Removal of Phenolic and Lignin Compounds from Bleached Kraft Mill Effluent by Fly Ash and Sepiolite

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Abstract. This study aimed to remove phenolic and lignin compounds from paper mill industry (4500 m^3/h) wastewaters, which is discharged to sea from a plant located in the western Turkey. As adsorbent, fly ash, raw sepiolite and heat-activated sepiolite were used. The effect of factors such as, particle size, temperature and pH on adsorption process was investigated. From kinetic studies, equilibrium time was found as 1 h for both. The kinetic data supports pseudo-second order model but shows very poor fit for pseudo-first order model. Intraparticle model also shows that there are two separate stages in sorption process, namely, external diffusion and pore diffusion. Adsorption isotherms for fly ash and activated sepiolite were obtained at two different temperatures. From experiments carried out at different pHs, it was observed that pH plays an important role in the adsorption process in removing of both lignin and phenolic compounds, providing both ionizating the compounds and modifying sorbent surfaces. It was also observed that heat-activated sepiolite is more effective than raw sepiolite and fly ash to remove these compounds. Adsorption of lignin and phenolic compounds increases with decreasing particle size. In addition, the efficiency of adsorption decreases with increasing adsorption temperature for both fly ash and untreated sepiolite.

Keywords: Bleached Kraft Mills Effluent, adsorption, sepiolite, fly ash, phenolic and lignin compounds

1. Introduction

Effluents from pulp and paper mills are highly toxic and are a major source of aquatic pollution. Bleached Kraft Mills Effluent (BKME) is discharged large volume of brown-colored effluent because of the different operations used in the processing of wood and pulp. The brown colour of the effluents results from the presence of lignin or polymerized tannins in the wastewater.

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The chromospheres groups on lignin are responsible for colour. BKME contains a complex mixture of organic constituents of various compound classes and in pulp mill effluents, more than 300 compounds have been identified to date. This wastewater causes three kinds of environmental impacts: biological oxygen demand (BOD), toxicity and color (Carlberg and Stuthridge, 1996; Diez et al., 1999; Ali and Sreekrishnan, 2001).

Lignin, which is a principal plant constituent and heterogeneous aromatic polymer interdispersed with hemicelluloses and occur surrounding microfibrils.

About 21 to 29% of wood is composed of lignin that ends up as waste during pulping processes. The effluent colour is primarily due to lignin and its degraded products, which are chemically stable, resistant to biological degradation (very high COD/BOD ratio), and are intractable to separation by conventional treatment methods (APHA, 1995; Mohan and Karthikeyan, 1997). Phenolic compounds, which are generated by petroleum industries, coal conversion, and phenolic compounds producing industries, are common contaminants in wastewaters including BKME. Phenols are considered as main pollutants since they are even harmful to organisms and human health at low concentrations (Bruce et al., 2001). Because of their toxicity, the U.S. Environmental Protection Agency (EPA) proposed limitations on the release from certain categories of pulp bleaching of twelve chlorinated phenolic compounds (USEPA, 1987; Bajpai and Bajpai, 1994; Rodriguez et al., 2000).

Physical and chemical processes to remove colour and toxicity from wastewaters are extensively studied. Some of these processes are adsorption, coagulation, flotation, biosorption, UV photodecomposition and ultrafiltration. Most of these processes are expensive and none of them is considered by pulp and paper industries to be commercially viable because of unfavorable economy. Adsorption has been found to be an efficient and economic method to remove dyes, pigments and other colorants and to control the bio-chemical oxygen demand. Activated carbons, inorganic oxides, natural adsorbents (such as clays and clay minerals, cellulose materials, chitin, and chitosan) have been extensively used as adsorbents to treat wastewaters (Al-Asheh et al., 2003; Naseem and Tahir, 2001). Despite its prolific use in water and wastewater industries, commercial activated carbon remains an expensive material. This has led to search for low-cost materials as alternative adsorbents in order to remove phenolic and lignin compounds (Montgomery, 1985; Bailey et al., 1999).

Sepiolite is a hydrous magnesium silicate characterized by its fibrous morphology and intracrystalline channels, having the ideal structural formula $Si_{12}Mg_8O_{30}(OH)_4(OH)_4(OH_2)_48H_2O$ for the half-unit cell (Brauner and Preisenger, 1956). Sepiolite has a common industrial application due to its molecular sized channels and large specific surface (more than 200 m^2g). It is an effective sorbent in the removal of compounds, such as aromatic amines, diquat, paraquat and methyl green from aqueous solutions (Sabah et al., 2002; Rytwo et al., 2002). Fly ash was extensively used

as an adsorbent material for removing various heavy metals and colours of organic compounds (Mott and Weber, 1992; Viraghavan and Alfaro, 1998). It was reported that the carbon content of fly ash plays a significant role during the sorption of organic compounds. In addition, fly ash and volcanic ash were used to remove phenolic compounds from polluted surface waters and wastewaters (Banerjee et al., 1997; Kao et al., 2000).

In the present study, it was aimed to study the removal of lignin and phenolic compounds from Bleached Kraft Mill Effluent by various sorbents, namely, fly ash, raw sepiolite and activated sepiolite, which are low-cost and abundantly available materials. In addition, the adsorption mechanism through various adsorption kinetics models was investigated. There is no study reported in the literature related to the use of fly ash and sepiolite as an adsorbent to remove lignin and phenolic compounds from Bleached Kraft Mill Effluents (BKME) discharged from the plant, which produce wastewater of 4500 m^3 per hour.

1.1. Adsorption Modeling

1.1.1. Pseudo-First-Order Model. In order to investigate the mechanism of adsorption, the pseudo-first-order adsorption, the pseudo-second order adsorption and the intraparticle diffusion model were used to test dynamical experimental data. The pseudo-first order rate expression of Lagergren (1898) is generally described by the following equation (Ho and McKay, 1998a, 1999; Chiou and Li, 2003; Jain and Sharma, 2002; Tseng et al., 2003)

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t) \qquad (1)$$

Where q_e and q_t are the amounts of phenolic and lignin compounds, (mg/g) adsorbed on sorbents at equilibrium, and at time t, respectively and k_1 is the rate constant (min^{-1}), respectively. Integrating and applying the boundary condition, $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$ Eq. (1) takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

The rate k_1 was obtained form slope of the linear plots of $(q_e - q_t)$ against t.

1.1.2. Pseudo-Second-Order Model. The pseudo-second order model is based on the assumption that

the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

The surface site-sorbate reaction may be represented as follows:

Active surface site $+$ sorbate

$\longrightarrow$ surface site-sorbate surface complex
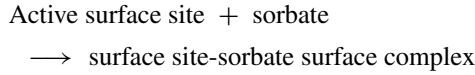
It is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent, then the kinetic rate law can be written as follows: (Ho and McKay, 1998b, 1998c, 2000; Ho, 2003; Ho and Chiang, 2001; Tseng et al., 2003)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

where k_2 the rate constant of pseudo-second order sorption (g/mgmin). Integrating and applying boundary conditions $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$ Eq. (3) becomes

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \qquad (4)$$

which has linear form of

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

If initial adsorption rate (Gündoğan et al., 2004) is

$$h = k_2 q_e^2 \qquad (6)$$

then Eqs. (5) and (6) become

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \qquad (7)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad (8)$$

If second-order kinetics is applicable, the plot of $\frac{t}{q_t}$ against t of Eq. (8) should give a linear relationship from which the constants q_e h and k_2 can be determined.

1.1.3. Intraparticle Diffusion Model. It has also been demonstrated that sepiolite has a highly porous structure. This type of adsorbent structure often results in intraparticle diffusion being the rate-limiting step. Intraparticle diffusion can be described by three consecutive steps.

 (i) The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.
 (ii) Internal diffusion, the transport of sorbate from the particles surface into interior sites.
(iii) The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and sorbent. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris (1963) is used. The rate constants, for intraparticle diffusion (k_i) are determined using equation given by Weber and Morris (1963). This equation can be described as Ho and McKay (1998d), Sivaraj et al. (2001), Jain and Sharma (2002), and Basibuyuk and Forster (2003)

$$q_t = k_i t^{0.5} + c \qquad (9)$$

where k_i and c is intraparticle diffusion rate constant (mg/gmin$^{0.5}$) and a constant, respectively. The k_i is the slope of straight-line portions of plot of q_t vs. $t^{0.5}$. These plots generally have a dual nature, i.e., an initial curved portion and a final linear portion. This is explained by the fact that the initial curved portion represents boundary layer diffusion effects. The final linear portions are a result of intraparticle diffusion effects. Extrapolating the linear portion of the plot to the ordinate yields the intercept (c) which is proportional to the extent of boundary layer thickness (Jain and Sharma, 2002).

2. Material and Methods

2.1. Wastewater

The paper mill effluents were provided from a modern bleached Kraft mill located in the western Turkey.

Table 1. Characteristics of Bleach Kraft Mill Effluent.

Parameter	Average value
Colour	Brown
Natural pH (average)	7.50
Compounds (mg/L)	
PO_4^{3-}	0.176
NO_2^-	0.213
NO_3^-	0.183
NH_4^+	9.88
Phenol	0.535
Lignin	13514.0
BOD (Biological Oxygen Demand)	25.5
COD (Chemical Oxygen Demand)	426.0

Wastewater (4500 m^3/h) is discharged into Gökova Gulf (Mugla-Turkey) by deep discharging. Wastewater samples from an aerated lagoon were taken before the discharging to the sea . The average effluent characteristics are given in Table 1.

2.2. Sorbents

The fly ash was obtained from the Yatağan Power Plant in Muğla, Turkey. The sepiolite sample, which is *Türktaciri* sepiolite deposit-sedimentary type, was collected from the west of Eskişehir, Turkey. Chemical compositions of the fly ash, sepiolite and activated sepiolite were determined by X-Ray diffraction and the results are given in Table 2.

The brown-coloured raw sepiolite samples were used for the all experiments except for the experiments in which activated sepiolite samples (at 120°C for 1 hour) were used. SEM (Scanning Electron Microscopy) analyses of the sepiolite were carried out before and after heat activation in order to see the change in the surface morphology (see Figs. 4 and 5).

2.3. Sorption Studies

Adsorption experiments were carried out in a 100-mL, flasks immersed in a thermostatic shaker bath at 293 and 313 K for 24 h. Fly ash and sepiolite samples of 2.0 g were mixed with wastewaters of 100 mL. At the end of each adsorption period, the suspension was centrifuged. The concentrations of phenolic and lignin compounds in the supernatant solution after and before adsorption were determined spectrophotometrically, as explained in the following section. The effect of pH on the removal of phenolic and lignin compounds was studied by conducting equilibrium sorption tests at different suspension pH values (3.0, 5.0, 7.0, 9.0 and 11.0). The suspension pH was adjusted by using NaOH and HCl solutions. To determine the effect of temperature, the isothermal experiments were carried out at two different temperatures (293 and 313 K) for 24 h. The effect of particle size was investigated by using

Table 2. Chemical composition and specific surface areas of raw sepiolite, activated sepiolite and fly ash.

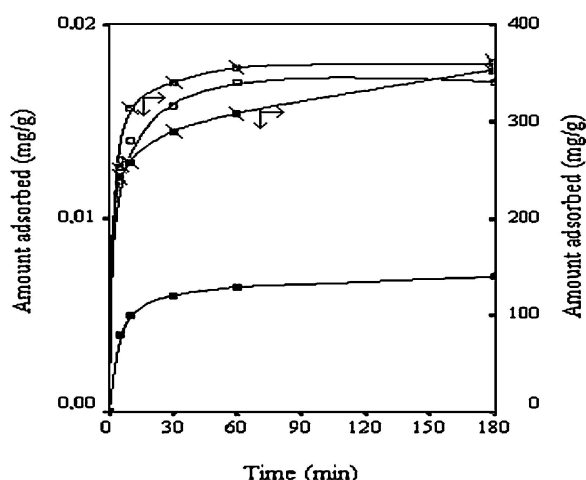| Chemical composition	Sepiolite (raw) (% wt)	Sepiolite (activated) (% wt)	Fly ash (% wt)
SiO_2	56.91	61.03	33.30
MgO	27.52	27.74	1.23
CaO	1.39	6.49	31.09
Al_2O_3	0.08	1.21	14.31
Fe_2O_3	0.04	0.50	4.11
Na_2O	0.02	0.02	0.34
K_2O	0.01	0.20	1.43
MnO_2	0.002	0.007	–
TiO_2	0.008	0.062	0.30
SO_3	0.00	0.03	6.28
Moisture (%)	14.00	–	–
Specific surface area (m^2/g)	200.0	276.0	2.1

Figure 1. The effect of contact time on the removal of phenolic compound and lignin compound by fly ash and sepiolite at fixed solid-liquid ratio 1 g/50 mL, pH 7.5, particle size 150 μm and 293 K (■ Fly ash-phenolic compound, □ Sepiolite-phenolic compound ◤ Fly ash-lignin compound, ◿ Sepiolite-lignin compound).

three different particle-sized samples, ranging from 35 to 150 μm size, of fly ash and sepiolite.

2.4. Determination of Phenolic and Lignin Compounds in Wastewater

The concentration of phenolic and lignin compounds was spectrophotometrically (Dr. Lange spectrophotometer) determined by analysis of the developed colour resulting from the reaction of phenol with 4-aminoantipyrine and from the reaction of lignin with folin phenol reagent (tungstophosphoric and molybdophosphoric acid) at λ_{max} 500 and 700 nm, respectively (APHA, 1995).

2.5. Kinetic Studies

Sorption kinetics was investigated at different experimental conditions such as fixed solid-liquid ratio, 1 g/50 mL, pH 7.5, particle size, 150 μm and tem-

perature, 293 K. The results are given in Fig. 1. As see from this figure, the adsorptive behaviour of lignin compounds on fly ash and sepiolite are similar. However, Fig. 1 indicates that the adsorption of phenolic compounds on sepiolite is three times more than that on fly ash. This difference could be explained by the significantly larger surface area of sepiolite compared to fly ash. The observed large differences between the amounts of adsorbed lignin and phenolic compounds on sepiolite could be attributed to the extraordinary differences between their initial concentrations in natural effluents (see Table 1). It could be said that both adsorbents did not show a special selectivity towards lignin and phenolic compounds.

3. Results and Discussion

It was observed that the first-order kinetic model did not adequately fit the experimental values. Therefore, its parameters are not given in Table 3. In contrast, the pseudo-second order rate equation for sorption of phenolic and lignin compounds onto sepiolite and fly ash agreed well with the data. Consequently, the correlation coefficients calculated by using the pseudo-second order model, i.e., $r2^2$, and the pseudo-second order parameters, k_2, h, $q_{e,\exp}$ and $q_{e,\mathrm{calc}}$, are shown in Table 3.

As seen from Table 3, the calculated equilibrium sorption capacity for the second-order model, $q_{e,\mathrm{calc}}$, 0.0172 mg/g, for the sepiolite-phenol system. That is close to the experimental value, $q_{e,\exp}$, 0.0171 mg/g, and the linear regression analysis of the second order rate equation gave a high r^2 value (0.9996). For the fly ash-phenol system, the calculated value of qe was 7.2×10^{-3} mg/g, compared with an experimental value of 7.1×10^{-3} mg/g, and $r^2 = 0.9980$. In addition, for the sepiolite-lignin and fly ash-lignin systems, the calculated and experimental equilibrium sorption capacities were found to be 360.5 mg/g versus 361.0 mg/g, and 355.6 mg/g versus 356.0 mg/g, respectively. These systems also exhibited high correlation coefficients, $r^2 = 0.9998$ and 0.9970, respectively.

Table 3. Pseudo second-order kinetics model parameters for the adsorption systems in the study.

Sorbent	Compounds	$q_{e,\exp}$ (mg/g)	$q_{e,\mathrm{calc}}$ (mg/g)	k_2 (g/mgmin)	h (mg/gmin)	r^2
Sepiolite	Phenolic	0.0171	0.0172	24.7	$7.3.1^{-3}$	0.9996
	Lignin	360.5	361.0	$2.2.10^{-3}$	282.5	0.9998
Fly ash	Phenolic	$7.1.10^{-3}$	$7.2.10^{-3}$	22.8	$1.2.10^{-3}$	0.9980
	Lignin	355.6	356	$5.6.10^{-4}$	70.4	0.9970

These results suggest that the sorption of both phenolic and lignin compounds onto sepiolite and fly ash follows the pseudo-second-order model. Therefore, it can be said that more than one-step may be involved in the sorption processes (Ho and McKay, 1998d; Ho, 2003). The sorption kinetic data was further processed to determine whether intraparticle diffusion is rate limiting. It was observed that the correlation coefficient, r^2, for the intraparticle model was much lower (<0.900) than for the pseudo second-order model for sorption of phenolic and lignin compounds onto sepiolite and fly ash. That suggests an activated sorption mechanism, which could occur because of chemical character of clay. On account of the relatively poor agreement with the data, the parameters and correlation coefficients related to the pseudo-first order model and the intraparticle diffusion model are not given in Table 3. The sorption of phenolic and lignin compounds by sepiolite and fly ash may occur chemically.

3.1.   *The Effect of Particle Size on Sorption Process*

Experiments were conducted with samples having three different average particle sizes for fly ash and sepiolite, ranging from 35 to 150 μm in order to determine the effect of particle size on sorption. The results are given in Fig. 2. As seen from Fig. 2, the adsorption of lignin compounds decreases rapidly with increasing
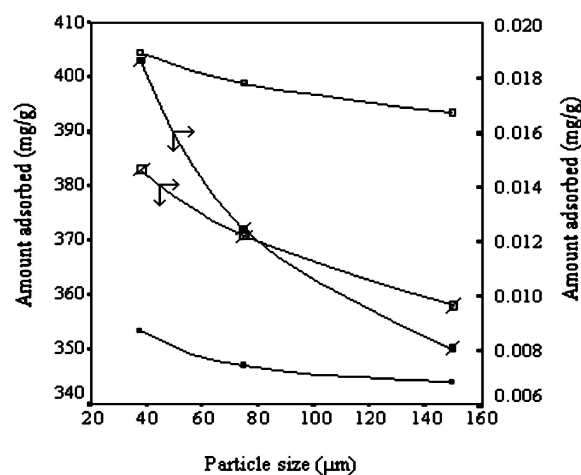
particle size of both fly ash and sepiolite. However, the sorption of lignin compounds is affected much more by the particle size of fly ash compared to sepiolite. This result could be attributed to the increasing accessibility of active sites with decreasing particle sizes of the adsorbents. In contrast to the removal of lignin, it is observed that the amount of phenolic compounds removed by the sepiolite is higher than that of fly ash for all particle sizes. From this figure, it is clear that the removal of phenolic compounds is not significantly affected by particle size for both adsorbents, considering the removal of lignin compounds.

3.2.   *Effect of pH on Sorption Process*

The effect of pH on removal of phenolic and lignin compounds for various sorbents is given in Fig. 3. In addition, to compare the adsorptive behaviours of activated and raw sepiolite and, adsorption experiments were conducted for both samples under similar conditions. It is well known that adsorption processes depend highly on pH because of the high sensitivity of functional groups on the adsorbent surfaces to hydrogen and hydroxyl ions.

A decrease in removal of phenolic compounds for all adsorbents with increasing suspension pH was
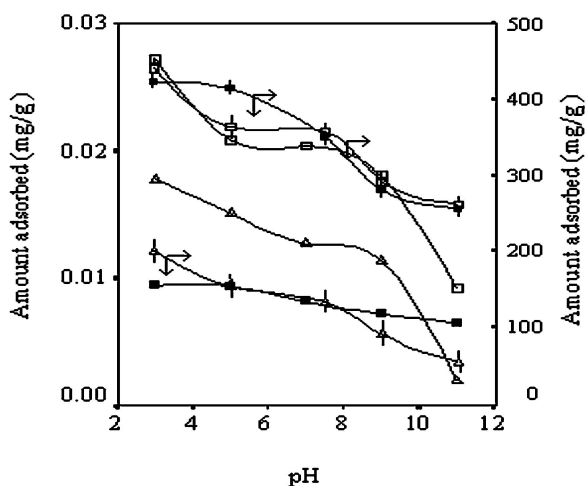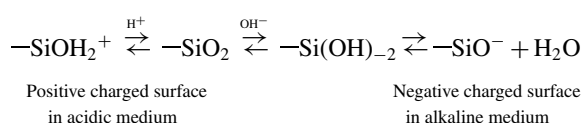
Figure 2. The effect of particle size on the removal of lignin compound and phenolic compound by fly ash and sepiolite (time: 24 h. temperature: 293 K, pH $\cong$ 7.5 and solid/liquid: 1/50g/mL) (■ Fly ash-phenolic compound, □ Sepiolite- phenolic compound, ▰ Fly ash-lignin compound, ▱ Sepiolite-lignin compound).

Figure 3. The effect of pH on the removal of phenolic compound and lignin compound by fly ash, raw and activated sepiolite (time: 24 h, temperature: 293 K, particle size: 150 μm and solid/liquid: 1/50 g/mL) (■ Fly ash-phenolic compound, □ Treated sepiolite-phenolic compound, △ Untreated sepiolite-phenolic compound, ■ Fly ash-lignin compound, ⊕ Treated sepiolite-lignin compound, ⟁ Untreated sepiolite-lignin compound).

observed (see Fig. 3). However, it is seen that the amount of adsorbed phenolic compounds by activated sepiolite was much higher than that of fly ash and raw sepiolite. This can be explained by the higher specific surface area of activated sepiolite. In addition, the observed higher sorption capacities for all adsorbents at the low pHs can be attributed to decreasing of the adsorption ability to active sites of chlorinated phenolic compounds at high pHs.

Aluminium and silicon oxides in sepiolite and fly ash can ionize as follows in acidic and alkaline conditions:

$$-\text{SiOH}_2{}^+ \overset{\text{H}^+}{\rightleftarrows} -\text{SiO}_2 \overset{\text{OH}^-}{\rightleftarrows} -\text{Si(OH)}_{-2} \rightleftarrows -\text{SiO}^- + \text{H}_2\text{O}$$

Positive charged surface   Negative charged surface
in acidic medium   in alkaline medium

As known, the phenolic functional group can ionize in basic aqueous medium as follows:

$$\text{Ø-OH} \rightleftarrows \text{Ø-O}^- + \text{H}^+ \quad (\text{Ø} \equiv \text{Phenyl group})$$
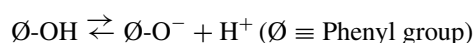
Thus, phenolic compounds can acquire a negative charge in aqueous medium. Lignin, a principal plant constituent, is a heterogeneous aromatic polymer interdispersed with hemicelluloses occurs surrounding with microfibrils. Thus, it includes many phenolic functional groups. Lignin and derivatives charge negatively at high pHs due to the functional groups. Therefore, it is expected that the adsorption with increasing pH will decrease, since the pH increases, the negative charge on both phenolic/lignin compounds and the sepiolite surface increases, which results in an electrostatic repulsion. The isoelectric point of sepiolite is nearly at pH 6. The slow change in removal rate of phenolic compounds at low pH is attributed to predominance of electrostatic interaction in sorption processes.

When sepiolite, which contains water in three kinds of habits, is heated, the channels enlarge by the zeolitic water removal. Crystal folding and micropore plugging occur at the same time. There is also water molecules associated with magnesium ions in the structure of sepiolite, and some of the hydroxyl ions undergo ion exchange with the H$^+$ ions under acidic conditions. It was reported that acid activation causes an approximate surface area increase of 2.5-times compared with raw sepiolite (Balci and Dinçel, 2002). The adsorption of phenolic compound by activated sepiolite is higher than that of fly ash and raw sepiolite. This is attributed to the large surface area of activated sepi-

olite. As seen from Fig. 3, thermal activation increases considerably adsorption capacity of sepiolite, leading to nearly 2 times in the adsorption.

In outer blocks, some of the corners of sepiolite mineral are Si atoms bound to hydroxyls (SiOH). These silanol groups at the "external surface" of the silicate are usually accessible to organic species, acting as neutral adsorption sites. In addition, some isomorphic substitutions in the tetrahedral sheet of the lattice of the mineral, such as Al^{3+} instead of Si^{4+}, form negatively charged adsorption sites. Such sites are occupied by exchangeable cations that compensate for the electrical charge. These characteristics of sepiolite make it a powerful sorbent for neutral organic molecules and organic cations. At low pHs (<6), high adsorption of neutral phenolic compounds is attributed to the process.

As seen from Fig. 3, as pH increases, the adsorption of lignin onto fly ash and treated sepiolite increased, relative to lignin onto raw sepiolite. When raw sepiolite was used for removal of lignin, a rapid decrease was observed with increasing pH. A decrease in the amount of lignin adsorbed onto treated sepiolite was also observed with increasing pH, but this decrease has continued till pH 5. The efficiency of adsorptions of lignin onto treated sepiolite and fly ash are much higher than that of untreated sepiolite. This could be attributed to both variation of surface morphology and increase of the surface area of treated sepiolite due to heating (see Table 2). Because of the heat treatment, a clear difference in the surface morphology was identified by Scanning Electron Microscope (SEM) analysis. SEM photographs for two temperatures are given in Figs. 4 and 5.
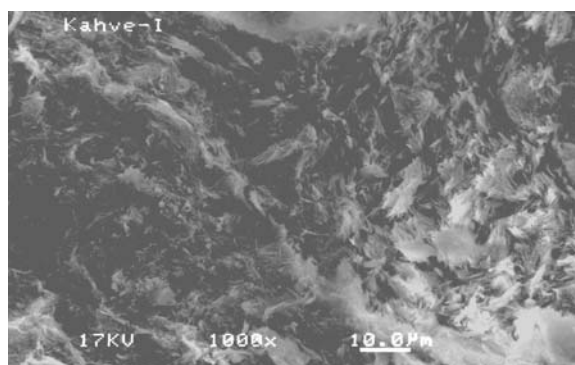

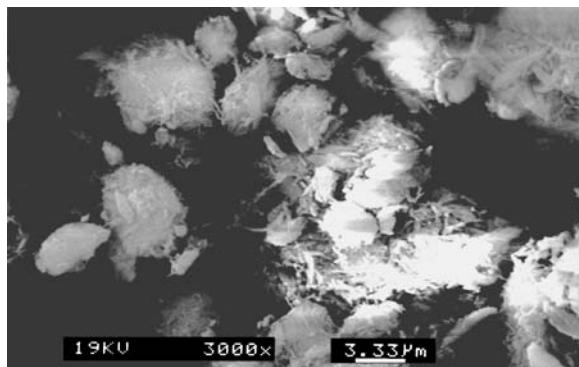*Figure 4.* SEM Micrographs of raw brown sepiolite.

Figure 5. SEM Micrographs of brown sepiolite activated at 120°C.

3.3. Equilibrium Studies

To obtain adsorption isotherms of phenolic and lignin compounds on sepiolite and fly ash additional experiments were performed at 293 and 313 K for 24 h. (see Figs. 6–9). A plateau in the phenol isotherm on sepiolite and fly ash appeared at both 293 and 313 K at equilibrium concentrations of nearly 0.20 mg/L and 0.02 mg/L (see Figs. 6 and 7), respectively. In addition, similar plateaus exist for lignin adsorption on sepiolite and fly ash (see Figs. 8 and 9) at both temperatures, at equilibrium concentrations of 6 and 3 g/L, respectively.

The isotherm experimental data were fit to the Langmuir model by using equation below:

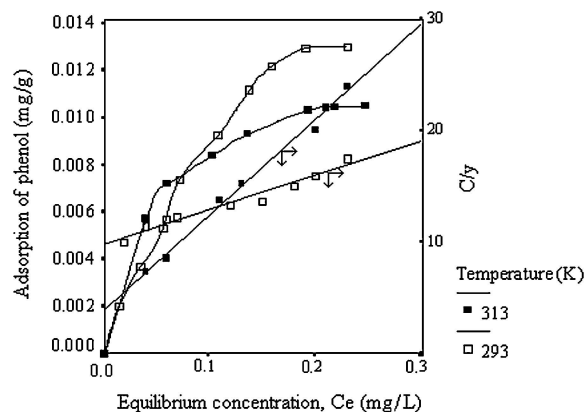$$\frac{C}{y} = \frac{1}{y_m K} + \frac{C}{y_m} \tag{10}$$

Figure 6. Adsorption isotherms and Langmuir adsorption isotherm for phenol-sepiolite system at different temperatures (time: 24 h, Particle size: 150 μm and solid/liquid ratio: 1/50 g/mL).
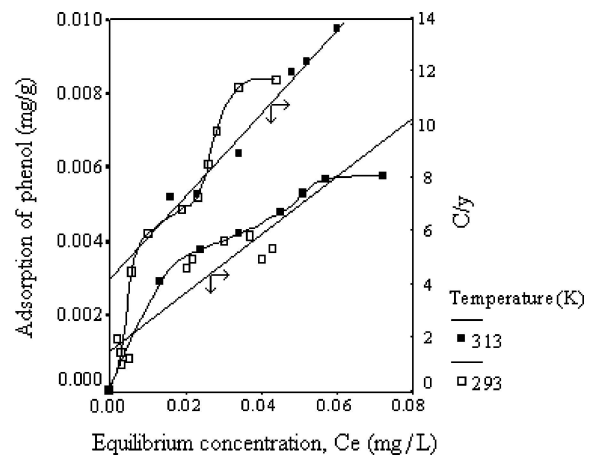

Figure 7. Adsorption isotherms and Langmuir adsorption isotherm for phenolic/fly ash system at different temperatures (time: 24 h, Particle size: 150 μm and solid/liquid ratio: 1/50 g/mL).
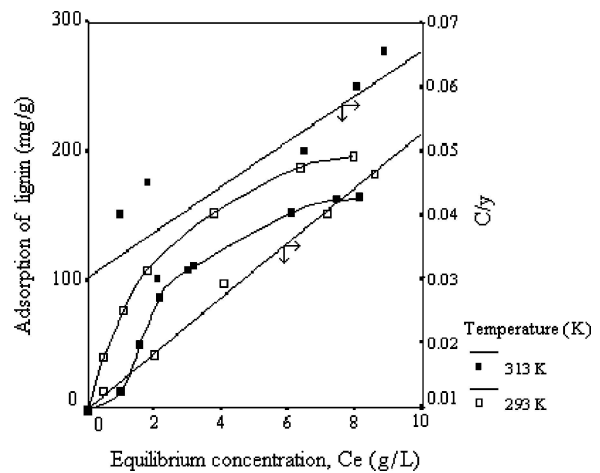

Figure 8. Adsorption isotherms and Langmuir adsorption isotherm for lignin-sepiolite system at different temperatures (time: 24 h. Particle size: 150μm and solid/liquid ratio: 1/50 g/mL)

The Langmuir parameters are given Table 4. As seen from Figs. 6–8, the Langmuir fits for sepiolite-phenol, sepiolite-lignin, and fly ash-phenol sorption pairs agreed well with the experimental data. That was not true for the fly ash-lignin system, and so the data related to the system is not given in Table 4. In addition, from the adsorption isotherms at two temperatures free energy of adsorption ΔG^0_{ads} can be calculated by means of the following equation (Gürses et al., 2004):

$$\Delta G^0_{ads} = -RT(\ln K + 4.02) \tag{11}$$

Table 4. Langmuir parameters and the values of the free energy of adsorption for three adsorption systems fitted to Langmuir model.

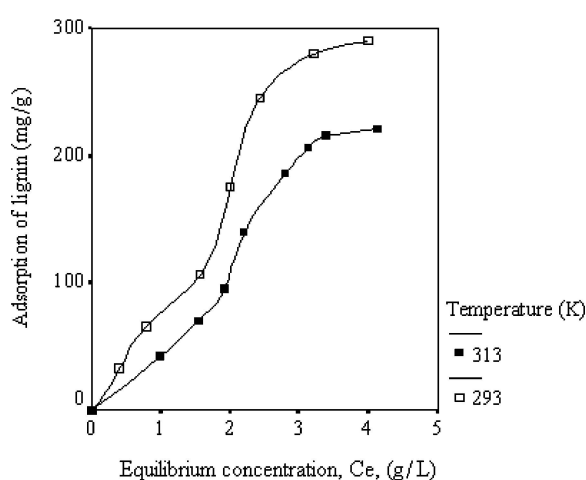| Sorbent	Compounds	Temperature (K)	y_m (mg/g)	K	ΔG^0_{ads} (kJ/mol)	r^2
Sepiolite	Phenolic	293	0.0325	3.14	−12.6	0.963
		313	0.0116	2.6	−18.6	0.993
	Lignin	293	233.1	0.44	−7.8	0.993
		–	–	–	–	–
Fly ash	Phenolic	–	–	–	–	–
		313	$6.4 \cdot 10^{-3}$	38.3	−19.9	0.981
	Lignin	–	–	–	–	–

Figure 9. Adsorption isotherms for lignin compound removal by fly ash at different temperatures (time: 24 h. Particle size: 150 μm and solid/liquid ratio: 1/50 g/mL).

where ΔG^0_{ads}, R, T and K represent the free energy of adsorption, ideal gas constant, absolute temperature, and the adsorption equilibrium constant, respectively. The Langmuir parameters and the values of the free energy of adsorption calculated from Eqs. (10) and (11) are given in Table 4. The negative sign of the free energy values indicates the spontaneous nature of sorption processes.

4. Conclusions

In this work, the sorption of phenolic and lignin compounds from Bleached Kraft Mill Effluents (BKME) on sepiolite and fly ash was studied for a better understanding of the kinetics and the removal efficiency. The results suggest that the removal of lignin and phenolic compounds decreases with increasing suspension pH. In addition, the amount of lignin and phenolic compounds adsorbed increases with decreasing particle sizes of fly ash and sepiolite. The sorption tends to attain equilibrium in nearly 1 h for these systems.

Because information from sorption kinetics studies is practically important for the design of more efficient wastewater treatment processes, the experimental data was applied to various kinetics models. A comparison of the kinetic models of the overall adsorption rate showed that the pseudo second-order rate model best described these sorption systems. In contrast, the intraparticle diffusion model and the pseudo first order model do not show a satisfactory fit to the experimental data. Therefore, it can be said that predominate adsorption mechanism is chemical sorption, including the interactions between the functional groups of phenolic and lignin compounds and surface functional groups of sorbents. It was also found that adsorption efficiency decreases with increasing temperature. This means that sorption has an exothermic character.

The results of this study suggest that sepiolite and fly ash, with low-cost and abundant availability, have a potential of being used as a sorbent for removing contaminants, such as phenolic and lignin compounds from BKME. In addition, it was shown that the sorption efficiency might be enhanced by changing key process parameters such as pH and particle size. Nevertheless, it is necessary to study desorption mechanism in order to design a suitable engineering process and to enhance the sorptive efficiency of these sorbents.

Nomenclature

q_t	Adsorbed amount at t time (mg/g)
q_e	Adsorbed amount at equilibrium (mg/g)
$q_{e,exp}$	Experimental adsorbed amount at equilibrium (mg/g)
$q_{e,calc}$	Calculated adsorbed amount at equilibrium (mg/g)

t	Time (min)
k_1	Rate constant for first order model ($min^{-1/2}$)
k_2	Rate constant for second order model (g/mg·min)
k_i	Rate constant for intraparticle model ($mg/gmin^{1/2}$)
$t_{1/2}$	Half-time for adsorption (min)
r_0	Mean size of sorbent (cm)
h	initial adsorption rate (mg/g·min)
C_0	Initial concentration (mg/L)
Ce	C Equilibrium concentration (mg/L)
y_m and y	The adsorbed amount in monolayer formation in Langmuir model
K	equilibrium constant in Langmuir model
r^2	Statistical correlation coefficient
SEM	Scanning Electron Microscopy
BKME	Bleached Kraft Mill Effluent
ΔG_{ads}^0	The free energy of adsorption (kJ/mol)
R	Universal gas constant (8,314 J/molK)
T	Absolute temperature (K)
K	The adsorption equilibrium constant
c	Intraparticle diffusion constant

References

Al-Asheh, S., F. Banat, and L.A. Aitah, "Adsorption of Phenol Using Different Types of Activated Bentonites," *Separation and Purification Technology*, 33, 1–10 (2003).

Ali, M. and T.R. Sreekrishnan, "Aquatic Toxicity from Pulp and Paper Mill Effluents: A Review," *Advances in Environmental Research*, 5, 175–196 (2001).

APHA, AWWA, WPCF, *Standard Methods for the Examination of Water and Wastewater for Lignin and Phenol*, 15th Ed., USA, vol. 5, pp. 54–67 (1980).

Bailey, S.E., J.T. Olin, R.M. Bricka, and D.D. Adrian, "A Review of Potentially Low-Cost Sorbents for Heavy Metals," *WaterResearch*, 33(1), 2469–2479 (1999).

Bajpai, P. and P.K. Bajpai, "Mini Review: Biological Color Removal of Pulp and Paper Mill Wastewaters," *J. Biotechnol*, 33, 211–220 (1994).

Balci, S. and Y. Dinçel, "Ammonium Ion Adsorption with Sepiolite: Use of Transient Uptake Method," *Chem. Eng. Process*, 4179–4185 (2002).

Banerjee, K., P.N. Cheremisinoff, and S.L. Cheng, "Adsorption Kinetics of O-Xylene by Fly Ash," *Water Research*, 31(2), 249–261 (1997).

Basibuyuk, M. and C.F. Forster, "An Examination of the Adsorption Characteristics of a Basic Dye (Maxilon Red BL-N) on to Live Activated Sludge System," *Process Biochemistry*, 38 (9), 1–6 (2003).

Brauner, K. and A. Preisenger, "Structur und Entstehung Des Sepioliths," *Tschermaks Miner Petrogr Min*, 6, 40–120 (1956).

Bruce, W., M.E. Meek, and A. Newhook, "Phenol: Hazard Characterization and Exposure-Response Analysis," *Environ. Carcino. & Ecotox. Revs*, C19(1), 305–324 (2001).

Carlberg, G.E. and T.R., Stuthridge, "Environmental Fate and Distribution of Substances," *Lucie Press ccc*, 169–177 (1996).

Chiou, M.S. and H.Y. Li, "Adsorption Behavior of Reactive Dye in Aqueous Solution on Chemical Cross-Linked Chitosan Beads," *Chemosphere*, 50, 1095–1105 (2003).

Diez, M.C., M.L. Mora, and S. Videala, "Adsorption of Phenolic Compounds and Colour from Bleached Kraft Mill Effluent Using Allophonic Compounds" *Water Research*, 33(1), 125–130 (1999).

Gündoğan, R., B. Acemioğlu, and MH. Alma, "Copper (II) Adsorption from Aqueous Solution by Herbaceous Peat," *Journal of Colloid and Interface Science*, 269(2), 303–309, (2004).

Gürses, A., S., Karaca, Ç., Doğar, R., Bayrak, M., Açıkyıldız, and M. Yalçın, "Determination of Adsorptive Properties of Clay/Water System," Journal of Colloid and Interface Science, 269, 310–314 (2004).

Ho, Y.S. and C.C. Chiang, "Sorption Studies of Acid Dye by Mixed Sorbents," *Adsorption*, 7, 139–147 (2001).

Ho, Y.S. and G. McKay, "Sorption of Dye from Aqueous Solution by Peat," *Chemical Eng Journal*, 70, 115–124 (1998a).

Ho, Y.S. and G. McKay, "The Kinetics of Sorption of Basic Dyes from Aqueous Solution by Sphagnum Moss Peat," *Canadian Journal of Chemical Engineering*, 76(4), 822–827 (1998b).

Ho, Y.S. and G. McKay, "Kinetic Model for Lead (II) Sorption on to Peat," *Adsorption Science & Technology*, 16(4), 243–255 (1998c).

Ho, Y.S. and G. McKay, "The Sorption of Lead (II) Ions on Peat," *Water Research*, 33, 578–584 (1999).

Ho, Y.S. and G. McKay, "The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Flat," *Water Research*, 34(3), 735–742 (2000).

Ho, Y.S. "Removal of Copper Ions from Aqueous Solution by Tree Fern," *Water Research*, 37, 2323–2330 (2003).

Ho, Y.S. and G. McKay, "Kinetic Models for the Sorption of Dye from Aqueous Solution by Wood," *Process Saf. Environ. Protect*, 76B, 183–191 (1998d).

Jain, C.K. and M.K. Sharma, "Adsorption of Cadmium on Bed Sediments of River Hindon: Adsorption Models and Kinetics," *Water Air and Soil Pollution*, 137, 1–19 (2002).

Kao, P.C., J.H. Tzeng, and T.L. Huang, "Removal of Chlorophenols from Aqueous Solution by Fly Ash," *Journal Hazardous Material*, 76(2–39), 237–249 (2000).

Lagergren, S., "Zur Theorie der Sogenannten Adsorption gelöster Stoffe. Kungliga Svenska Vetenskapsakademiens," *Handlingar, Band*, 24(4), 1–39 (1898).

Mohan, S.V. and J., Karthikeyan, "Removal of Lignin and Tannin Colour from Aqueous Solution by Adsorption onto Activated Charcoal," *Environmental Pollution*, 97(1–2), 183–187 (1997).

Montgomery J.M., *Consulting Engineers Water Treatment Principles and Design*, Wiley Interscience, New York, NY (1985).

Mott, H.V. and W.J. Weber, "Sorption of Low Molecular Weight Organic Contaminants by Flyash: Consideration of Enhancement of Cut-Off Barrier Performance," *Environmental Science & Technology*, 26(6), 1234–1242 (1992).

Naseem, R. and S.S. Tahir, "Removal of Pb (II) From Aqueous/Acidic Solutions by Using Bentonite as an Adsorbent," *Water Research*, 35(16), 3982–3986, (2001).

Rodriguez, I., M.P. Llompart, and R. Cela, "Solid-Phase Extraction of Phenols," *Journal of Chromatography*, 885, 291–304 (2000).

Rytwo, G., D. Trop, and C. Serban, "Adsorption of Diquat, Paraquat and Methyl Green on Sepiolite: Experimental Results and Model Calculations," *Applied Clay Science*, **20**, 273–282 (2002).

Sabah E., M. Turan, and M.S. Celik, "Adsorption Mechanism of Cationic Surfactants onto Acid-and Heat-Activated Sepiolites," *Water Research*, **36**, 3957–3964 (2002).

Sivaraj, R., C. Namasivayam, and K. Kadirvelu, "Orange Peel as an Adsorbent in the Removal of Acid Violet 17(Acid Dye) from Aqueous Solutions," *Waste Management*, **21**, 105–110 (2001).

Sun, Q. and L. Yang, "The Adsorption of Basic Dyes from Aqueous Solution on Modified Peat-Resin Particle," *Water Research*, **37**, 1535–1544 (2003).

Tseng R.L., F.C. Wu, and R.S. Juang, "Liquid-Phase Adsorption of Dyes and Phenols Using Pinewood-Based Activated Carbons, *Carbon*, **41**, 487–495 (2003).

US EPA. *Federal Register*. vol. 52, pp. 25861–25962, Washington, D.C, USA, (1987).

Viraghavan, T. and F.M. Alfaro, "Adsorption of Phenol from Wastewater by Peat, Fly Ash and Bentonite," *Journal of Hazardous Materials*, **57**, 59–70 (1998).

Weber, W.J. and Morris, J.C. "Kinetics of Adsorption on Carbon from Solution," *J Sanit Eng Div Am Soc Civ Eng*, **89**, pp. 31–60 (1963).