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Removal of Phenol and Chlorophenols from Aquatic System Using Activated Clinoptilolite

Aktive Edilmiş Klinoptilolit Kullanılarak Sulu Ortamdan Fenol ve Klorofenollerin Uzaklaştırılması

Research Article

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ABSTRACT

Chemical contamination of water from a wide range of toxic compounds, in particular aromatic molecules, is a serious environmental problem owing to their potential human toxicity. In this study, activated clinoptilolite from Manisa-Gördes region (AMGC) was investigated for removal of phenol and chlorophenols (i.e. o-chlorophenol, m-chlorophenol and p-chlorophenol). AMGC was characterized by FT-IR, TG/DTA, BET Surface Area, SEM, XRD, and XRF methods. Adsorption rates of phenol and chlorophenols were very high, and equilibrium was achieved in about 45 min. The maximum adsorptions of phenol and chlorophenols onto the AMGC were 7.977 mg/g for phenol, 9.846 mg/g for o-chlorophenol, 9.981 mg/g for m-chlorophenol, and 8.241 mg/g for p-chlorophenol. The effect of various parameters like adsorbent dose, pH and initial concentration were studied for their optimization. The adsorption values of phenol and chlorophenols decreased with increasing pH. Desorption of phenol and chlorophenols was achieved using ethanol solution (30%, v/v). The rate of adsorption of phenol and chlorophenols were found to be maximum at pH 6.25. Equilibrium adsorption data for phenol and chlorophenols were analyzed by using Freundlich and Langmuir adsorption isotherms. It was found that Freundlich adsorption isotherm is the most suitable model.

Key Words
Clinoptilolite, removal of phenols, activation, adsorption isotherms and kinetics.

ÖZET

İnsanlar açısından zehirli olması nedeniyle suyun kimyasal kirliliği çok geniş toksik bileşiklerden dolayı, özellikle aromatik moleküller, ciddi bir çevresel problemdir. Bu çalışmada, Manisa-Gördes bölgesinden alınan (AMGC) aktive edilmiş klinoptilolit, fenol ve klorofenollerin (o-klorofenol, m-klorofenol ve p-klorofenol) uzaklaştırılmasında araştırılmıştır. Klinoptilolit, FT-IR, TG/DTA, BET yüzey alanı, SEM, XRD ve XRF metodları yardımıyla karakterize edilmiştir. Fenol ve klorofenollerin adsorpsiyon hızları çok yüksektir ve yaklaşık 45 dakikada dengeye ulaşmıştır. Klinoptilolit üzerine fenol ve klorofenollerin maksimum adsorpsiyonu, fenol için 7.977 mg/g, o-klorofenol için 9.846 mg/g, m-klorofenol için 9.981 mg/g ve p-klorofenol için 8.241 mg/g'dır. Adsorbant dozajı, pH ve başlangıç derişimi gibi çeşitli parametrelerin etkisi optimize edilmiştir. Fenol ve klorofenollerin adsorpsiyon değerleri pH arttıkça azalmıştır. Fenol ve klorofenollerin desorpsiyonu için %30 (v/v)'luk etanol çözeltisi kullanılmıştır. Fenol ve klorofenollerin adsorpsiyon hızları pH 6.25'de maksimum olarak bulunmuştur. Fenol ve klorofenoller için denge adsorpsiyon verileri, Freundlich ve Langmuir adsorpsiyon izotermleri kullanılarak analiz edilmiştir. En uygun modelin Freundlich adsorpsiyon izotermi olduğu bulunmuştur.

Anahtar Kelimeler
Klinoptilolit, fenollerin uzaklaştırılması, aktivasyon, adsorpsiyon izotermleri ve kinetik.

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INTRODUCTION

In the beginning of the 21st century, the mankind had to face an important threat of water shortage. According to World Health Organization (WHO), the shortage of water due to political, economical and climatological reasons affects more than 40% of the world population [1].

Phenolic compounds are very toxic, and most of them are known as potential carcinogens. Large-scale coal gasification and carbonization plants generate huge quantities of waste water with high phenolic content [2-6]. They cause adverse effects on digestive, nervous and respiratory systems, lead to cancer and disrupt the thyroid functions according to the report of International Program on Chemical Safety (IPCS) [7,8]. It became necessary to find an effective method to remove these compounds from waste or polluted waters. Monochlorophenols (MCPs) appeared to be effective cancer promoters and they are listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) [9]. US Environmental Protection Agency (EPA) regulations call for lowering the phenol content in the waste waters to less than 1 μg/L from the several thousand μg/L often present [10,11].

The conventional pollutant removal technologies include biological, thermal and physico-chemical treatments. Biological treatments usually require a long residence time for microorganisms to degrade the pollutant, because they are affected by toxicity of chlorophenols (CPs) [12]. Various methods have been proposed for the removal of phenolic compounds. These methods are based on chemical–biological oxidation and solvent extraction. The main limitation of these methods is their low efficiency in the removal of trace levels of phenols. Adsorption technology is currently being used extensively for the removal of phenols in a low concentration such as ppm level [13]. Non-specific sorbents, such as activated carbon, metal oxides, silica and ion-exchange resins have been employed for this purpose [14]. However, recently, specific sorbents have been found to be very promising [13]. Specific sorbents consist of a ligand (e.g. ion-exchange material) that interacts with the organic and inorganic pollutants specifically, and a carrier matrix that may be an inorganic material (e.g. aluminium oxide, silica or glass) or polymer microbeads (e.g. polystyrene, starch, chitosan, cellulose, poly(maleic anhydride) or polymethylmethacrylate) [10,15,16].

In recent years usage of low cost adsorbents in the removal of aromatic compounds [17-22] especially phenols [5,6], chlorophenols [5,10,17, 23] and other substituted phenols [16] have been widely investigated [5,6,10,13, 6-19,21,23-25].

Zeolites have appeared as attractive options for removal of organic compounds from the wastewater, because of their superior advantages [26]. Zeolites consist of more than 40 natural species. The most abundant and frequently studied zeolite is clinoptilolite. Clinoptilolite has been shown to have high selectivity for certain pollutants. The characteristics and applications of zeolites have been reviewed by Breck [27]. Natural zeolites have valuable properties such as ion exchange ability and high surface area. There are large deposits of natural zeolites in Greece, UK, Italy, Mexico, Iran, and Jordan [6]. Turkey has approximately 50 billion tons of zeolite deposits mainly present as clinoptilolite ores. There are large reserves of clinoptilolite in Bigadiç, Balıkesir, and Manisa-Gördes regions [28]. According to the General Directorate of Mineral Research and Exploration of Turkey, the reserves of clinoptilolite in the Manisa-Gördes region are estimated to be 2 billion tones [29]. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites attractive adsorbents. Their price is about US$ 0.03–0.12/kg, depending on the quality of the mineral [30-31].

Kuleyin has studied the adsorption characteristics of phenol and 4-chlorophenol (4-CP) by surfactant-modified zeolite [17]. Su et al. [32] studied the adsorption behaviors of phenol in aqueous solution on zeolite-templated porous carbons with different pore structures and surface properties. The adsorption of o-, m- and p-nitrophenols on clinoptilolite type natural zeolite has been studied as a function of the solution concentration and temperature [33] This study deals with the removal of phenols

Table 1. EDXRF results of AMGC.

Component	%	Component	%	Component	%	Component	%
SiO_2	70.370	MnO	0.040	K_2O	2.280	SO_3	0.040
TiO_2	0.117	MgO	1.220	P_2O_5	0.014	*LOI	10.509
Al_2O_3	10.430	CaO	3.440	Cr_2O_3	0.001		
Fe_2O_3	1.468	Na_2O	0.065	V_2O_5	0.006		

*LOI : Lost of ignition

and chlorophenols from the aqueous media in a batch system by the use of activated clinoptilolite. Another aim of this paper is to investigate thermal, structural and spectral properties of natural clinoptilolite and its H-form samples. Therefore, the equilibrium time of the adsorption of phenol and chlorophenols, the effect of the initial concentration upon the adsorption rate, the effect of the pH and the possibility of its regeneration have been examined.

EXPERIMENTAL

Materials

Natural zeolitic tuffs from Manisa-Gördes region (NMGC), western Anatolia, Turkey used in this study.

Reagents

Phenol, chlorophenols, 4-aminoantipirin (4-AAP), potassium ferricyanide $K_3[Fe(CN)_6]$, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Merck AG (Darmstadt, Germany) and were used without further purification. The water used in the preparation of the solutions was distilled and deionized by an ELGA Option S7BP water purification system.

ANALYTICAL METHODS

Activation of Clinoptilolite

AMGC was crushed and sieved to obtain < 63 μm fractions. First, clinoptilolite rich samples boiled in deionized water (100 mL deionized water for 5 g of clinoptilolite) at 60°C for 2 h in order to remove the soluble salts. In the second stage, the washed zeolite was activated by 100 mL of 0.2 M HCl solution and rewashed with de-ionized water. Third, Na^+, K^+, Ca^{2+} and Mg^{2+} ionic forms of clinoptilolites were prepared by the batch method, using 1 M solutions at 80°C for 4 h. Finally, the treated samples were rinsed with de-ionized water and dried at room temperature. Before the experimental procedure, all samples were dried in an oven at 110°C for 16 h and stored in desiccators.

After activation, the sorbents were placed in acid solutions, thoroughly washed by distilled water up to pH about 5.5–6.0 and dried in air. The samples of natural zeolite do not possess microporous structure but they are observed to form hydrogen forms of clinoptilolite [34].

Chemical composition of natural zeolite is given in Table 1. AMGC sample has high calcium and potassium and low magnesium and sodium contents. Ming and Dixon have reported that the main cations were Na^+, K^+ and Ca^{2+} [35]. In addition, iron is present. Iron has been associated with impurities present in zeolitic tuffs such as iron oxides. The sorbent has a high SiO_2 content with SiO_2/Al_2O_3 ratio of 6.75.

The experimental values of cation exchange capacity (CEC) were measured according to ASTM 837C Standard. The total CEC of zeolite was found to be 27.174 meq/ 100 g.

N_2 adsorption and surface area (BET)

The total surface areas for the NMGC and AMGC (H-clinoptilolite) samples were 28.22 m^2/g and 80.51 m^2/g, respectively. The total surface area of AMGC was higher than NMGC [36]. The natural adsorbent has a small specific surface area which increases significantly after the activation [34].

X-ray diffraction (XRD) analysis

XRD measurements were taken by Rigaku D-max 2200 model diffractometer. XRD analysis was performed on the natural and activated clinoptilolite sample to confirm the crystal structure and identity.

Thermogravimetric analysis

Thermal analysis of clinoptilolite was conducted with a Shimadzu TGA/DSC 60H at a heating rate of 20 K/min under nitrogen (99.99% purity) with aluminum pans at temperatures from ambient 25°C to 900°C. The powdered sample, about 40 mg in weight was packeted into the aluminum pan, and the gas flow rate was kept at 5 L h^{-1}.

Scanning electron microscopy (SEM) and EDX (Energy-dispersive X-ray)

The surface morphology and internal structure of the AMGC was observed by a scanning electron microscope (LEO 1430VP). The AMGC was dried at room temperature and coated with a thin layer of carbon (about 100 Å) in vacuum and photographed in the electron microscope at X5000 magnification.

FT-IR photoacoustic spectroscopy

Spectral data were collected by a Perkin Elmer 460 Spectrum BXI spectrometer and a helium-purged MTEC 300 photoacoustic cell. All the spectra were recorded over the 4000–400 cm^{-1} region at a spectral resolution of 8 cm-1 and with the 1024 scans co-added. The spectra were normalized proportioning the sample spectrum with a carbon black spectrum [34].

Zeta Potential

The zeta potential of the AMGC particles was measured without any pretreatment by a MALVERN Nano-Z equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation [37]. The zeta potential measurements were carried out as a function of pH. A sample of 0.05 g AMGC and 50 mL distilled water containing the desired electrolyte was added to a beaker and stirred with a magnetic stirrer for 10 min at 20±1 C. The samples were allowed to stand for 5 min to let larger particles settle.

Adsorption Studies

Monochlorophenols are solid at room temperature, except for 2-MCP, which is a liquid. Phenol and chlorophenols concentrations in the samples were determined using a colorimetric assay where the phenolic compounds within a sample react with 4-AAP in the presence of potassium ferricyanide reagent under alkaline conditions [5,24]. The phenolic compound assay contained sample solution (1.0 mL), 4-AAP (1.0 mL, 2.0 mM), and potassium ferricyanide reagent (1.0 mL, 6 mM). The latter two reagents were prepared in phosphate buffer solution (pH 10, 100 mM). The absorbance of the assay mixture was measured using a DR-5000 spectrophotometer. A blank containing distilled water, 4-AAP, and potassium ferricyanide reagent was used in each set of the assay. The experiments were carried out over the pH range 2.0–12.0 and temperature range 25–45°C to determine the effect of pH and temperature on the removal of phenol and chlorophenols. Each set of experiments was carried out in triplicate and the arithmetic mean values were calculated.

The AMGC was weighed and placed in flasks containing phenol or chlorophenols solutions at desired concentration. In order to evaluate kinetic data, separate flasks were prepared for each period from 15 min to 24 h. For each adsorption isotherm experiment, a known amount of the adsorbent was added to 20 mL of the solution ranging from 50 to 1000 mg/L in phenol and chlorophenol concentrations. The mixture was shaken in a temperature-controlled shaking water bath at a constant speed of 400 rpm for 24 h. The solution and sorbent were separated by centrifugation at 5000 rpm and analyzed for phenol and chlorophenols concentrations. The concentration of phenol and chlorophenols was determined spectrophotometrically at a wave length of 510 nm.

RESULTS AND DISCUSSIONS

XRD Results

Figure 1 shows the X-ray diffraction patterns of AMGC. According to the most intense diffraction peaks, It contains clinoptilolite and heulandite as well as quartz, feldspar and smectite group clay mineral. The sharpness of the peaks and the negligible variation of their positions after the activation suggest a high crystallinity degree and structural stability of the materials. Thus,

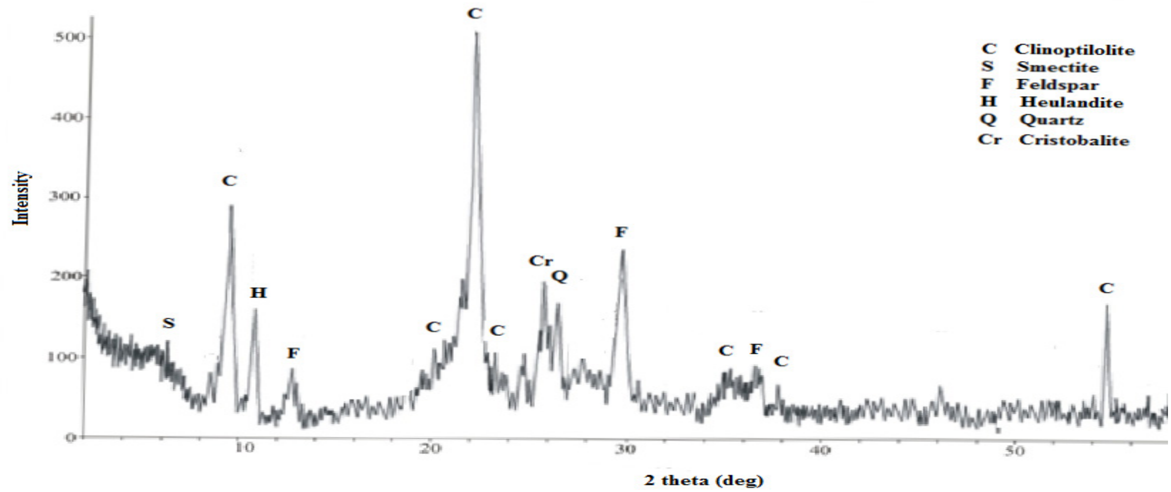


Figure 1. XRD spectrum of AMGC.

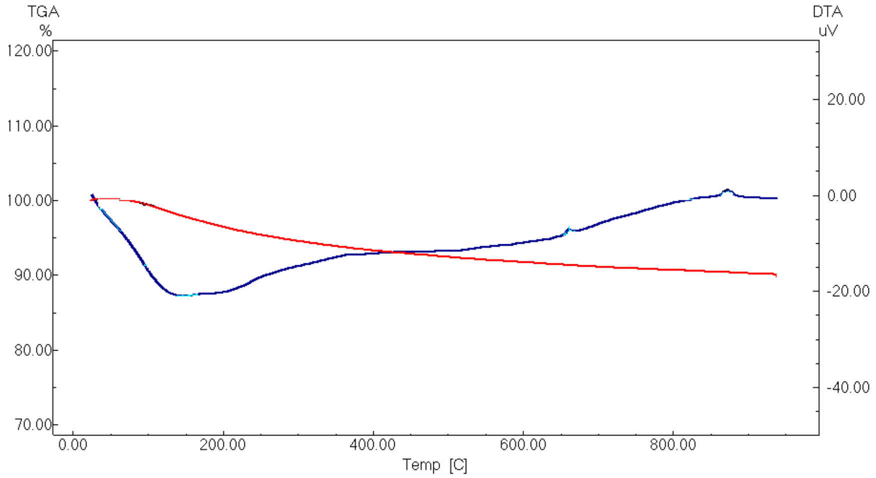


Figure 2. DTA-TG curve of AMGC sample.

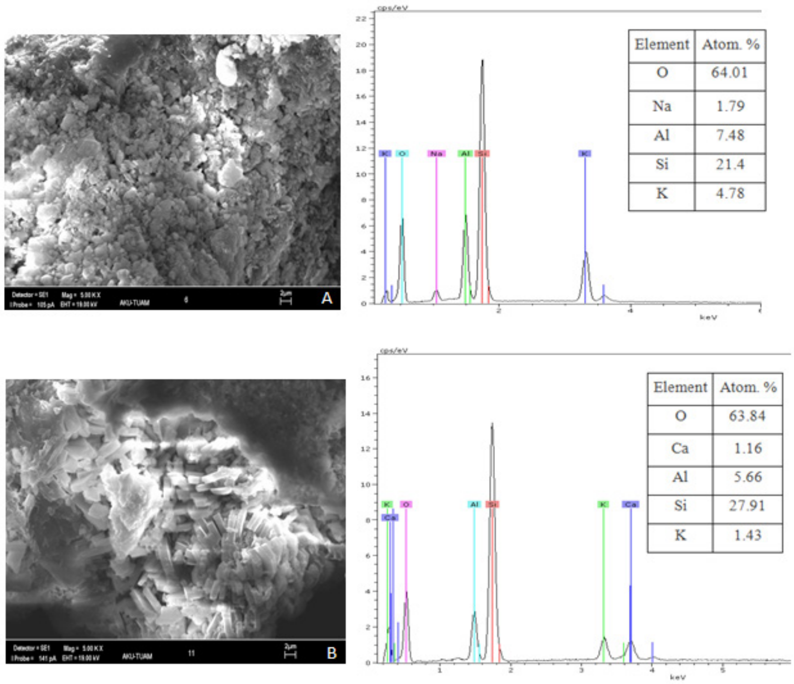
the applied treatments do not seem to provoke collapse or significant destruction of the zeolitic structure, at least detectable by this technique [38,39].

TG-DTA Experimental Results

The thermo analytical techniques TG/DTA can help us to understand the interactions between adsorbed water ion as well as the thermal behavior of zeolite. The thermogravimetric analysis shows the presence of various types of intact water and surface hydroxy species. Figure 2 shows TG-DTA curves of AMGC.

The DTA curves of the AMGC forms display a single endotherm at temperature ranging from 35 to 146°C as a result of a single-step dehydration process. This shows the presence of water, and larger amounts of water desorbed from zeolite. Clinoptilolite belongs to the zeolite group that does not show major structural changes during dehydration process which exhibits continuous mass-loss curves as a function of temperature. Clinoptilolite structure remains stable up to temperatures between 700 and 800°C [29]. As can be seen in the Figure 2, the main structural changes occur at temperatures below or around 250°C while the mass loss is constant at temperatures higher than 700°C [34].

In the temperature between 20-230°C desorption of zeolitic water is assumed to occur according to the Equation 1



Element	Atom. %
O	64.01
Na	1.79
Al	7.48
Si	21.4
K	4.78

Element	Atom. %
O	63.84
Ca	1.16
Al	5.66
Si	27.91
K	1.43

Figure 3. SEM micrograph and EDX analysis of AMGC. A: Before adsorption of phenol; B: After adsorption of phenol.

$$H_2O\text{-clinoptilolite(cr)}\ \ \text{clinoptilolite(cr)} + H_2O\ (g) \qquad (1)$$

The mass losses recorded by thermogravimetric analysis (TG) are shown in Figure 2. In the temperature range from 100 to 250°C, the rapid mass loss is documented by the steep slope of the TG curve as it is attributed to the loss of the water located in the zeolite cavities and bound to the nonframework cations. In the temperature range from 250 to 600°C, the mass loss is less and it is indicated by the slight slope of the TG curve. In the temperature range from 600 to 950°C, the rate of loss is even slower. In this temperature range, the remaining water is gradually removed.

SEM-EDX Microscopy Studies

The mineralogical and geochemical analysis showed that the clinoptilolite is the only zeolite mineral in tuff samples where the volcanic ash shards were altered to the aggregates of clinoptilolite crystallizes. SEM micrograph of AMGC is shown in Figure 3. The zeolitized tuffs have a texture with very high microporosity. The orthorhombic geometry of clinoptilolite has not changed much; probably there are changes in sharp edges and corners.

In microphotos of samples (Figure 3), it is shown that conditions are favorable for development of clinoptilolite crystals. The fact that clinoptilolite minerals are intensely found in samples and there is no other high-temperature mineral in the environment may indicate that clinoptilolites were developed in low temperature. The average silica concentrations of AMGC are 70.37%. The wide distribution of zeolites in both regions is indicative of glass-enrichment of the volcanic products. In SEM microphotos of Figure 3A, AMGC is shown to complete their crystal development under favorable conditions.

FT-IR Experimental Results

FT-IR spectra is shown in Figure 4. It shows the presence of the same typical bands after and before adsorption of AMGC [25].

There are two groups of frequencies of vibrations in all clinoptilolite: internal vibrations of T–O (considered insensitive to structure) and vibration of external linkages between tetrahedral bridges, due to topology and the mode of structural arrangement. The FT-IR band connected with the internal Si–O(Si) and Si–O(Al)

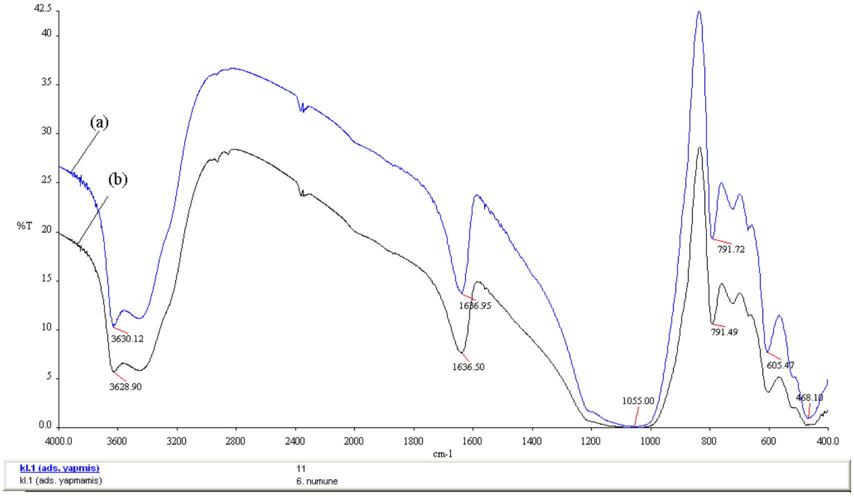


Figure 4. AMGC'in Infrared spectrum. a) After adsorption of p-chlorophenol, b) Before adsorption.

vibrations in tetrahedral or alumina- and silica-oxygen bridges lies in the range of 791.49-1055 cm^{-1}. The bands due to the presence of zeolite water lie in the range of 1600–3700 cm^{-1}. There are several types of zeolitic water. The OH- group is less acidic if the number of aluminum atoms increases because Al is less electronegative. The OH stretching vibrations in the range of 3340-3400 cm^{-1} are inherent for less acidic groups than that at 3630 cm^{-1}. There are bands due to pseudo-lattice vibrations of structural units (500-700 cm^{-1}). Embedding of non-tetrahedral cations into the aluminosilicate framework can change the FT-IR spectra in the range of pseudolattice vibrations at 700–500 cm^{-1}. These changes are more often characterized by shifts in the bands of the framework vibrations [9,34].

The Zeta Potential Measurements

The variation of the zeta potential of AMGC is shown in Figure 5. The zeta potential measurements revealed that the AMGC surface acquires a negative charge in water at pH 3-11. This negative charge results from substitutions within the AMGC lattice of Al^{3+} for Si^{4+}, the broken bonds at the Si– O–Si (siloxane group) of AMGC particularly generated at the particle surface during grinding (Figure 5) and the lattice imperfections.

AMGC can be considered as a permanently charged mineral because of the isomorphic substitution. The decrease of the suspension pH results in a decrease of the negative potential due to the H^+ adsorption on the negative charge centers. At around pH 3, the zeta potential is about -18 mV; this shows that the AMGC surface maintains its negative character even in very acidic conditions though most silicate or clay minerals have the isoelectric point (iep) of pH 2–4. This is attributed to the number of substitution, of Al^{3+} for Si^{4+}, to be more than those of clay minerals and also to the higher positive charge deficiency of AMGC. As a result, the negatively charged surface of AMGC even at very acidic pH values may be an advantage for the electrostatic interactions of organic or inorganic cationic contaminants with AMGC [37].

Phenol and Chlorophenols Adsorption

AMGC was separated from the adsorption medium at the end of each experiment, and the concentration of the phenol and chlorophenols in the aqueous phase was measured by UV.

In order to reduce measurement errors the UV absorption intensity of each equilibrium solution sample was measured three times and the average value was used to calculate the

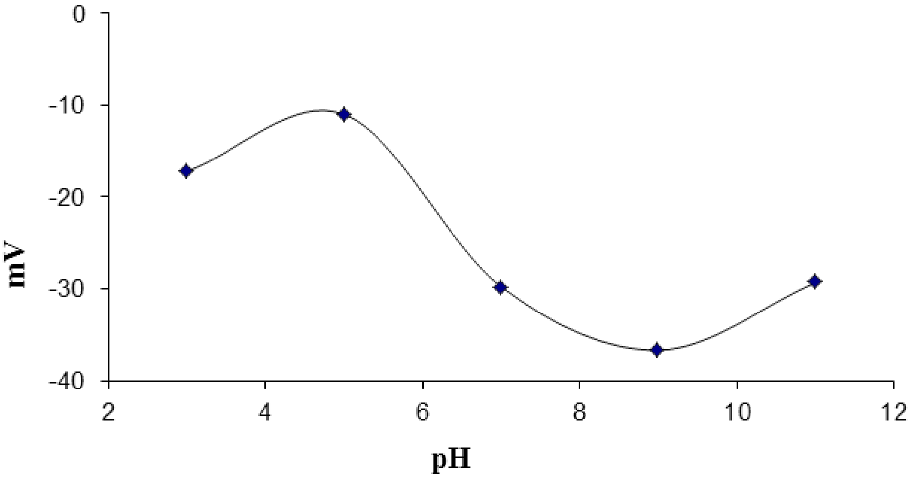


Figure 5. The variation of the zeta potential of AMGC versus pH.

equilibrium concentration based on a standard calibration curve, which correlation coefficient (R^2) was 0.99. The amount of phenol and chlorophenols adsorbed onto the adsorbate qe (mg/g) were calculated according to: (Eq. 2)

$$q_e=[(C_0-C_A)V]/m \quad (2)$$

where qe is the amount of phenol and chlorophenols adsorbed onto the unit amount of AMGC (mg/g); Co and CA are the concentrations of the phenol and chlorophenols in the initial solution and in the aqueous phase after adsorption, respectively (mg/L); V is the volume of the aqueous phase (L); and m is the weight of the AMGC (g) [10,15].

The AMGC loaded 7.977 mg/g for phenol, 9.846 mg/g for o-chlorophenol, 9.981 mg/g for m-chlorophenol and 8.241 mg/g for p-chlorophenol were placed in this adsorption medium and stirred at 400 rpm for 45 min at room temperature. The difference in adsorption behavior of the chlorophenol species compared to each other can be explained by the different affinity of the phenolic species for the reactive functional groups in AMGC. A difference in geometrical structure is most probably also the case for the AMGC, resulting in a relatively high adsorption of m-chlorophenol [10]. The final phenol and chlorophenols concentrations in the aqueous phase were determined by using UV. The desorption ratio was calculated from the amount of phenol and chlorophenols initially loaded on the AMGC and the final concentration of phenol and chlorophenols in the desorption medium [25].

Recent literature on the methods of removal of phenol and their compounds from wastewater focuses on adsorption process[40]. As with other materials, clay materials can be modified to improve their adsorption capacity. Kaleta [41] utilized modified Clarion clay and clinoptilolite as adsorbents for the removal of phenolic compounds from water. Adsorption capacities are substantially improved by modifying the clay materials. The amount of adsorption was found to be dependent on the relative energies of adsorbent–adsorbate, adsorbate solvent and adsorbate–adsorbate interaction. The removal of phenol from aqueous solutions by adsorption using three different adsorbents, clinoptilolite, montmorillonite, and hydrotalcite (HT) was studied by Yapar and Yilmaz [42]. Clinoptilolite was modified using cetyltrimethylammonium bromide (CTAB) and hydrotalcite was calcined by heating to 550°C. Calcined hydrotalcite (HTC) was found to be the best among the studied adsorbents. Naturally occurring bentonite is able to adsorb phenol from aqueous solutions [43].

Adsorption Time

The equilibrium adsorption time of phenol and chlorophenols (i.e. o-chlorophenol, m-chlorophenol, p-chlorophenol) on the AMGC was investigated (Figure 6). Note that these batch experiments were performed by using

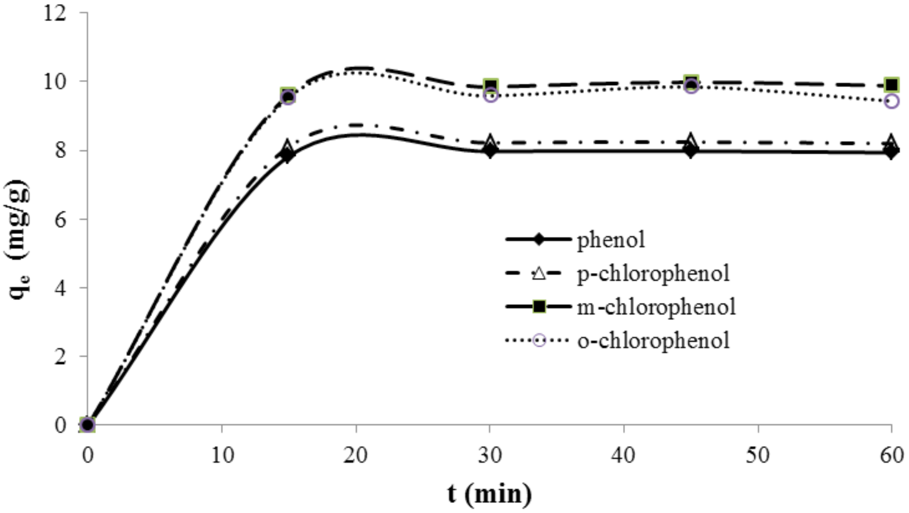


Figure 6. Adsorption rates of phenol on the AMGC at 25°C. (Initial concentration: 200 mg/L; pH= 6.25).

single solutions of the concerned phenol and chlorophenols. The initial concentrations of the phenol and chlorophenols within the aqueous phase were kept constant at 200 mg/L. These kinetic studies point out that the phenol adsorption is carried out at a rapid rate in the first 15 min. Then the adsorption is slower down, possibly due to the less active adsorption sites being available and/or the difficulty of the edge molecules in diffusing the small adsorbents' pores [16]. Saturation levels are gradually reached within 30 min for all phenol and chlorophenols. Notice that m-chlorophenol was adsorbed much faster than other chlorophenols due to the much higher affinity of the AMGC. The adsorption rate order was as follows: m-chlorophenol, o-chlorophenol, p-chlorophenol and phenol. Adsorption of phenolic species was quite fast especially when the initial solution concentration was high.

Note that there are several parameters that determine the adsorption rate such as stirring (or flow) rate of the aqueous phase, structural properties of the sorbent (e.g. porosity, surface area), amount of sorbent, adsorbate properties (e.g. molecular weight), initial concentration of phenolic species and of course existence of other species that may compete with the phenolic species of interest for the active adsorption sites. Therefore, it is very difficult to compare the adsorption rates reported. However, the adsorption rates obtained with the AMGC produced by us seem to be very satisfactory [25].

Effect of Initial Concentration of Phenol and Chlorophenols

The phenol and chlorophenols adsorption capacities of the AMGC are given as a function of the initial concentration of phenol and chlorophenols within the aqueous phase in Figure 7. It was observed that the amount of adsorption was significantly increased with the initial concentration from 50 to 10000 mg/L.

The maximum adsorption capacities of the AMGC in the studied range are 7.977 mg/g for phenol, 9.846 mg/g for o-chlorophenol, 9.981 mg/g for m-chlorophenol, and 8.241 mg/g for p-chlorophenol at 6.25 pH, which correspond to an initial concentration of 200 mg/L. The results suggest that the affinity of phenol and chlorophenols toward adsorption follows the order m-chlorophenol > o-chlorophenol > p-chlorophenol > phenol.

The difference in adsorption behavior of phenol and chlorophenol species compared to each other can be explained by the different affinity of the phenolic species for the reactive functional groups in the AMGC. A difference in geometrical structure is the most probably also the case for AMGC, resulting in a relatively high adsorption of m-chlorophenol [10].

The phenol and chlorophenols removal by the AMGC are given as a function of the initial concentration of phenol and chlorophenols

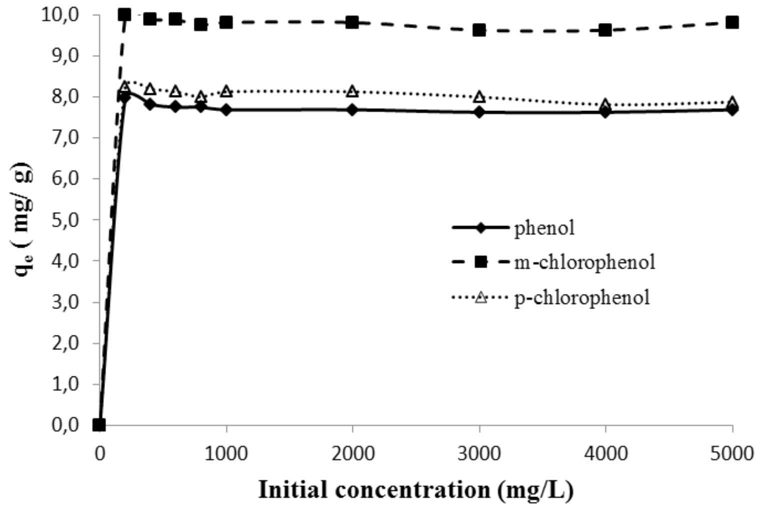


Figure 7. Phenol and chlorophenols adsorption capacity of the AMGC at 25°C. (pH= 6.25, s/l : 2.5 gr/L, 400 rpm, t= 45 min).

within the aqueous phase in Figure 8. Phenol and chlorophenols maximum removal efficiency by AMGC were 89.01 for phenol, 99.21 for m-chlorophenol, and 96.41 for p-chlorophenol.

Effect of pH

The effect of pH on adsorption of phenol and chlorophenols is shown in Figure 9. The effect of pH less than 5 was not investigated because zeolite is not stable at pH below 5.0 [19]. It was observed that the adsorption capacities decreased with increasing pH. The maximum adsorption of phenol and chlorophenols were at approximately pH 6.25 for all species. However, the adsorption capacity was considerably decreased when the pH of the initial solution was above 8.0. The interaction forces between chlorophenols and clinoptilolite are rather weak in the neutral solutions. The decrease in adsorption capacity may also be due to the competing hydroxide ions [10].

Effect of Thermodynamic Parameters

Thermodynamic parameters free energy of sorption (G) can be evaluated with the following equations [17]:

$$K_d=q_e/C_e$$

where K_d is the sorption distribution coefficient. The K_d values are used in following equation to determine the Gibbs free energy of sorption process at different temperatures.

$$\Delta G^0=-RT\ln K_d$$

where ΔG is the free energy of sorption (kJ/mol), T is the temperature in Kelvin, and R is the universal gas constant (8.314 J/mol.K). Thermodynamic parameters for phenol and chlorophenols adsorption on AMGC were given in Table 2.

The negative values of free energy change (ΔG) indicate the spontaneous nature of the adsorption process. The negative values of G confirm the feasibility of the process and the spontaneous nature of sorption with a high preference of phenol and chlorophenols on AMGC [44,45] However, the negative ΔG value decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature.

In conclusion, the usage of AMGC as an adsorbent could be an alternative for commercially available carbon due to its low cost and good efficiency.

Reusability of the Adsorbent

In order to determine the adsorptive capacity of the adsorbent after each cycle an experiment was performed with the used adsorbent to determine its reusability. Desorption of phenol and chlorophenols was achieved by using ethanol solution (30% v/v). Significant decline in the

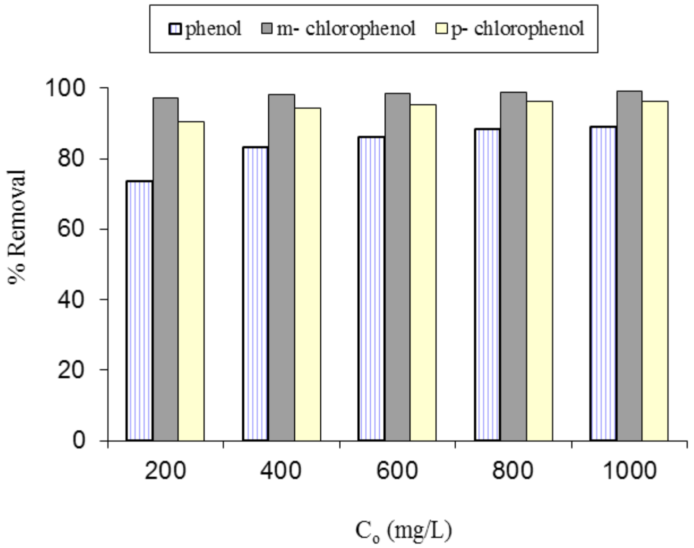


Figure 8. Comparison of phenol and chlorophenols removal by AMGC at 25°C. (pH= 6.25, s/l : 2.5 gr/L, 400 rpm, t= 45 min).

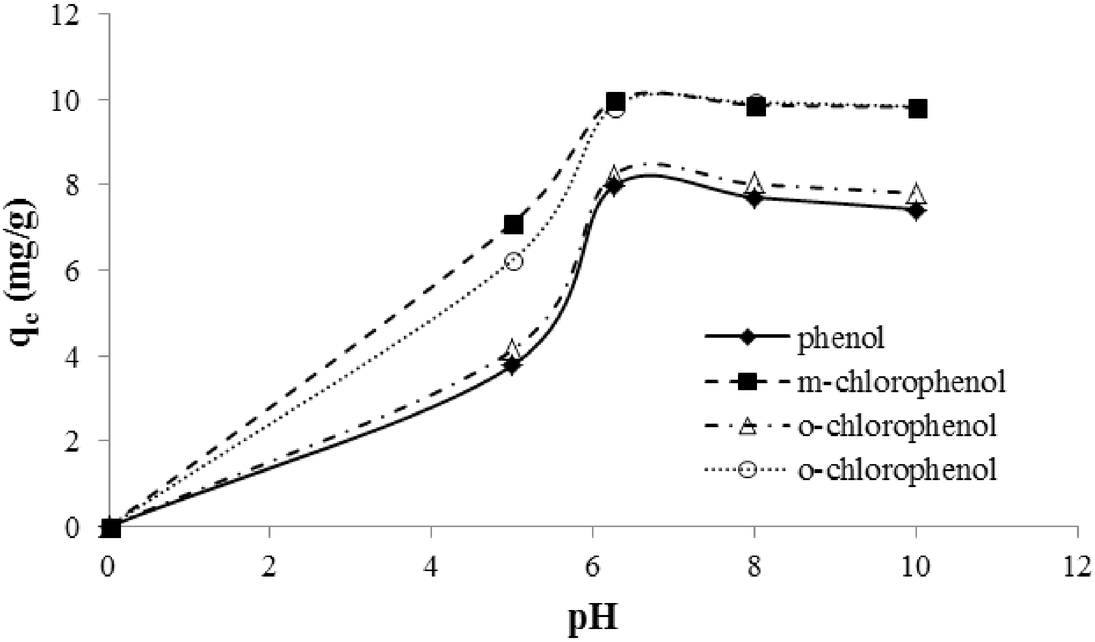


Figure 9. Effect of pH on adsorption of phenol and chlorophenols on the AMGC at 25°C. (Initial concentrations of chlorophenols: 200 mg/L s/l : 2.5 g/L, t= 45 min , 400 rpm).

Table 2. Gibbs free energy of AMGC.

Gibbs Constant	Phenol	m-Chlorophenol	p-Chlorophenol
K_o	1.576	4.463	1.552
R^2	0.984	0.958	0.942
ΔG°(kj/mol)	-1.128	-3.706	-1.089

removal efficiency was observed for subsequent adsorption. As the number of adsorption cycles increases the adsorptive capacity of the adsorbent decreases because with successive adsorption the active sites of the adsorbent decreases which results in the decrease in its removal efficiency [19].

Adsorption Isotherms

Freundlich Adsorption Isotherms

This isotherm developed by Freundlich (1906) describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. It is given by (Eq. 5).

$$q_e=K_F C_e^{1/n} \qquad (5)$$

where qe is the equilibrium amount of solute adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of solute in bulk solution (mg/L), K_F is a constant indicative of the relative adsorption capacity of the adsorbent (mg/g) (mg/L)n, and the constant 1/n indicates the intensity of the adsorption (Table 3) [6].

It was found that Freundlich adsorption isotherm is the most suitable model and adsorption mechanism is physical.

Mechanism of Adsorption

The results showed that kinetic data were followed more closely the pseudo-second order model than the pseudo-first order. Kinetic studies have been performed to understand the mechanism of adsorption. The adsorption occurred via a film diffusion mechanism at lower concentrations and via particle diffusion at higher concentrations.

The pseudo-second order reaction model based on sorption equilibrium capacity may be expressed as

$$d_q/d_t=k_2 (q_e-q_t)^2 \qquad (6)$$

After integrating Eq. (6) for the following boundary condition and rearranging it to obtain the linearized form which is shown as follows: t=0, qt =0, t = t, qt = qt

$$t/(q_t=1/(k_2 q_e^2)+1/(q_e t)) \qquad (7)$$

$$h=k_2 q_e^2 \qquad (8)$$

where q_e is the amount of the solute sorbed at equilibrium (mg/g), k_2 is the equilibrium rate constant of pseudo-second order (g/mg min), h is the initial sorption rate (mg/g min).

These constants can be determined by plotting t/qt against t [17,46].

The values of kinetic constants for phenol and chlorophenols sorption onto AMGC are presented in Table 4. Good correlation coefficients were obtained for the pseudo-second order kinetic model, which shows that the uptake process follows the pseudo-second order rate expression with the correlation coefficients higher than 0.99 [17].

MCPs are represented by a Cl atom and an OH group, bound to the aromatic ring. Functional group position of the molecule affects vibrational frequencies. It was obtained that the closer the Cl atom to OH group of the ring, the higher the wave number of OH group for MCPs [9]. Hydrogen bonding refers to a stronger than usual dipole attraction between molecules in which hydrogen is bonded to a highly electronegative atom. Chlorophenols and polar solvent molecule (e.g., water, alcohol) could act as proton donors as well as proton acceptors and two types of hydrogen bonds are possible. When chlorophenol is the proton donor, electronic charge is transferred from the solvent to the phenolic oxygen and in consequence intermolecular hydrogen bonds may be formed. The influence of hydrogen bonding on rate of reaction, especially radicals reaction, is discussed in various papers. Due to type of polar group, in chlorophenol two types of intermolecular hydrogen bonds, between two chlorophenol molecules, i.e., HO· · ·HO, and OH· · ·Cl can be formed. The interactions between hydrogen and chlorine atoms are weaker than those between hydrogen and oxygen atoms, therefore strong shifts of these bands can be observed in the case of HO· · ·HO type of hydrogen bonds [47]. There isn't electron attractive group such as chlorine in phenol, so it is observed less adsorption than other chlorine derivatives on clinoptilolite.

Table 3. Freundlich Isotherm parameters for the removal of phenol and chlorophenols by AMGC at 25°C. (natural pH=6.25, 400 rpm, s/l=2.5 g/L).

Freundlich Coefficients	Phenol	m-Chlorophenol	p-Chlorophenol
KF	0.004	0.670	0.027
1/n	2.445	2.840	2.711
R2	0.980	0.949	0.908

Table 4. Pseudo-second-order constants for the adsorption of phenol and chlorophenols on AMGC at 25°C. (Co= 200 mg/L, natural pH=6.25, 400 rpm, s/l=2.5 g/L).

Phenols	qe_2 (teo.)	qe_2 (den.)	k^2	R^2
Phenol	66.660	63.813	0.059	0.9999
o-Chlorophenol	75.758	78.768	-0.033	0.9983
m-Chlorophenols	78.740	79.848	0.043	0.9998
p-Chlorophenol	67.567	65.927	0.033	0.9995

CONCLUSIONS

Wastewaters containing phenolic compounds present a serious problem. Phenol-containing wastewater may not be conducted into open water without treatment because of the toxicity of phenol.

The present studies lead to the following conclusions: AMGC materials are proving to be an effective new class of adsorbents for the adsorption of phenolic compounds. It has good physical as well chemical stability; hence it can be used for various environmental applications.

The structural stability of the zeolite was not significantly affected by the acid treatment. A considerable increase in the micropore volume was also observed in AMGC after the acid treatment.

The removal of phenol and chlorophenols at neutral pH is high as compared to alkaline pH and this may be attributed to the fact that at higher pH it form phenolate ion, which decrease its adsorption. The adsorption of phenol and chlorophenols decreased with increasing pH after neutral pH.

The sorption of chlorophenols was high as compared to phenol, which may be due to more hydrophobic nature of chlorophenols. The maximum adsorption capacities of these AMGC from their single solutions were 9.981 mg/g for m-chlorophenol, 9.846 mg/g for o-chlorophenol, 8.241 mg/g for p-chlorophenol and 7.977 mg/g for phenol. The affinity order was as follows: m-chlorophenol > o-chlorophenol > p-chlorophenol > phenol. The difference in adsorption order of chlorophenols compared to each other can be explained by the different affinity of the phenolic species in AMGC.

For AMGC the elimination of greater amounts of physically bonded water is observed up to 120°C. Thermogravimetric curves showed no noticeable breaks in the mass-loss curve. The mass losses above 500°C may be caused by dehydroxylation. In general, the dehydroxylation of the clinoptilolite is slow and occurs in this case in the range 600–800°C.

In conclusion the use of low-cost adsorbents may have a great contribute to the sustainability of the surrounding environment. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future.

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References

1. M. P. Titus, V. G. Molina, M. A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B-Environ., 47 (2004) 219–256.
2. HEW Publication No. (N1OSH), Center for Disease Control, N1OSH, Washington, 1976.
3. M.W. Slein, E.B. Sansone, Degradation of Chemical Carcinogens, Van Nostrand Reinhold, New York, 1980.
4. N.N. Dutta, S. Borthakur, R. Baruah, A novel process for recovery of phenol from alkaline wastewater: laboratory study and predesign cost estimate, Water Environ. Res., 70 (1998) 4-9.
5. G. Bayramoğlu, M.Y. Arıca, Enzymatic removal of phenol and p-chlorophenol in enzyme reactor: Horseradish peroxidase immobilized on magnetic beads, J. Hazar. Mater., 156 (2008) 148–155.
6. S.H. Lin, R.S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review, J. Environ. Manage., 90 (2009) 1336–1349.
7. Environmental Health Criteria 93: Chlorophenol Other Than Pentachlorophenol, World Health Organization, Geneva, 1989, 208.
8. International Programme on Chemical Safety (IPCS), Poisons Information Monograph (PIM), 1989, 405.
9. B. Bardakçı, FTIR-ATR Spectroscopic Characterization of Monochlorophenols and Effects of Symmetry on Vibrational Frequencies, Çankaya Üniversitesi Fen-Edebiyat Fakültesi, J. Art. Sci., 7 (2007) 13-19.
10. A. Denizli, G. Özkan, M. Uçar, Removal of chlorophenols from aquatic systems with dye-affinity microbeads, Sep. Purif. Technol., 24 (2001) 255–262.
11. D. Tang, Z. Zheng, K. Lin, J. Luan, J. Zhang, Adsorption of p-nitrophenol from aqueous solutions onto activated carbon fiber, J. Hazar. Mater., 143 (2007) 49–56.
12. V. G. Molina, J. Kallas, S. Esplugas, Wet oxidation of 4-chlorophenol Kinetic study, Chem. Eng. J., 126 (2007) 59–65.
13. M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: A review, Adv. Colloid Interfac., 143 (2008) 48–67.
14. E.G. Furuya, H.T. Chang, Y. Miura, K.E. Noll, A fundamental analysis of the isotherm for the adsorption of phenolic compounds on activated carbon, Sep. Purif. Technol., 111 (1997) 69-78.
15. A. Denizli, G. Özkan, M. Uçar, Microbeads for Removal of Phenols and Nitrophenols from Aquatic Systems, J. Appl. Polym. Sci., 83 (2002) 2411–2418.
16. S. Şenel, A. Kara, G. Alsancak, A. Denizli, Removal of phenol and chlorophenols from water with reusable dye-affinity hollow fibers, J. Hazar. Mater. B, 138 (2006) 317–324.
17. A. Kuleyin, Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite, J. Hazar. Mater., 144 (2007) 307–315.
18. S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J., 156 (2010) 11–24.
19. S.P. Kamble, P.A. Mangrulkar, A.K. Bansiwal, S.S. Rayalu, Adsorption of phenol and o-chlorophenol on surface altered fly ash based molecular sieves, Chem. Eng. J., 138 (2008) 73–83.
20. M.L. Soto, A. Moure, H. Dominguez, J.C. Parajo, Recovery, concentration and purification of phenolic compounds by adsorption: A review, J. Food Eng., 105 (2011) 1–27.
21. R.I. Yousef, B. El-Eswed, The effect of pH on the adsorption of phenol and chlorophenols onto natural zeolite, Colloids Surface A., 334 (2009) 92–99.
22. L. Damjanovi , V. Raki , V. Rac, D. Stoši , A. Auroux, The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents, J. Hazar. Mater., 184 (2010) 477–484.
23. A. Denizli, N. Cihangir, N. Tüzmen, G. Alsancak, Removal of chlorophenols from aquatic systems using the dried and dead fungus Pleurotus sajor caju, Bioresource Technol., 96 (2005) 59-62.
24. K. Tatsumi, S. Wada, H. Ichikawa, Removal of chlorophenols from wastewater by immobilized HPR, Biotechnol. Bioeng., 51 (1996) 126–130.
25. S. Uçar, Sulu Ortamda Bulunan Fenol ve Klorofenollerin Aktive Edilmiş Klinoptilolit Kullanılarak Uzaklaştırılması, Master Thesis, Afyon Kocatepe University, 2009.
26. M. Ghiaci, A. Abbaspur, R. Kiaa, F. Seyedeyn-Azad, Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM- 41 Sep. Purif. Technol., 40 (2004) 217-219.
27. D.W. Breck, Zeolite molecular sieves: structure, chemistry, and use. New York: Wiley; 1974.
28. A.D. Bahaallddin, Ammonium and Lead Exchange in Clinoptilolite Zeolite Column, Master Thesis, METU, 2010
29. B.E. Alver, M. Sakızcı, E. Yörükoğulları, Investigation of clinoptilolite rich natural zeolites from Turkey: a combined XRF, TG/DTG, DTA and DSC study J. Therm. Anal. Calorim., 100 (2010) 19–26.
30. A. Evcin, O. Tutkun, Pervaporation Separation of Ethanol-Water Mixtures by Zeolite Filled Polymeric Membranes, Ceram-Silikaty., 53 (2009) 250-253.
31. Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water, J. Hazard Mater., 97 (2003) 219-243.
32. F. Su, L. Lv, M.H. Tee, X.S. Zhao, Phenol adsorption on zeolite-templated porous carbons with different pore-structural and surface properties, Carbon., 43 (2005) 1156-1164.
33. T. Şişmanoglu, S. Pura, Adsorption of aqueous nitrophenols on clinoptilolite, Colloid Surface A., 180 (2001) 180, 1-6.
34. O. Korkuna, R. Leboda, J. Skubiszewska-Zi ba, T. Vrublevs'ka, V.M. Gun'ko, J. Ryczkowski, Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite, Micropor. Mesopor. Mat., 87 (2006) 243–254.
35. D. Ming and J. Dixon, Quantitative Determination of Clinoptilolite in Soils by a Cation-Exchange Capacity Method, Clay. Clay Miner., 35 (1987) 463-468.

36. M. Yılgın, D. Akkoca, "Bigadiç Klinoptilolitik Tüfün Kimyası, Yüzey Alanı ve Gözeneklilik Özelliklerine Farklı Asitlerin Etkilerinin İncelenmesi", Sci Eng J., 20 (2008) 175- 184.
37. B. Ersoy, M. S. Çelik, Electrokinetic properties of clinoptilolite with mono- and multivalent electrolytes, Micropor. Mesopor. Mat., 55 (2002) 305–312.
38. A. Rivera, T. Farías, L. C. de Ménorval, G. Autié-Castro, H. Y. Madeira, J. L. Contreras, M. A. Pérez, Acid natural clinoptilolite: Structural properties against adsorption/separation of n-paraffins, J. Colloid Interface Sci., 360 (2011) 220–226.
39. O.E. Petrov, Cation exchange in clinoptilolite: An X-Ray powder diffraction analysis, in: D. W. Ming, F.A. Mumpton (Eds.), Natural Zeolite'93: Occurrence, Properties, Use, International Committee on Natural Zeolites, Brockport, NY, 1995, pp. 271–279.
40. Doğal Zeolitlerin Katalizör ve Adsorbent Sentezi ve Ekonomik Açıdan Kullanılabilirlikleri, DPT Proje no 2003K12019014-5, 2005-2008.
41. J. Kaleta, Removal of phenol from aqueous solution by adsorption, Can. J. Civil Eng. 2006, 33, 5, 546-551.
42. S. Yapar, M. Yılmaz, Removal of Phenol by Using Montmorillonite, Clinoptilolite and Hydrotalcite. Adsorption, 10 (2005) 287-298.
43. S. Al-Asheh, F. Banat, L. Abu-Aitah, Adsorption of phenol using different types of activated bentonites. Sep. Purif. Technol., 33 (2003) 33, 1-10.
44. Donat R., Akdoğan A., Erdem E and H. Çetişli, Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions, J. Colloid İnterf. Sci., 286 (2005) 43-52.
45. G. Varank, A. Demir, K. Yetilmezsoy, S. Top, E. Sekman, M.S. Bilgili, Removal of 4-nitrophenol from aqueoussolution by natural low-cost adsorbents, Indian Journal of Chemical Technology, 19 (2012) 7-25
46. Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.
47. M. Czaplicka, B. Kaczmarczyk, Infrared study of chlorophenols and products of their photodegradation, Talanta, 70 (2006) 940–949.