

## Adsorption of phenol and chlorophenols on pure and modified sepiolite

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**Abstract:** In this work, pure sepiolite and sepiolite modified by nitric acid (HNO<sub>3</sub>), ethylenediaminetetraacetic acid (EDTA) and hexadecyltrimethylammonium (HDTMA) were used as adsorbents. The changes on the surface were studied by IR spectroscopy. The adsorption of solutions of phenol and phenol derivatives in pure ethanol on these adsorbents were examined by means of gas chromatography. It was found that the adsorption capacities of the clay–organic complexes (sepiolite–EDTA and sepiolite–HDTMA) were higher than those of pure sepiolite and sepiolite–HNO<sub>3</sub>.

**Keywords:** adsorption, clay, sepiolite, phenol, chlorophenol.

### INTRODUCTION

In our world, organic pollutants are still a problem for the environment and drinking water. Clay minerals possess a net negative electrical charge, which is compensated for by exchange cations on their surface. In nature, these exchange ions are mainly alkaline and alkaline earth metal ions, such as Na<sup>+</sup> and Ca<sup>2+</sup>. The hydration of these metal-exchange cations imparts a hydrophilic nature to the mineral surface. In the presence of water, such mineral surfaces are given often not good adsorbents for sparingly soluble organic species which cannot compete with highly polar water for adsorption on the clay mineral surface.<sup>1</sup> Organic modified smectites are used for the removal of organic pollutants from waste water because of their hydrophobicity and their high surface area. It has been suggested that the sorptive properties of soil and subsurface materials may be enhanced by placing organic cations, such as HDTMA, on exchange sites. When organic metal cations are adsorbed on the cation exchange sites of clays, the surface properties of the clays may be significantly modified. Long chain alkylammonium cations adsorbed on clays, for instance, change the nature of the surface from hydrophilic to more hydrophobic. As a result, the organo–clay complex becomes an excellent sorbent for sparingly soluble organic species.<sup>2</sup>

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The adsorption properties of smectites modified by alkylammonium ions increase with increasing length of the alkyl substituent. Different pollutants were adsorbed on modified smectite with respect to the chain length of the alkyl groups and the layer charge.<sup>3</sup> Quaternary ammonium cations of the general form  $[(\text{CH}_3)_3\text{NR}]^+$  or  $[(\text{CH}_3)_2\text{NR}_2]^+$  were used as exchange ions on smectite clay and the uptake of phenol, chlorophenol, and pentachlorophenol from water was studied. It was shown that quaternary ammonium cations with relatively large R groups, as for example hexadecyltrimethylammonium ( $\text{R} = [\text{CH}_3-(\text{CH}_2)_{15}-\text{N}(\text{CH}_3)_3]^+$ ), imparted very significant sorptive capabilities to the organo-smectite complexes. However, smectite saturated with smaller organic cations, such as tetramethylammonium, showed very weak sorptive capabilities for the tested phenolic compounds.<sup>4</sup> Activated carbon was used as the adsorbent for the removal of *p*-chlorophenol and *p*-nitrophenol from aqueous solutions.<sup>5,6</sup> Despite the fact that many adsorbents have been used for the removal of *p*-chlorophenol and *p*-nitrophenol from waste water, organo-clays are widely used as the adsorbent for the removal of phenolic compounds.<sup>7-9</sup> Different methods for the treatment of waste water based on organic clays have been proposed.<sup>10,11</sup>

In another work, it was shown that *p*-nitrophenol adsorbed on an adsorbent can form stronger hydrogen bonds than *p*-chlorophenol.<sup>12</sup> Furthermore, the sorption of phenol, as well as of 2,3- and 4-chlorophenol from water by tetramethylammonium (TMA)-smectite and tetramethylphosphonium (TMP)-smectite was studied. It was shown that TMP-smectite is a better sorbent than TMA-smectite.<sup>13</sup> The hydration of exchangeable alkali and alkaline earth metal cations (*e.g.*,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , *etc.*) creates a hydrophilic environment on the surface and in the interlayer region of natural montmorillonite clay. This renders the clay relatively ineffective as an adsorbent of natural organic contaminants (NOCs) such as chlorinated phenols. The adsorbent properties of montmorillonite clay for NOCs can be greatly improved by replacing the natural inorganic interlayer cations with organic cations such as quaternary ammonium cations (QACs) of the form  $[(\text{CH}_3)_3\text{NR}]^+$  or  $[(\text{CH}_3)_2\text{NR}_2]^+$ . This results in a more organophilic clay as compared to the natural clay.<sup>14</sup>

The adsorption of *p*-chlorophenol and *p*-nitrophenol on organophilic bentonite (dodecylammonium-bentonite, DDAB) was studied as a function of solution concentration and temperature.<sup>15</sup> In a study of the adsorption of environmental toxicants by modified clays, pillared, delaminated and hydroxy interlayered smectites were suggested for the removal of toxic compounds.<sup>16</sup> It was shown that different kinds of organo-clay complexes possess varying adsorption properties for benzene, chlorobenzenes and phenol.<sup>17</sup> In another investigation improved adsorption properties for 2-chlorophenol as a pollutant were obtained with rigid organic cations on smectites. Good adsorption results were also achieved using pillaring cations in combination with low charged smectites, especially at low pollutant concentrations.<sup>18</sup>

In this paper, the adsorption of phenol and phenol derivatives from alcoholic solutions by sepiolite–HNO<sub>3</sub>, sepiolite–EDTA, sepiolite–HDTMA and pure sepiolite was investigated. The aim was to investigate the adsorption capacity of modified sepiolites.

TABLE I. Name and structural formula of the organic cations and anion present in the sepiolite exchange complexes

Name	Abbreviation	Structure
Hexadecyltrimethylammonium	HDTMA <sup>+</sup>	
Ethylenediaminetetraacetic acid	EDTA	
Nitric Acid	HNO <sub>3</sub>	
Phosphorous pentachloride	FPK	

### EXPERIMENTAL

The sepiolite used in the study was from Eczacibasi, Turkey. The samples were characterized by X-ray diffraction and thermogravimetry.<sup>19</sup> The natural sepiolite was dried at 100 °C, ground and then passed through a sieve with a mesh size of 0.038 mm (400 Mesh). The cation-exchange capacity (CEC) (equivalents) of the sepiolite samples, determined according to the ammonium acetate saturation method, was found to be 82 mmol per 100 g dry clay. The sample had a BET specific surface area of 162 m<sup>2</sup>/g.<sup>20</sup>

The natural sepiolite sample was divided into 4 samples of 10 g. The first sample of natural sepiolite was put aside and kept for the adsorption experiments. The second sample of sepiolite was washed with water, mixed with 100 ml 0.75 M HNO<sub>3</sub>, stirred for 6 h under a condenser and then filtered at room temperature without being washed.

The third group of sepiolite was stirred with 100 mL 0.3 M phosphorous pentachloride under a condenser for 6 h, and then stood for 24 h. Chlorination of the sepiolite sample was thus achieved. After filtering without prior washing, the sepiolite sample was dried at room temperature.<sup>21–23</sup> It was then stirred with 300 mL of 0.4 M EDTA, for 6 h under a condenser and stood for 24 h. The sepiolite sample treated with EDTA was washed 8 times with distilled water until it contained no free chloride ions and then freeze-dried.

To the fourth sample of sepiolite, HDTMA was added in an amount equivalent to 70 % or 40 % of the cation exchange capacity (CEC) of the sepiolite. Again, the treated clay was washed on filter paper with distilled water 8 times and freeze-dried.

The modified sepiolite samples were passed through a 400 mesh sieve and their IR spectra recorded in order to examine the changes that had occurred on their surfaces.

The adsorbents used in the adsorption process (3-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and phenol) were dissolved in pure ethanol at concentrations varying from 0.01 M to 0.05 M for all the prepared adsorbents. For each concentration, 0.02 g of sepiolite sample was weighed and the mixture was stirred for 30 min and left standing for 24 h in order that the adsorption equilibrium could be established and then the formulation was filtered. Quantitative analysis of the adsorption was determined by gas chromatography of the filtrate.

## RESULTS AND DISCUSSION

The IR spectra of the pure and modified sepiolites are shown in Fig. 1.

It can be seen from the IR spectrum of pure sepiolite that the adsorption band of  $\text{OH}^-$  within the crystal structure appear at  $3642\text{--}3693\text{ cm}^{-1}$ , while the  $\text{OH}^-$  adsorption bands of the bound and zeolitic forms of water appear at  $3438\text{ cm}^{-1}$  and  $3591\text{ cm}^{-1}$ , respectively.

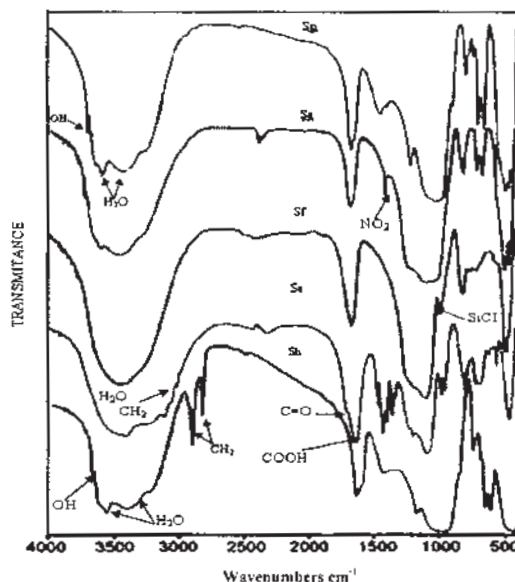


Fig. 1. IR Spectra of the sepiolites: Sp: pure sepiolite, Sa: sepiolite-nitric acid, Sf: sepiolite-FPK, Se: sepiolite-EDTA, Sh: sepiolite-HDTMA.

Figure 1. clearly shows that the bands of the  $\text{OH}^-$  groups at  $3438\text{--}3591$  and  $3642\text{--}3693\text{ cm}^{-1}$  become a little smaller when the surface of sepiolite had been altered by nitric acid. Another adsorption band belonging to the  $\text{NO}_2^-$  group of nitric acid is also observed at  $1395\text{ cm}^{-1}$ . These observations can be interpreted as being the consequence of nitric acid exchanging with the  $\text{OH}^-$  groups of the crystal structure of the sepiolite and those of the bound and zeolite water. The state is different with respect to the case of nitric acid in the sample obtained by chlorination of the (phosphorous pentachloride). In the spectrum of the nitric acid modified sample, four adsorption bands at  $3438\text{--}3591$  and  $3642\text{--}3693\text{ cm}^{-1}$  are present, whereas in that of the chlorinated sepiolite, the adsorption bands at  $3489$ ,  $3693$  and  $3438\text{--}3591\text{ cm}^{-1}$  have disap-

peared and a new wide band at  $3350\text{ cm}^{-1}$  is observed. This fact leads to the conclusion that the  $\text{OH}^-$  groups on the surface of sepiolite, as well as great number of the  $\text{OH}^-$  groups belonging to the Si-OH band and of the  $\text{OH}^-$  groups belonging to the bound and zeolitic water had been exchanged with chlorine. The reason for this exchange is that phosphorous pentachloride is a powerful chlorinating agent.

The treatment of the chlorinated sepiolite with EDTA resulted in a small decrease in the intensity of the broad band at  $3350\text{ cm}^{-1}$ , accompanied by the appearance of new adsorption peaks in the region around  $3000\text{ cm}^{-1}$ . This led to the conclusion that the chlorine on the surface of the sepiolite had been replaced by EDTA. In addition, small adsorption bands are also observable at 2825, 1625 and  $1421\text{ cm}^{-1}$ . Those are due, respectively, to C-H and C=O bonds in the EDTA and C-N groups bound to EDTA in different ways. From this, it can be inferred that the surface of the had been replaced by EDTA.

After the sepiolite had been treated with HDTMA, the absorption band at  $3693\text{ cm}^{-1}$  and the band at  $3591\text{ cm}^{-1}$  become smaller. Also, absorption bands at  $2856\text{--}2929\text{ cm}^{-1}$  appear. These newly-formed bands can be considered as belonging to the C-H groups of HDTMA in free positions in the clay or bound in various ways to the sepiolite. Due to these observations of the changes in the IR spectra, it is thought that the surface of sepiolite had been replaced by HDTMA.

The results of the adsorption onto pure sepiolite, sepiolite-nitric acid, sepiolite-EDTA and sepiolite-HDTMA of, respectively, 3-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and phenol are shown in Figs. 2-5.

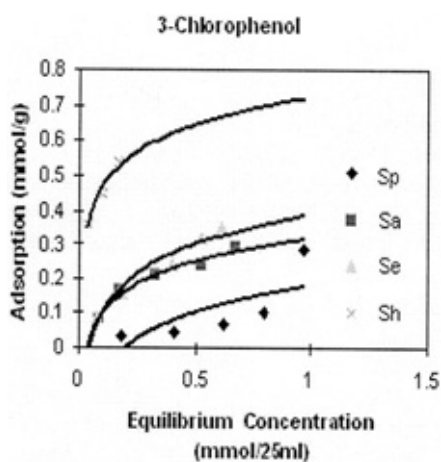


Fig. 2. The adsorption isotherms of 3-chlorophenol in ethanol at  $20\text{ }^{\circ}\text{C}$  onto Sp: pure sepiolite, Sa: sepiolite-nitric acid, Se: sepiolite-EDTA and Sh: sepiolite-HDTMA.

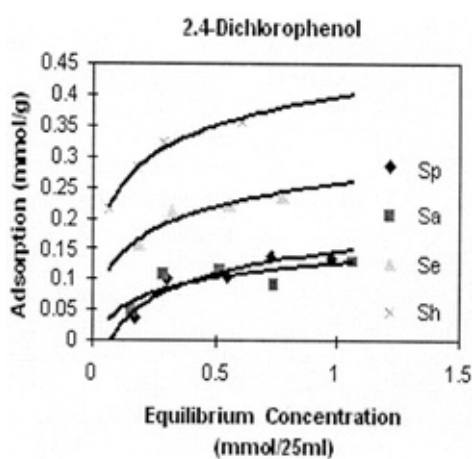


Fig. 3. The adsorption isotherms of 2,4-dichlorophenol in ethanol at  $20\text{ }^{\circ}\text{C}$  onto Sp: pure sepiolite, Sa: sepiolite-nitric acid, Se: sepiolite-EDTA and Sh: sepiolite-HDTMA.

The adsorption of 3-chlorophenol onto sepiolite-HDTMA, sepiolite-EDTA, sepiolite- $\text{HNO}_3$  and pure sepiolite are shown in Fig. 2, from which it can be seen

that the order of the adsorptions properties is: sepiolite–HDTMA > sepiolite–EDTA > sepiolite–HNO<sub>3</sub> > pure sepiolite.

The adsorption of 2,4-dichlorophenol onto sepiolite–HDTMA, sepiolite–EDTA, sepiolite–HNO<sub>3</sub> and pure sepiolite are shown in Fig. 3, from which it can be seen that the order of the adsorptions properties is: sepiolite–HDTMA > sepiolite–EDTA > pure sepiolite > sepiolite–HNO<sub>3</sub>. As a result of the interaction of the sepiolite surface with nitric acid, the surface of the sepiolite became positive and, hence, interacted much more with the solution and thus sepiolite–HNO<sub>3</sub> adsorbed less 2,4-dichlorophenol than pure sepiolite (Fig. 3).

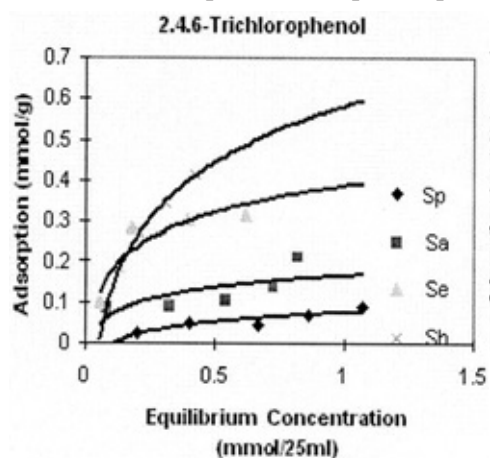


Fig. 4. The adsorption isotherms of 2,4,6-trichlorophenol in ethanol at 20 °C onto Sp: pure sepiolite, Sa: sepiolite–nitric acid, Se: sepiolite–EDTA and Sh: sepiolite–HDTMA.

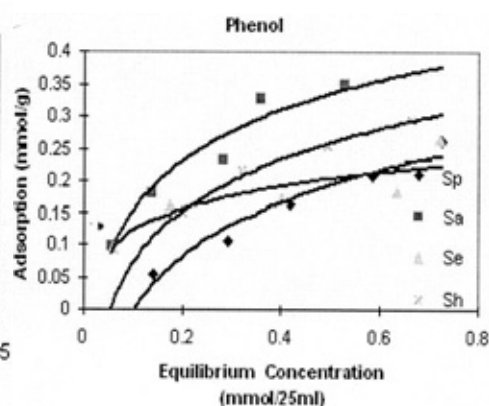


Fig. 5. The adsorption isotherms of phenol in ethanol at 20 °C onto Sp: pure sepiolite, Sa: sepiolite–nitric acid, Se: sepiolite–EDTA and Sh: sepiolite–HDTMA.

As can be seen from Fig. 4, sepiolite–HDTMA was the best of the studied adsorbants for 2,4,6-trichlorophenol. Sepiolite–HDTMA was also the best adsorbant for phenol, followed by sepiolite–HNO<sub>3</sub>, sepiolite–EDTA and pure sepiolite, respectively.

As seen in Figs. 2–5, 3-chlorophenol was the best adsorbed, followed by 2,4-dichlorophenol, 2,4,6-trichlorophenol and finally phenol.

In the case of the alteration of the sepiolite surface by HDTMA and EDTA, the sepiolite surface changes from hydrophilic towards hydrophobic. Hydrophobic surfaces adsorb the hydrophobic adsorbents existing in their environment to a greater degree than hydrophilic surfaces. Since the surface of sepiolite–HNO<sub>3</sub> is hydrophilic, lower amounts of phenol and phenol derivatives were adsorbed by this adsorbant with respect to sepiolite–HDTMA and sepiolite–EDTA.

## CONCLUSIONS

Developing technology shows that, in the future, studies will focus on further modification and design of metal oxide-delaminated and pillared clays for the adsorption of organic toxicants.

According to results presented here, complexes such as sepiolite–HDTMA can be used as sorbents for the removal of organic contaminants. Furthermore, the present investigation shows that modified sepiolite can be employed as an effective adsorbent for the removal of aromatic compound. The data obtained can be useful for environmental decontamination and chromatographic applications.

## ИЗВОД

## АДСОРПЦИЈА ФЕНОЛА И ХЛОРОВАНИХ ФЕНОЛА НА ЧИСТОМ И МОДИФИКОВАНОМ СЕПИОЛИТУ

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У раду су коришћени као адсорбенти чисти сепиолит и сепиолит модификован азотном ( $\text{HNO}_3$ ) и етилендиаминтетрасирћетном (ЕДТА) киселином, као и хексадецилтриметиламонијум јонима (НДТМА). Промене на површини испитиване су ИР спектроскопијом. Гасном хроматографијом испитивана је адсорпција раствора фенола и деривата фенола у чистом етанолу на овим адсорбентима. Утврђено је да су адсорпциони капацитети система глина–органски комплекс (sepiolite–EDTA и сепиолит–HDTMA) већи од капацитета чистог сепиолита и система сепиолит– $\text{HNO}_3$ .

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