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Adsorption of Phenol and Phenol Derivatives on Pure and Modified Kaolinite

A. YILDIZ* and A. GÜR
Department of Chemistry, Science-Literature Faculty,
Yüzüncü Yil University, Van, Turkey
E-mail: adnanyildiz@yahoo.com

In the present work, pure kaolinite and that modified by HNO_3, EDTA and HDTMA, were used as the adsorbents.The changes on the surfaces were studied by IR spectroscopy. The adsorption of solutions of phenol and phenol derivatives in alcohol on these adsorbents was examined by means of gas-chromatography. As a result of these examinations, it was seen that the adsorption capacities of the clay-organic complexes (kaolinite-EDTA and kaolinite-HDTMA) were higher than pure kaolinite and kaolinite-HNO_3.

Key Words: Adsorption, Clay, Kaolinite, Phenol, Phenol derivatives.

INTRODUCTION

Organic pollutants are still a problem for the environment and for drinking water. Organic modified smectites are used for the removal of organic pollutants from wastewater due to their hydrophobicity and their large surface area[1]. Clays are widely used as adsorbents, because their specific surface area is very high. The sorptions of clay are very low for organic molecules that have highly cationic or polar surface because the mineral surfaces of clay are hydrophilic are well established. Such minerals are not good sorbents in the presence of water, for organic sorts that weakly dissolve in water. In recent years, there has been an increasing interest in organo-clay because of the cation exchange on the surface of clay minerals, negative charge develops in their structures. This case is caused in nature generally by the alkaline ions, such as Na^+ and Ca^{2+}, and by the soil alkaline metal-ions in the soil.

Generally, the adsorbtion properties of smectites modified by alkylammonium ion increase with the length of the alkyl substituents. Different pollutants were adsorbed by modified smectite with respect to the chain length of the alkyl groups and the layer charge[2, 3]. The hydration of these cations altered by metals gives a hygrophilous nature on to the surface of minerals[4]. Quaternary ammonium cations of the general form $[(CH_3)NRR]^+$ or $[(CH_3)_2NR_2]^+$ were used as exchange ions on smectite clay and the uptake of phenols, chlorophenols and pentachlorophenols from water was studied. It was seen that quaternary ammonium cations with relatively large R groups, for example, haxadecyltrimethylammonium

[R = $(CH_2)_{15}CH_2$], compared very significantly with the sorptive capabilities of organo-smectite complex. The smectite saturated with smaller organic cations like tetramethylammonium ion showed very weak sorptive capabilities for the phenolic compounds tested[3]. Organic cations may enter into ion exchange reaction with metal cations on the exchange edges of clay[6, 7]. 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 reactions[2]. Activated carbon was used as adsorbent for removal of *p*-chlorophenol and *p*-nitrophenol from aqueous solution[8, 9] despite the fact that many adsorbents have been used of removal of *p*-chlorophenol and *p*-nitrophenol from wastewater organo-clay have been used widely as adsorbents for removal of phenol compounds[2, 10–12]. Different methods for treating wastewater based on organic clays were proposed by many workers[13, 14].

In another work[15], it was seen that *p*-nitrophenol adsorbed on adsorbent could form a stronger hydrogen bonding than *p*-chlorophenol. Furthermore, sorption of phenol and 2-, 3- and 4-chlorophenol from water by tetramethylammonium (TMA)-smectite and tetramethyphosphonium (TMP)-smectite was studied and it was determined that TMP-smectite was a better sorbent than TMA-smectite[12].

As a function of solution concentration and temperature, the adsorption of *p*-chlorophenol and *p*-nitrophenol on organophilic bentonite (dodecylammonium bentonite, DDAB) was studied[16]. Modified clays were studied for the adsorption of environmental toxicants suggesting that the pillared, delaminated and hydroxy inter-layered smectites are better for removal of toxic compounds[17]. It has been shown that different kinds of organo-clay complexes possess varying adsorption properties for benzene, chlorobenzenes and phenol[18]. Meir *et al.*[19] obtained improved adsorbtion properties for rigid organic cations on smectites using 2-chlorophenol as pollutant. Good adsorption results are achieved using pillaring cations in combination with low charged smectites, especially at low pollutant concentrations[19].

In the present work, the adsorption of phenol and phenol derivates by kaolinite-HNO_3, kaolinite-EDTA, kaolinite-HDTMA and pure kaolinite in alcohol has been described. The present work was carried out to investigate the adsorption capacity of modified kaolinite.

EXPERIMENTAL

The kaolinite used in the study was provided by Eczacibaşi, Turkey. The samples were characterized by X-ray diffraction and thermo gravimetric analyses. The natural kaolinite was picked up, dried at 100°C and ground and then passed through a sieve with a mesh size of 0.038 mm (400 mesh).

Natural kaolinite samples were divided into 4 groups, each being 10 g. The first group of the natural kaolinite was put aside and kept for the adsorbents. The second group of kaolinite was washed in water after being mixed with 100 mL of 0.75 M HNO_3 and stirred for 6 h under re-cooling conditions and then drained and dried at room temperature without being washed.

The third group of kaolinite was also stirred, being immersed in water under re-cooling conditions for 6 h after the addition of 100 mL of 0.3 M PCl_5 and then kept for 24 h. Thus, the chlorination process of the kaolinite sample was achieved. The kaolinite sample was dried at room temperature. After the addition of 300 mL 0.4 M EDTA, the kaolinite sample was stirred for 6 h under re-cooling conditions and kept for 24 h. The kaolinite sample treated with EDTA was washed 8 times with distilled water until it contained no free chloro ions and then freeze-dried[8].

Considering the cation exchange capacity (CEC) of the kaolinite of group 4, some HDTMA of 30–40% of CEC was added and stirred with magnetic irritator for 6 h and then the mixture was kept for 24 h. The kaolinite, treated with HDTMA, was washed with distilled water 8 times until it contained no free HDTMA and then freeze-dried. The kaolinite samples whose surface had been altered were passed through a sieve of 400 mesh and then their IR spectra were taken in order that the changes occurred on their surfaces could be examined.

The adsorbents to be used in the adsorption process (3-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol) were dissolved in pure alcohol and the serial-solutions varying from 0.01 to 0.05 M of all adsorbents were prepared. For each concentration unit, 0.02 g of kaolinite sample was weighed and the mixture was stirred for 30 min and left for 24 h in order that the adsorption equilibrium could be established and then the formation was drained. The quantitative analysis of adsorption in the filtrate was determined through gas-chromatography method.

RESULTS AND DISCUSSION

It is seen in the IR spectra of pure kaolinite that the infrared adsorption band of OH^- within the crystal texture observed at 3719 cm^{-1}, while the OH^- stretching adsorption bands of the bound and zeolitic forms of water are formed at 3693 and 3489 cm^{-1} respectively. The infrared spectrum clearly shows that the bands at 3489, 3693 and 3719 cm^{-1} get a bit smaller and the absorption bands decreases when the surface of kaolinite was altered by nitric acid. Another adsorption band at 1395 cm^{-1} belonging to NO_2^- group of nitric acid was also observed. This can be interpreted as that the groups of crystal texture of the kaolinite and the OH^- groups belonging to the bound and zeolitic waters have exchanged with nitric acid. It is seen that in the infrared spectra of kaolinite samples impregnated with chlorination by phosphopentachlorine, there is a different state with respect to nitric acid for the sample obtained as a result of chlorination of kaolinite (phosphopentachlorine). In the former position, it is interpreted that three absorption bands occurred at 3489, 3693 and 3719 cm^{-1}, but now as a result of chlorination of kaolinite it is observed that almost all the absorption tension bands of 3489, 3693 and 3719 cm^{-1} have disappeared and there has appeared a new wide band at 3350 cm^{-1}. From this fact we can reach this conclusion: the OH^- groups on the surface of kaolinite 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 tension bands located in the fingerprint zones.

The infrared adsorption bands at 3489, 3693 and 3719 cm^{-1} which was disappeared after the treatment of chlorinate kaolinite with EDTA, occurring absorption band of 3350 cm^{-1} got a little smaller. The resulting adsorption band disappeared and was observed at a different location, which leads us to the conclusion that the chlorine and EDTA have replaced each other on the surface of kaolinite. The reason for this exchange is that the agent of phosphoropentachlorine is a powerful chlorinating agent.

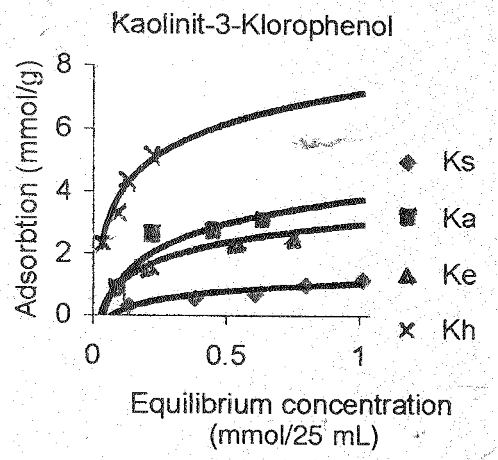
In addition, small adsorption bands are also observed at 2989, 1625 and 1651 cm^{-1} respectively due to the C—H, C═O bonded to the EDTA and the OH$^-$ groups bonded to kaolinite in different ways. From this, it can be inferred that the surface of kaolinite has been replaced by EDTA.

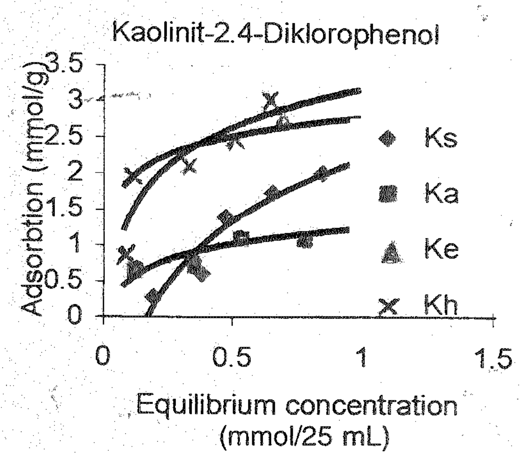
In the infrared spectra of pure kaolinite (a) and kaolinite-HDTMA (b), show thatin pure kaolinite, the adsorption band at 2375 cm^{-1} had disappeared and in kaolinite-HDTMA the adsorption bands of 3719, 3693 cm^{-1} and of 3489 cm^{-1} which were bounded to kaolinite had been more sharp than in the pure sample. This state can be interpreted as in kaolinite the OH$^-$ groups belonging to crystal waters, the OH$^-$ groups belonging to bonded waters and the OH$^-$ groups belonging to zeolitic waters, then the appearing of the absorption bands of 2924–2854 cm^{-1} belonging to the groups of C—H of HDTMA, have exchanged with HDTMA. From these bands, looking at this alteration, it is suggested that the surface of kaolinite has been replaced by HDTMA.

As seen in Fig. 1, kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite have been determined to be adsorbents for 3-chlorophenol; then it was seen that the best adsorbents, respectively, kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite at the adsorption isotherms. As seen in Fig. 2. kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite have been determined to be adsorbents for 2,4-dichlorophenol; then it was seen that the best adsorbants, respectively, kaolinite-HDTMA, kaolinite-EDTA, pure kaolinite and kaolinite-HNO_3 at the adsorption isotherms. As a result of interaction of surface of kaolinite with nitric acid, the surface of kaolinite got positive and more interactive with solution and so kaolinite-HNO_3 less adsorbed 2,4-dichlorophenol than pure kaolinite.

As seen in Fig. 3, kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite have been determined to be adsorbents for 2,4,6-trichlorophenol. It was seen that the best adsorbent was kaolinite-HDTMA. As seen in Fig. 4, kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite have been determined to be adsorbents for 3-chlorophenol; then it was seen that the best adsorbents are kaolinite-HDTMA, kaolinite-HNO_3, kaolinite-EDTA, pure kaolinite, respectively, at the adsorption isotherms. As seen in Figs. 1–4, kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite have been determined to be the adsorbents that give the highest adsorption at the adsorption isotherms belonging respectively to 3-chlorophenol 2,4-dichlorophenol and 2,4,6-trichlorophenol and kaolinite-HDTMA, kaolinite-EDTA, kaolinite-HNO_3 and pure kaolinite less adsorbed phenol than phenol derivative, due to the acidic nature of phenol.

Clay minerals hold the OH$^-$ groups in many various forms (bound water,

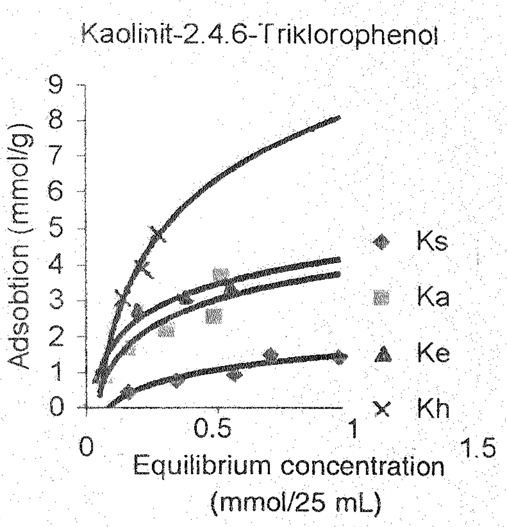




The adsorption isotherms of kaolinite samples belonging to different surfaces:

Fig. 1. The pure kaolinite (Ks), kaolinite (Ka) solutions of nitric acid-kaolinite, kaolinite-EDTA (Ke) and kaolinite-HDTMA (Kh) adsorption isotherms of the nitric acid solutions of 3-chlorophenol that dissolved in 20°C alcohol

Fig. 2. The adsorption isotherms of 2,4-dichlorophenol in 20°C alcohol on pure kaolinite (Ks), kaolinite (Ka), kaolinite-EDTA (Ke) and kaolinite-HDTMA (Kh)



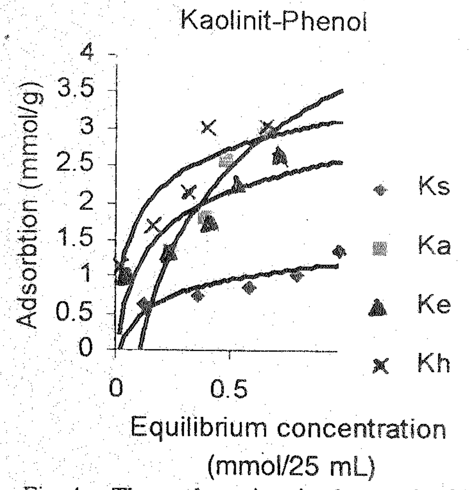


Fig. 3. The adsorption isotherms of 2,4,6-trichlorophenol in 20°C alcohol on pure kaolinite (Ks), kaolinite (Ka), nitric acid-kaolinite, kaolinite-EDTA (Ke) and kaolinite-HDTMA (Kh)

Fig. 4. The adsorption isotherms in 20°C alcohol on pure kaolinite (Ks), kaolinite (Ka), nitric acid-kaolinite, kaolinite-EDTA (Ke) and kaolinite-HDTMA (Kh)

zeolitic water, etc.). In the IR spectra of all, the adsorption bands are seen in the OH^- zones. After changing the surface of clays, the surface-changing agents then change their places mutually with the water of different binds in the clays. The adsorption bands belonging to the water are bound in different ways to the clays either get smaller after their interaction with the clay-surface changing agents or completely disappear.

Adsorbents attach to the surfaces of clays in three ways: (a) Adsorbents are bound to the active points of clay by enveloping surrounding all sides of the solvent molecules in the solvent condition they act. (b) The positive active points of the clay surfaces are bound to the negative points of the adsorbents in the solution and, likewise, the negative active points on the surfaces are bound to the positive points of adsorbents. (c) There occur dipole-dipole and dipole-ion interactions between the clay surfaces and adsorbent in the solution. The interactions between the clay-surface and the adsorbent are of the type of van der Waals' forces.

In the surface alteration of the kaolinite by nitric acid, the bands belonging to OH^- group being at 1719–1693 and 1489 cm^{-1} got a bit smaller. Almost all of the tension bands belonging to the bound and zeolitic water vanished as a result of chlorination of pure kaolinite. This case justifies the fact that phosphorpentachloride, which is known as a strong chlorinating agent, easily exchanges places with OH^- groups.

The chloride groups that are bound to the chlorinated kaolinite are known to be changing places more easily with the anion and cation adsorbents and the surface altering agents compared to pure kaolinite.

The adsorption bands which had disappeared after treatment of the chlorinated kaolinite with EDTA have now formed at various places, which makes us think that a (Si—O—C) linkage has been formed instead of the (Si—C) linkage whereas the fact that the EDTA adsorption band belonging to the (C=O) linkage has formed at 1625 cm^{-1} causes us to think that a (Si—O—C) bridge linkage has been formed. In the light of these data we can infer that the surface of kaolinite clay is altered by EDTA.

Two sharp adsorption bands of the (C—H) linkage belonging to HDTMA are observed at 2924–2854 cm^{-1} as a result of the alteration of kaolinite by HDTMA. We can consider these newly formed adsorption bands to be 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 kaolinite as the free HDTMA has been removed away from the kaolinite through washing it eight times.

In the case of alteration of the kaolinite surface by HDTMA and EDTA, an increase on kaolinite surfaces from hydrophilic towards hydrophobic has been observed. Hydrophobic surfaces adsorb the hydrophobic adsorbents existing in their own environment at greater degrees since the surfaces of kaolinite-HNO_3 have a hydrophilic property, they have achieved less adsorption in the adsorption of phenol and phenol derivatives with respect to kaolinite-HDTMA and kaolinite-EDTA, whereas the highest rate of adsorption has been demonstrated in the aniline adsorption case, by kaolinite-HNO_3. This is so due to the fact that the hydrophilic property of the kaolinite-HDTMA and kaolinite-EDTA surfaces has enhanced, they adsorb more the phenol and phenol derivatives, while less adsorbing aniline because of its hydrophilic property because similar surfaces adsorb similar matters more greatly.

Conclusions

The future studies will focus on further modification and design of metal oxide-delaminated and pillared clay for the adsorption of organic toxicants. In the comparison of the adsorption of aniline, phenol and its derivatives by kaolinite-HNO_3, kaolinite-EDTA and kaolinite-HDTMA, certain conclusions are obtained.

According to results presented here that complexes such as kaolinite-HDTMA can be used as sorbents for removing organic contaminants and the present investigation shows that modified kaolinite can be employed as an effective adsorbent for the removal of aromatic compounds. The data obtained can be useful for environmental contaminants and chromatographic applications.

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