h at each temperature. XRD diffractograms were recorded by using a Phillips Automatic Diffractometer (PW 1710) with a Cu tube anode.

ICP measurements Determination of Si, Al, Mg, Co, Ni and Cu in the supernatants of the different monoionic montmorillonite suspensions, before and after the loading with increasing amounts of alizarinate, was carried out by ICP analysis (Inductively Coupled Plasma). Si, Al, Mg compose the clay framework and their presence in the supernatants is due to the presence of peptized clay. Exchangeable Co, Ni and Cu may be released from the clay after the treatment with alizarinate by cation exchange with Na of the alizarinate salt due to their extraction by the excess organic dye. For this purpose series of the different mono-ionic montmorillonites, containing a constant amount of clay (0.1 wt%) and increasing amounts of dye (final concentrations between 5×10^{-5} and 4.5×10^{-4} mol/l) were prepared. The final pH of the clay-dye suspension was 8.8 ± 0.2. When necessary, it was adjusted with a few micro-drops of NaOH. All suspensions were centrifuged (4000 rpm) for 10 min after an aging period of 24 h. The ICP measurements of the supernatants were carried out on a Perkin Elmer Optima 3300 instrument after the addition of scandium oxide as an internal standard. The peptized clay should lead to a mistake (high results) in the determination of Co, Ni and Cu in the supernatants because of the presence of these cations on the peptized clay and because of light scattering. This mistake should be very small because of the very small amounts of peptized clay.

Exchangeable Co, Ni and Cu in Co-, Ni- and Cu-montmorillonite, respectively, were determined after their extraction from 100 mL 1% aqueous clay suspension with 10 mL glacial acetic acid. The suspension was heated to boiling and after an aging period of 48 hours at room temperature it was centrifuged and the three elements were determined by ICP. The clay capacity of these three elements is 38 mmol (or 76 meq) per 100 g clay.

Spectroscopy study of the adsorption of alizarinate Electronic spectra of the supernatants, containing the non-adsorbed dye, were recorded and their absorbance determined in order to calculate the amounts of dye, which were adsorbed by the clay. For this purpose series of the different monoionic montmorillonites, loaded by a constant amount of dye (5×10^{-5} M) and increasing amounts of clay (final concentrations between 0.005 and 0.5%) were prepared. Another series of the different monoionic montmorillonites was prepared with a constant amount of clay (0.04%) and increasing amounts of dye. The supernatants were separated after an aging period of 24 h in a refrigerator (4 °C). This aging period in the refrigerator leads to the flocculation of most of the peptized montmorillonite leaving the supernatant free from most of the peptized material. After the separation of the sediments the supernatants were centrifuged twice for additional 10 min. Spectra of the supernatants were recorded by a Milton Roy Genesis 2 scanning spectrometer, in the 300–700 nm range, using quartz 10 mm cells. The spectrometer operation program made integration of areas under curves. The area under a peak at 515–535 nm, due to n-π^* transition [14], was used to determine the amounts of non-adsorbed alizarinate. In this integration, the calculation is made relative to an extrapolated base-line of the alizarinate spectrum, thus minimizing the effect of light scattering of peptized particles which were not flocculated at 4 °C. It should be noted that the presence of small amounts of transition cations in the supernatants results in a slight shift in the band maximum and in the absorbance and consequently there is a slight inaccuracy in the determination of non-adsorbed dye. These amounts were calculated by subtracting the peak area in the spectrum of the supernatant from that of a clay-free NaH-alizarinate solution with a concentration similar to that of the solution used for the equilibrium system.

Results

Adsorption of alizarinate by the clay

Figure 1 shows the adsorption curves of alizarinate by Co-, Ni- and Cu-clays, calculated from the amounts of residual non-adsorbed dye in the supernatants, determined by visible spectroscopy measurements. For comparison adsorption curves of Na- and Al-montmorillonite from our previous work [8] are also shown in the figure. Na-montmorillonite adsorbs alizarinate up to 4 mmol per 100 g clay; however, this adsorption is achieved when the loading (the total amount of dye in the equilibrium system) is equivalent to 10 mmol per 100 g clay (curve a). Ni- and Co-montmorillonite adsorb up to 13 ± 1 mmol per 100 g clay (curves b and c, respectively), but it should be noticed that in Ni-montmorillonite

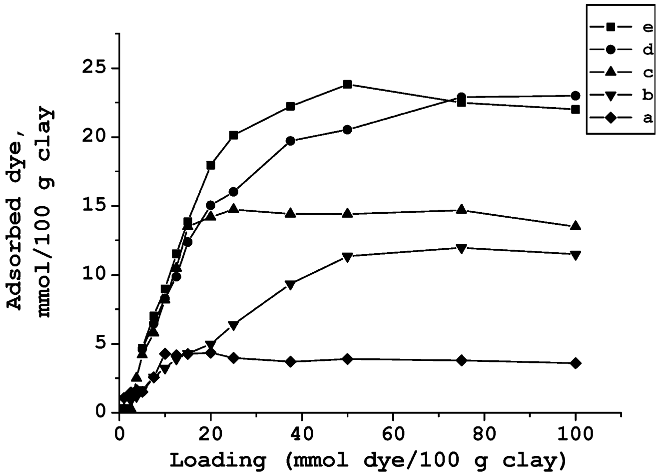


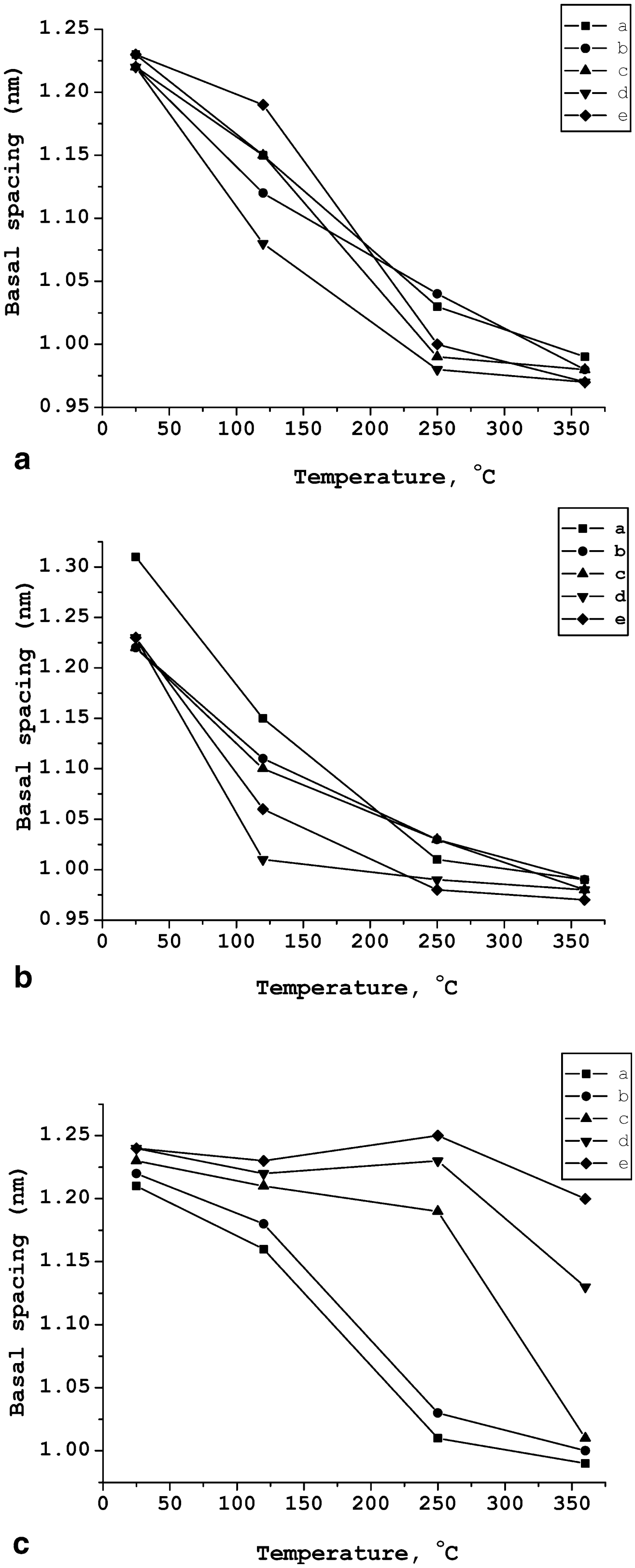
Fig. 1 Adsorption of alizarinate by Na-, Ni-, Co-, Cu- and Al-montmorillonite (curves a, b, c, d and e respectively) as a function of the loading of the clay in aqueous suspension by NaH-alizarinate. The adsorptions and loadings are expressed in mmol dye per 100 g clay

saturation is achieved at a loading of 50 mmol per 100 g clay, while in Co-montmorillonite it is achieved at a loading of 20 mmol per 100 g. Cu- and Al-montmorillonite both adsorb up to about 25 ± 1 mmol per 100 g clay (curves d and e, respectively); however, in Cu-montmorillonite saturation is achieved at a loading of 75 mmol per 100 g clay, whereas in Al-montmorillonite it is already achieved at a loading of 50 mmol per 100 g clay.

X-ray diffraction

Co-, Ni- and Cu-montmorillonite, unloaded and loaded with different amounts of alizarinate, were examined by XRD. Figure 2 shows the basal spacings as recorded at room temperature, before and after heating the samples to different temperatures (thermo-XRD-analysis curves). For comparison thermo-XRD-analysis curves of Na- and Al-montmorillonite based on data from our previous work [8] are also discussed. In the diffractograms of thermal treated Na-, Ni- and Co-montmorillonite a sharp *001* peak was recorded whereas in those of thermal treated Al- and Cu-montmorillonite the *001* peak was broad.

Fig. 2A–C The effect of temperature on the basal spacings of Ni-, Co-, and Cu-montmorillonite unloaded (curves a) and saturated with different amounts of alizarinate: **A**—Ni-montmorillonite saturated with 2, 3, 5 and 13 mmol alizarinate per 100 g clay (curves b–e, respectively); **B**—Co-montmorillonite saturated with 4, 8, 13 and 13 mmol alizarinate per 100 g clay (curves b–e, respectively); **C**—Cu-montmorillonite saturated with 5, 8, 15 and 21 mmol alizarinate per 100 g clay (curves b–e, respectively)



The thermo-XRD-analysis curves of Na-montmorillonite, unloaded and loaded with different amounts of alizarinate (see [8]) showed that before the thermal treatment there were no significant differences in the basal spacings of the alizarinate loaded samples compared with that of unloaded Na-montmorillonite. The basal spacing of 1.19–1.25 nm is characteristic for a water monolayer in the interlayer space [16]. After thermal treatments at 360 °C it decreased to about 0.97–1.00, due to the evolution of water from the interlayer, suggesting the absence of organic matter in this space [16].

The thermo-XRD-analysis curves of Co- and Ni-montmorillonite, unloaded and loaded with different amounts of alizarinate (Fig. 2A,B) show that these clays behave similar to the Na-clay. Before the thermal treatment the basal spacings are characteristic for the presence of water monolayer in the interlayer space and after the thermal treatment at 360 °C they decreased to about 0.97–1.02 nm, indicating a collapse of the interlayer [16]. Concerning the samples treated with alizarinate, these observations suggest that already before the thermal treatment, the adsorbed alizarinate in any loading used in the present study was located outside the interlayer space [17, 18, 19].

In Al-montmorillonite the adsorption of the dye resulted in slightly smaller basal spacings (measured at room temperature and air atmosphere) compared with that of the untreated clay (1.40–1.47 nm in the loaded clay and 1.50 nm in the unloaded clay [8]). A basal spacing of 1.52 nm is characteristic for a bilayer of water in the interlayer space [16]. In Al-montmorillonite we showed previously that adsorbed alizarinate was located inside the interlayer space [8]. As a consequence, the hydrophobicity of the interlayer space increased and the amount of interlayer water in ambient atmosphere decreased [5].

When unloaded Al-montmorillonite was heated at 360 °C, the basal spacing drastically decreased to 1.02 nm, indicating that the clay collapsed [16]. The basal spacings of Al-alizarinate-montmorillonite containing 5, 9, 18 and 25 mmol alizarinate per 100 g clay, after a thermal treatment at 360 °C, became 1.07, 1.13, 1.16 and 1.15 nm, respectively [8]. These spacings are significantly large suggesting the formation of a charcoal layer inside the interlayer space [17, 18, 19, 20]. Charcoal in the interlayer space can be formed only if the adsorbed organic matter was initially located there. The charcoal is the thermal oxidation-condensation product of the organic dye, which was partially oxidized during the heating. After the thermal treatment the Al-alizarinate-clay samples became completely black. The gradual increase of the basal spacing with the loading (up to 20 mmol per 100 g) indicates that larger amounts of charcoal were obtained inside the interlayer space with increasing amounts of adsorbed organic matter.

In Cu-montmorillonite, as shown in Fig. 2C, there are no significant differences between the alizarinate loaded and the unloaded samples at room temperature. The basal spacing of 1.21–1.23 indicates the presence of a water-alizarinate mono-layer inside the interlayer space [16]. The thermo-XRD-analysis curve of the unloaded clay shows that at 360 °C the basal spacing became 0.99 nm, indicating dehydration and collapse of the clay while in the Cu-alizarinate-montmorillonite complexes the basal spacings were 1.00, 1.01, 1.13, 1.20 and 1.20 nm, after the adsorption of 5, 8, 15, 21 and 25 mmol of alizarinate per 100 g clay (loadings of 5, 10, 20, 50 and 75 mmol per 100 g clay), respectively. From these results it is obvious that in samples with more than 8 mmol dye per 100 g clay the adsorbed alizarinate is located inside the interlayer space [17, 18, 19, 20].

Chemical analysis of Al, Mg and SiO_2 in the supernatants

Figure 3 (A, B and C) shows the concentrations of Al, Mg and SiO_2, respectively, in the supernatants of Co-, Ni- and Cu-montmorillonite as a function of the loading of the clay by alizarinate. All the supernatants contain the three principal elements of the clay framework besides oxygen, indicating that under the present conditions the centrifuge did not separate some of the suspended clay fine particles. The non-separated fraction is considered here as the peptized clay. This is supported by the molar ratios of Mg and Al to SiO_2. In the untreated clay they are 0.068 ± 0.02 and 0.37 ± 0.01, respectively. After any of the treatments with alizarinate, these ratios are 0.067 ± 0.02 and 0.38 ± 0.01, very similar to the ratios found for the untreated clay. We therefore consider the analysis of these three elements as a tool for getting information on the peptization of the clay and the curves of Fig. 3 as peptization curves.

In Co- and Ni-montmorillonite treated with increasing amounts of the dye, Al, Mg and SiO_2 concentrations in the supernatants increased with adding alizarinate from the very beginning, up to loadings of 20 and 50 mmol dye per 100 g Co- and Ni-clay, respectively. In Cu-montmorillonite, the concentrations of Al, Mg and SiO_2 in the supernatants did not change with the loading of the clay by alizarinate.

Chemical analysis of Co, Ni and Cu in the supernatants

Figure 4 shows the concentrations of Co^{2+}, Ni^{2+} and Cu^{2+}, which were detected in the supernatants of Co-, Ni- and Cu-montmorillonite, respectively, as a function of the loading of the clay by alizarinate. The figure shows that with small loadings the concentrations of the transition metal cations did not change significantly.

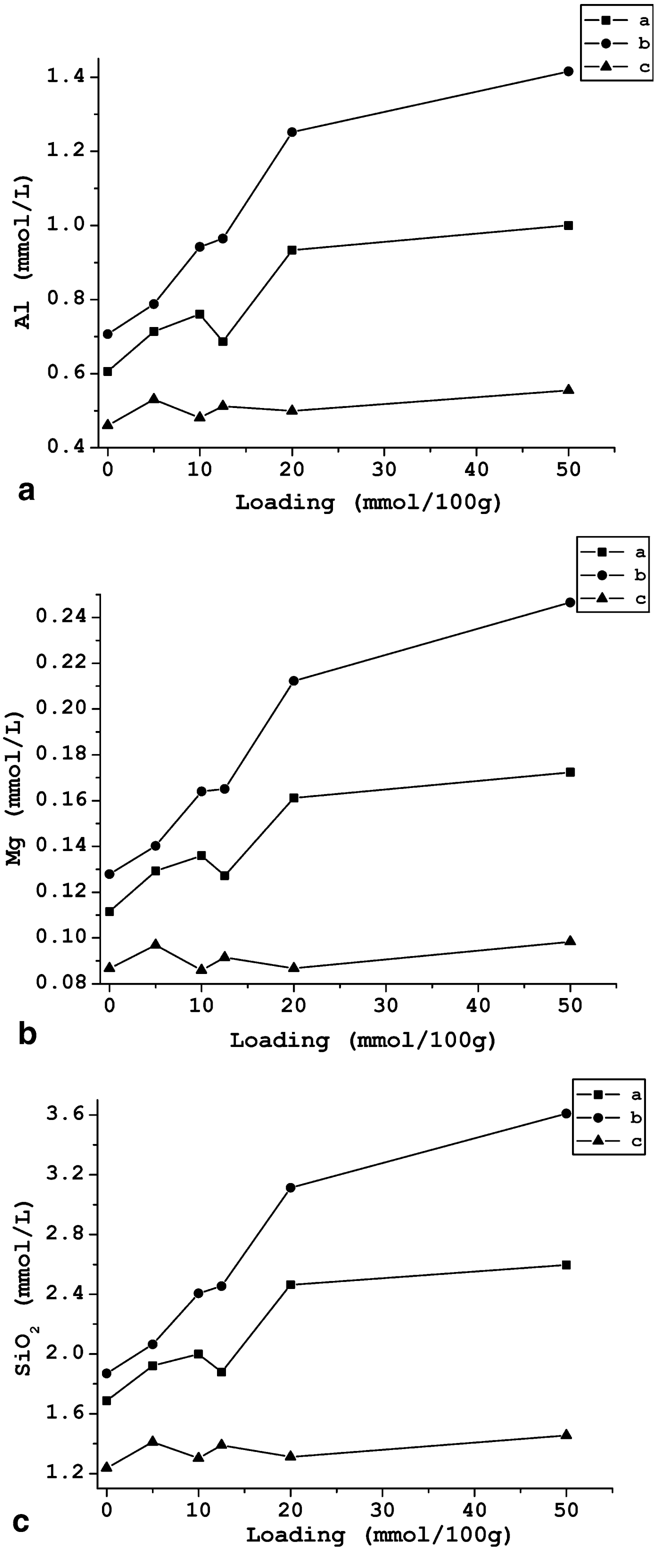


Fig. 3A–C The amounts of: **A** Al; **B** Mg; **C** SiO_2 (in mmol per 1000 ml) in the supernatants of Cu-, Co- and Ni-montmorillonite (curves a–c, respectively) as a function of the loading of the clay by alizarinate

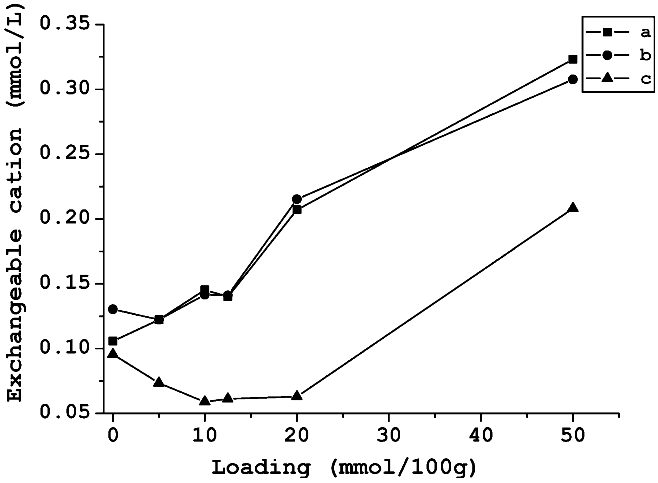


Fig. 4 The amount of Cu^{2+}, Co^{2+} and Ni^{2+} (in mmol per 1000 ml) in the supernatants of Cu-, Co- and Ni-Montmorillonite as a function of the loading of the clay by alizarinate (curves a–c, respectively)

Co^{2+} and Ni^{2+} in the respective supernatants increased mainly when the loadings were above 13 mmol dye per 100 g clay and that of Cu^{2+} increased mainly when the loadings were above 25 mmol dye per 100 g clay.

Discussion

When aqueous suspensions of mono-ionic montmorillonites are loaded by alizarinate aqueous solutions, there is a partition of the organic anion between the aqueous and the solid phases. Visible spectroscopy analysis of the supernatants proved that all the investigated mono-ionic montmorillonites adsorb alizarinate anion, under the conditions described here. However, the maximum adsorption and its mechanism depend on the exchangeable cation. Alizarinate adsorption of Ni- and Co-montmorillonite is thrice than that of Na-clay, and adsorption of Cu- and Al-montmorillonite is almost twice than that of Co- or Ni-montmorillonite, indicating different modes of adsorption.

The dependency of the alizarinate adsorption on the exchangeable cation may be associated with the formation of metal-ligand *d*-complexes between alizarinate and the exchangeable cations [9, 10, 11, 12, 13, 14]. Divalent transition metal cations form stable six-member chelate ring complexes with this ligand through the deprotonated 1-hydroxyl oxygen and the adjacent carbonyl oxygen. When these complexes were precipitated from aqueous-ethanol solutions, the metal:ligand molar ratio was 1:2 [21] and they were non-charged. Since the capacity of the clay for these cations is 38 mmol per 100 g clay, the present saturations indicate that only part of the transition metal cations form positively monovalent cationic charged *d*-coordination chelate complexes with metal:ligand ratio of 1. This is in agreement with our previous conclusions that anions are adsorbed by smectites as long as they form positively charged coordination species [6].

Na^+ does not form complexes with alizarinate and, consequently, only small amounts of alizarinate are adsorbed by Na-montmorillonite and are located on the broken bonds surfaces. The relatively high alizarinate adsorption capacity of Al-montmorillonite was previously attributed to the formation of a stable coordination complex between alizarinate and Al^{3+}. A similar interpretation can be applied in the present study for the high alizarinate adsorption capacities of Co-, Ni- and Cu-montmorillonite. During the loading of the clay suspension by alizarinate, anions are adsorbed by the clay forming *d*-coordination chelate complexes. The complex cations can be located inside the interlayer spaces or on the broken bonds surfaces. Thermo-XRD-analysis and peptization studies of the clay water systems are used here to identify the adsorption sites.

The thermo-XRD-analysis showed that by heating the unloaded montmorillonites at 360 °C, the basal spacings drastically decreased to ≈0.99 nm, indicating that most of the interlayer water evolved during the thermal treatment and the clay collapsed.

After the adsorption of alizarinate by these montmorillonites the basal spacings of the thermal treated organo-clay-complexes depended on the metallic exchangeable cation and on the amount of adsorbed alizarinate. In the present paper we discuss only the spacings, which were obtained when the adsorption was equivalent to the alizarinate adsorption capacity (maximum adsorption). This is sufficient for getting the necessary information on the different adsorption sites of the organic anion. Since the XRD peaks are not always sharp and the diffraction series are sometimes non-integral, a curve-fitting treatment is required for an accurate study of the effect of loading on the location of the adsorbed organic ion. This will be presented in a separate paper.

The basal spacing of Na-, Ni- and Co-montmorillonite saturated with 4, 13 and 13 mmol alizarinate per 100 g clay, respectively, was before the thermal treatment 1.19–1.25 nm, characteristic for one water layer in the interlayer space, and after a thermal treatment at 360 °C it decreased to about 0.98 nm, suggesting the absence of organic matter in this space, already before the thermal treatment. It may be concluded that with these exchangeable cations adsorbed alizarinate is located outside the interlayer.

Al- and Cu-alizarinate-montmorillonite containing 25 mmol alizarinate per 100 g clay, after a thermal treatment at 360 °C, become 1.20 nm. This spacing suggests the formation of a charcoal layer inside the interlayer space. The formation of charcoal in the interlayer space indicates that the adsorbed alizarinate has been initially located there.

Chemical analysis of Al, Mg and SiO_2 in the supernatants obtained after centrifugation may give information on the presence of peptized clay in these systems. In spite of the dependency of the content of these elements on the loading of the system by alizarinate, the molar ratios Al/SiO_2 and Mg/SiO_2 remained constant in the whole series, proving that these elements are components of the peptized clay. The mechanism of peptization of Na-montmorillonite by pyrogallol (1,2,3-trihydroxybenzene) in the form of the sodium salt was described by van Olphen [22]. He suggested that the adsorption of the organic anions on the positive sites at the broken-bonds, neutralizes the positive charge of the broken-bonds surface and consequently, edge-to-face flocs are peptized. In our study we use the clay peptization as a proof to the adsorption of the organic anion on the broken-bonds surface. In our previous study [8] we showed that Na-montmorillonite was peptized by alizarinate up to a loading of 5 mmol dye per 100 g clay. Al-montmorillonite peptization increased up to 50 mmol dye per 100 g clay.

In Cu-montmorillonite, where the thermo-XRD-analysis showed that the dye was adsorbed into the interlayer space, the concentration of the peptized clay in the supernatants did not change with the loading of the clay by alizarinate, indicating that in this case alizarinate did not serve as a peptizer and probably was not adsorbed on the broken-bonds surface.

In Co- and Ni-montmorillonite, where the thermo-XRD-analysis showed that the adsorbed dye was not located inside the interlayer space, loading with increasing amounts of alizarinate resulted in increasing amounts of peptized clay from the very beginning, up to loadings of 20 and 50 mmol dye per 100 g Co- and Ni-clay, respectively. The fact that the peptization of these clays increased with the adding of alizarinate suggests that the adsorbed organic anion reacts as a peptizing agent and was adsorbed on the broken-bonds surface. It should be noticed that the latter loadings are much above the anion adsorption capacities of the clays but they occur at the stage when the maximum loading is obtained.

The differences between the shapes of the peptization curves of Co- and Ni-montmorillonite are compatible with the differences between the shapes of their adsorption curves (compare curves b and c in Fig. 1 with curves b and c, respectively, in Figs. 3A, B and C). In Ni-montmorillonite maximum adsorption (13 mmol alizarinate per 100 g clay) and maximum peptization are achieved at a loading of 50 mmol per 100 g clay, while in Co-montmorillonite maximum adsorption (13 mmol alizarinate per 100 g clay) and maximum peptization are achieved at a loading of 20 mmol per 10 g clay.

Co^{2+}, Ni^{2+} and Cu^{2+} were detected in the supernatants (Fig. 4). The concentrations of Co^{2+} and Ni^{2+} in the respective supernatants increased mainly when the loadings were above 13 mmol dye per 100 g clay and that of Cu^{2+} increased mainly when the loadings were above 25 mmol dye per 100 g clay. These loadings are similar to the adsorption capacities of alizarinate by the respective clays. However, it should be remembered that the maximum adsorption of alizarinate occurs at higher loadings.

There are two possibilities for the appearance of Co^{2+}, Ni^{2+} and Cu^{2+} in the supernatants: (1) as the exchangeable cations of peptized clay and (2) as a result of being extracted into the sodium alizarinate solution. This extraction occurs due to the affinity of Co^{2+}, Ni^{2+} and Cu^{2+} to form aqueous soluble *d*-complexes of alizarinate. In the latter case, the clay adsorbs Na^+ from the sodium alizarinate, replacing the exchangeable transition cation. In Fig. 5 the effect of loadings on the molar ratios between Co^{2+}, Ni^{2+} or Cu^{2+} and SiO_2 in the supernatants are shown. For the first possibility, since SiO_2 in the supernatant results from the peptized clay, it is expected that this ratio remains constant and does not depend on the loadings. For the second possibility, it is expected that this molar ratio will increase with the loadings. The decrease in this ratio in loadings up to 5.0 mmol dye per 100 g clay, is not clear and may be due to experimental errors. Comparing between Fig. 4 and 5 indicates that the extraction of Co^{2+} from Co-montmorillonite begins at very small loadings. The extraction of Ni^{2+} and Cu^{2+} from Ni- and Cu-clay, respectively, begins only with loadings equivalent to the adsorption capacities of alizarinate by the respective clays.

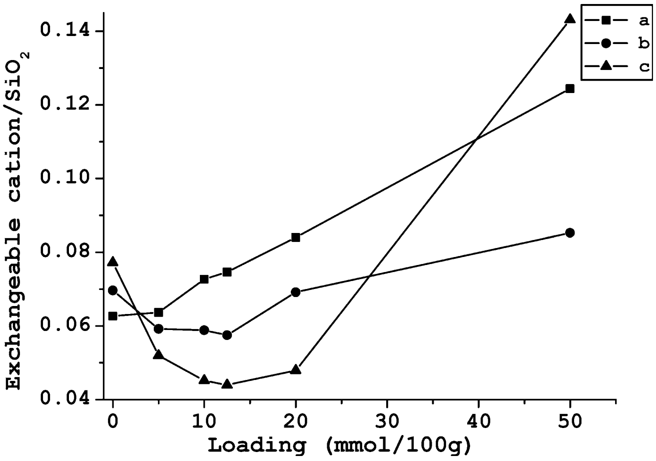


Fig. 5 The Cu^{2+}, Co^{2+} and Ni^{2+}/SiO_2 molar ratio in the supernatants of Cu-, Co- and Ni-Montmorillonite as a function of the loading of the clay by alizarinate (curves a–c, respectively)

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