

Sorbition of aniline onto organophilic sepiolite

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ABSTRACT

In this study, sepiolite was modified with nitric acid, ethylene diamine tetra acetic acid and hexa decyl trimethyl ammonium. The changes on the surfaces of sepiolite samples were studied in the IR spectroscopy. Pure and modified sepiolite were used as adsorbents. The adsorption of aniline was examined by means of gas chromatography. As the result of these examinations, it was seen that the adsorption capacities of the clay-organic complexes; sepiolite-HDTMA was higher than sepiolite-EDTA. The least adsorption was observed on surface of sepiolite-HNO₃. Off all sepiolite-samples it was determined that the pure sepiolite adsorbed the highest amount of aniline.

Key words: Sepiolite, aniline, adsorption, clay.

INTRODUCTION

In the industrial area the using of the clays as adsorbents are very important, because they have high specific surface area. It has been known that the sorption of clays is very low for organic molecules which are highly cationic or polar surface, owing to their hydrophilic capacities. Such minerals are not a good sorbent in the presence of water for organic sorts that weakly dissolve in water. In the recent years there has been an increasing interest in organo-clay because of the their effect of cation-exchange. Clay minerals have got a net negative electrical charge which is compensated by exchange cations on their surfaces. In the nature these exchange ions are mainly alkaline metal ions, and alkaline earth ions such as Na⁺ and Ca⁺⁺. The hydration of these metal- exchanged cations imparts a hydrophilic nature to the mineral surface¹. Quarternary ammonium cations of the general form is [(CH₃)₃ NR R]⁺ or [(CH₃)₂ NR₂]⁺. It was used as exchange ion on smectite clay and studied the uptake of phenol, chlorophenols, and pentachlorophenol from water. It was shown that quaternary ammonium cations with relatively large R groups, as for example hexadecyl-trimethylam-

monium-bromide (R is CH₃(CH₂)₁₅N (CH₃)₃Br), impared very significant sorptive capabilities of organo-smectite complex. However, smectite saturated with smaller organic cation like tetramethylammonium showed very weak sorptive capabilities for the phenolic compounds tested². Organic cation may enter into ion exchange reaction with metal cations on the exchange edges of clay³⁻⁴. 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 reactions⁵. Activated carbon was used as adsorbent for removal of p-chlorophenol and p-nitrophenol from aqueous solution⁶⁻⁷. Despite the fact that many adsorbents have been used for removal p-chlorophenol and p-nitrophenol from waste water, organo-clay has been used widely as adsorbent for the removal of phenol compounds⁸. Furthermore sorption of phenol, 2-,3- and 4-chlorophenol from water by tetramethylmonium (TMA)-smectite and tetramethylphosphanium (TMP)-smectit was studied, and it was determined that TMP-smectit was better sorbant than TMA-smectit⁹. The adsorption of p-chlorophenol and p-nitrophenol (p-Np) on organophilic bentonite (dodecylammonium

bentonite DDAB) was studied as function of solution concentration and temperature¹⁰. Modified clay were studied for the adsorption of environmental toxicants it is suggested in that the pillared, delaminated and hydroxyl interlayer smectites were used for removal of toxic compounds¹¹. It has been shown that different kinds of organo-clay complexes possess varying adsorption properties for benzene, chloro benzenes and phenol¹². In another work, the characterization of tetraethylammonium bentonite and the adsorption of p-chlorophenol (p-CP) onto organophilic bentonite (tetraethylammonium bentonite) was studied as a function of solution concentration and temperature. The observed adsorption rates were found to fit first-order kinetics and the rate constants were calculated for temperature ranging between 15 °C and 35 °C at constant concentration. The amount of adsorption of p-chlorophenol on organophilic bentonite was found to be dependent on the relative energies of adsorbent-adsorbate, adsorbate-solvent, and adsorbate-adsorbate interactions¹³.

In others studies; Adsorption of aniline, phenol and chlorophenols on pure and modified bentonite, adsorption of phenol, phenol derivatives on pure and modified kaolinite, adsorption of phenol, phenol derivatives on pure and modified sepiolite were investigated and obtained values from these investigations were evaluated as detailed comparatively. In this study we aimed to investigate the adsorption of aniline on sepiolite-HNO₃, sepiolite-EDTA, sepiolite-HDTMA and the pure sepiolite and to determine the capacity of sepiolite modified.

MATERIAL AND METHODS

Sepiolite sample used in the study was provided from a region of Eczacıbaşı, Turkey. The samples were characterized by X-ray diffraction and thermogravimetric analysis. The natural sepiolite was picked up, dried at 100°C and ground, and then passed through a sieve with mesh size of 0,038 mm (400 Mesh). Firstly natural sepiolite samples were divided into 4 groups. The first group of the natural sepiolite was put aside and kept for the adsorbents. The second group of sepiolite was washed in water after being mixed with 100 ml. 0,75 M. HNO₃ and stirred for 6 hours and then dried at room temperature without being washed. The third group

of sepiolite was also stirred, immersed in water under re-cooling conditions for six hours after the addition of 100 ml. 0,3 M PCl₅, and then rested for 24 hours. Thus the chlorination process of the sepiolite sample was achieved. Having been drained without a prior wash, the sepiolite sample was dried at room temperature. Then 300 ml, 0,4 M EDTA, was added, stirred for 6 hours under re-cooling conditions and rested for 24 hours. The sepiolite sample treated with EDTA was washed 8 times with distilled water, until it contains no free chlor ions, and then freeze dried⁶.

The cation exchange capacity (C.E.C.) of the sepiolite of group 4, some HDTMA the amounts of which was up to 30-40 % of C.E.C. was added to sepiolite sample and stirred with magnetic mixer for 6 hours and then the mixture was rested for 24 hours. Then the sepiolite treated with HDTMA was washed with distilled water 8 times until it contains no free HDTMA, and then freeze dried. The sepiolite samples the surface of which had been altered were passed through a sieve of 400 mesh, and then the changes of IR spectrums were taken. The adsorbents used in the adsorption process (Aniline) was dissolved in pure alcohol. The serial-solution of adsorbents were prepared vary from 0,01 M to 0,05 M. For each concentration unit, 0,02 g of sepiolite sample was weighed then it was stirred for 30 minutes in the mixture and left to rest for 24 hours to establish the adsorption equilibrium and then drained. The quantitative analysis of the adsorption in the filtrate was determined by means of gas chromatography.

RESULTS AND DISCUSSION

It is seen in the IR spectrum of pure sepiolite that the adsorption band of OH⁻ within the crystal texture are formed at 3642-3693 cm⁻¹, while the OH⁻ adsorption bands of the bounded and zeolitic forms of water are formed at 3438cm⁻¹ and 3591 cm⁻¹, respectively.

Fig. 1 show clearly that the bands at 3438-3591 and 3642-3693cm⁻¹ get a bit smaller and the absorption bands decreases when the surface of sepiolite was altered by nitric-acid. Another stretching adsorption band of 1395cm⁻¹ belonging to NO₂⁻ group of nitric acid is also observed at

1395 cm^{-1} . This state can be interpreted as that the groups of crystal texture of the sepiolite and the OH^- groups belonging to the bound and zeolitic waters have exchanged with nitric acid. It is seen in figure: 2 that there is a different state, respecting to the nitric acid for the sample obtained in the result of chlorination of sepiolite (Phosphopentachlorine). In the former positions, it could be seen four absorption stretching bands at 3438-3591 and 3642-3693 cm^{-1} , but now in result of chlorination of the sepiolite, it is observed that almost the absorption stretching bands of 3489, 3693 and 3438-3591 cm^{-1} have disappeared and have been occurred a new wide band at 3350 cm^{-1} . From the fact that we can reach to this conclusion: the OH^- groups on the surface of sepiolite have exchanged with chlorine. A great portion of the OH^- groups belonging to Si-OH band and of the OH^- groups that belong to the bound and zeolitic water have been replaced by chlorine. In addition, there has occurred a decrease in the strength of the adsorption stretching bands located in the finger-print zones. The adsorption stretching bands at 3438-3591 and 3642-3693 cm^{-1} which had disappeared after the treatment of chlorinate sepiolite with EDTA, occurring absorption band of 3350 cm^{-1} get a little

smaller. The result adsorption stretching bands have disappeared and then, it has been seen at a different location which leads us to the conclusion that the chlorine and EDTA have replaced each other on the surface of sepiolite. The reason for this exchange is that the agent of Phosphopentachlorine is a powerful chlorinator. In addition, small adsorption stretching bands are also observable at 2825, 1625 and 1421 cm^{-1} . Those are respectively the C-H, C=O bounded to the EDTA and C-N groups bounded to EDTA in different ways. From this, it can be infer that the surface of the sepiolite has been replaced by EDTA.

In Fig. 3(a), the adsorption stretching band at 3693 cm^{-1} get smaller and (b) the adsorption stretching band of 3591 cm^{-1} become smaller. This state can be interpreted as in sepiolite the OH^- groups belonging to crystal waters, the OH^- groups belonging to bounded waters and , then the appearing of the absorption bands of 2856-2929 cm^{-1} belonging to the groups of C-H of HDTMA, have exchanged with HDTMA. From these bands, looking at this alteration, it is thought that the surface of sepiolite has been replaced by HDTMA.

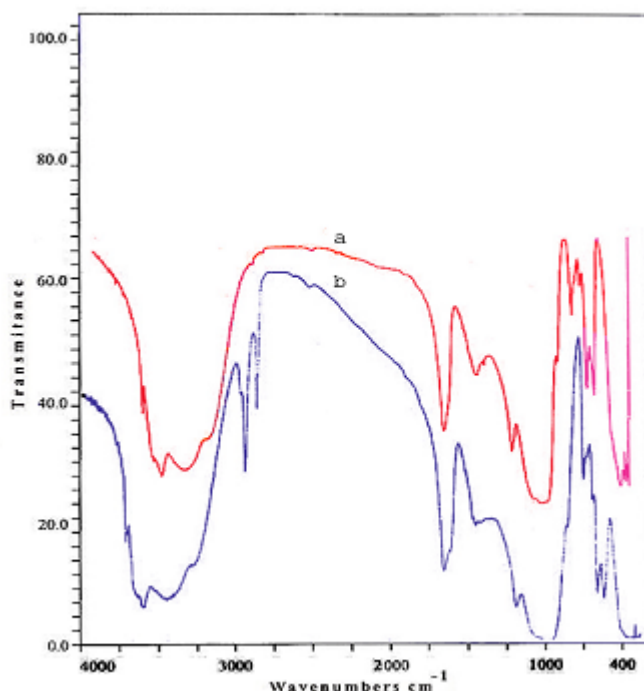


Fig. 1: The IR Spectrums of Sepiolite: a) Pure sepiolite b) Sepiolite-nitric acid

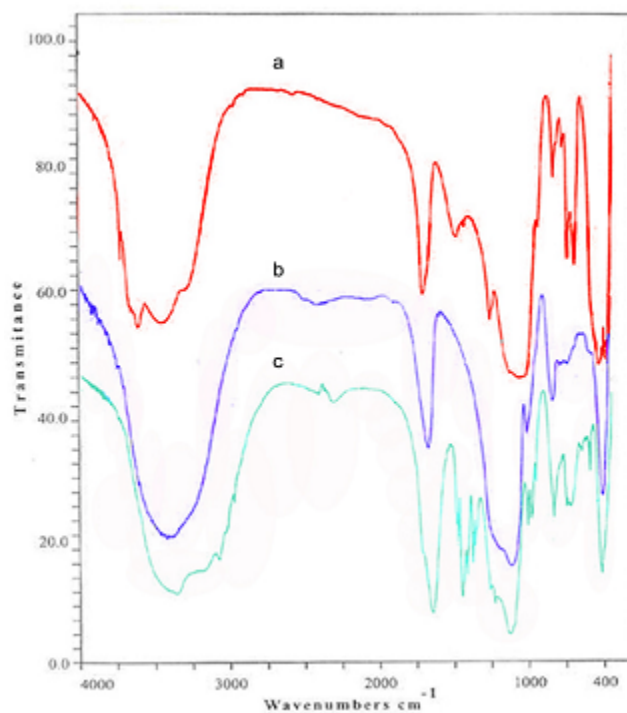


Fig. 2: The IR spectrums of Sepiolite: a) Pure sepiolite b) Sepiolite-FPK c) Sepiolite-EDTA

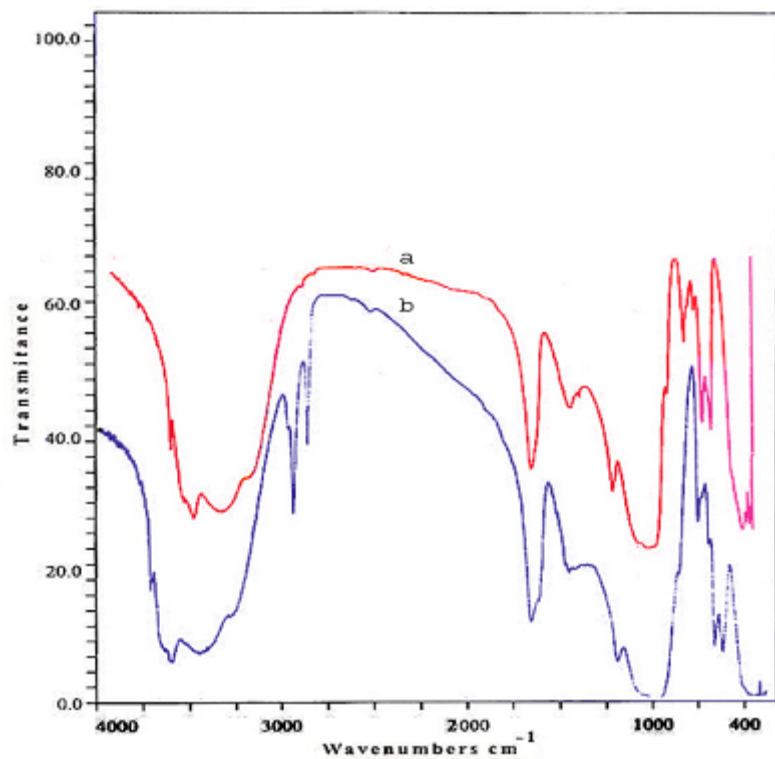


Fig. 3: The IR spectrums of sepiolite a) Pure Sepiolite b) Sepiolite-HDTMA

As seen in Fig. 4, sepiolite-HDTMA, sepiolite EDTA, sepiolite-HNO₃ and the pure sepiolite have been determined to be adsorbents for Aniline, then it was seen that the best adsorbents pure sepiolite, sepiolite-HDTMA, sepiolite EDTA, sepiolite-HNO₃ respectively, at the adsorption isotherms. Off all sepiolite-samples It has been observed that the pure sepiolite has adsorbed the highest amount of aniline (Figures 4).

In the surface alteration of the sepiolite by nitric-acid, the bands belonging to OH⁻ group being at 1719-1693 and 1489 cm⁻¹ got bit smaller. Almost all of the stretching bands belonging to the bound and zeolitic water vanish in result of chlorination of the pure sepiolite. This case justifies the fact that phosphorpentachloride, which is known as strong chlorinating agent, easily exchange places with OH⁻ groups. The chloride groups that are bound to the chlorinated sepiolite are known to be changing places more easily with the anion and cation adsorbents and the surface altering agents comparing to the pure sepiolite. The adsorption bands which had disappeared after treatment of the chlorinated sepiolite with EDTA have new formed at various places, which makes us think that a Si-O-C bind has been formed instead of the Si-Cl bind

where as the fast that the EDTA adsorption band belonging to the C=O bind has formed, at 1625 cm⁻¹ causes us to think that a Si-O-C bridge bind has been formed. In the light of these data we can infer that the surface of sepiolite clay is altered by EDTA. Two sharp adsorption bands of the C-H bind belonging to HDTMA are observed at 2854-2924 cm⁻¹ in result of the alteration of the sepiolite by HDTMA. We can consider these newly formed adsorption bands to the those belonging to, HDTMA, which is in a free position in the clay, yet we can also consider these adsorption bonds belong to the HDTMA, which is bound in various ways to the sepiolite as the free HDTMA has been removed a way from the sepiolite through washing it 8 times.

In the case of alteration of the sepiolite surface by HDTMA and EDTA, on sepiolite surfaces from hydrophilic towards hydrophobic an increase has been observed. Hydrophobic surfaces adsorb the hydrophobic adsorbents existing in their own environment at greater degrees since the surfaces of sepiolite-HNO₃ have a hydrophilic property, they have achieved less adsorption in the adsorption of phenol and phenol derivatives with respect to sepiolite-HDTMA and sepiolite-EDTA. This has been so, due to the fact that the hydrophilic property of

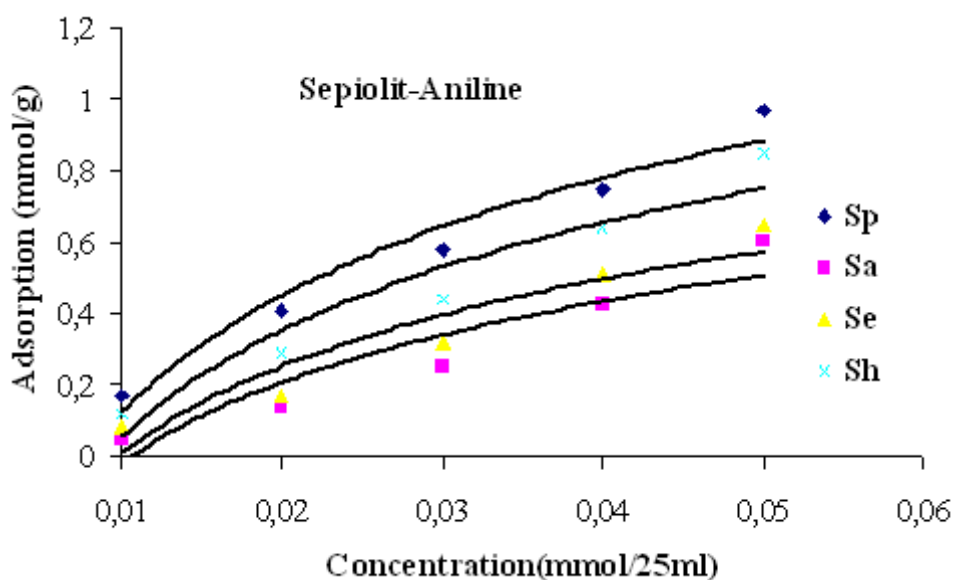


Fig. 4: The Adsorption isotherms of aniline solutions, Sp: Pure Sepiolite; Sa: Sepiolite-Nitric acid, Se: Sepiolite-EDTA, Sh: Sepiolite-HDTMA.

the sepiolite-HDTMA and sepiolite-EDTA surfaces has enhanced, they adsorb more greatly the phenol and phenol derivatives, while less adsorbing the aniline because of its hydrophilic property.

Conclusion

The result reported here show that clay minerals can be treated with specific organic cations that have specific adsorption properties for particular molecules, e.g., aniline. Such adsorption specificity is applicable in the removal of a particular target molecule from a solvent or in the chromatographic separation of closely related molecules. The

sensitivity of this organo-clay complexes for particular purposes is of great interest for future development. These synthetic organo-clay complexes also appear to be useful in fundamental studies on the interactions of organic molecules with specific kinds of surface which can be varied with respect to hydrophobicity, aromaticity and polarity. The results get here also suggest that complexes such as Sepiolite-HDTMA can be used as adsorbents for removing organic contaminants, and finally it can be said that modified sepiolite can be used as an effective adsorbent for the removal of organic pollutant.

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