

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231377205>

Removal of Lignin from Wastewater Generated by Mechanical Pulping Using Activated Charcoal and Fly Ash: Adsorption Isotherms and Thermodynamics

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JUNE 2011

Impact Factor: 2.59 · DOI: 10.1021/ie200378s

CITATIONS

17

READS

42

3 AUTHORS, INCLUDING:



Marie Eriksson

Svenska Cellulosa Aktiebolaget SCA

6 PUBLICATIONS 68 CITATIONS

SEE PROFILE



Magnus Norgren

Mid Sweden University

62 PUBLICATIONS 884 CITATIONS

SEE PROFILE

Removal of Lignin from Wastewater Generated by Mechanical Pulping Using Activated Charcoal and Fly Ash: Adsorption Isotherms and Thermodynamics

Kerstin I. Andersson,^{*,†,‡} Marie Eriksson,[‡] and Magnus Norgren[†]

[†]Department of Natural Sciences, Engineering and Mathematics, FSCN, Mid Sweden University, SE-851 70 Sundsvall, Sweden

[‡]SCA R&D Centre, SE-851 21 Sundsvall, Sweden

ABSTRACT: Lignin-related material found in wastewater from thermomechanical pulping resists conventional biological treatment, entailing the use of advanced removal methods. In this work, the use of adsorption for removing lignin-related material was investigated. Activated charcoal and fly ash were used to study the adsorption behavior of lignin and to determine the adsorption capacities of these two adsorbents. Experimental data were fitted to various isotherm equations to find the best description of the sorption systems, and the corresponding thermodynamic parameters were calculated. Fly ash exhibited good sorption properties, although its sorption capacity was inferior to that of activated charcoal. Both the Freundlich and Langmuir equations provided reasonable models of the sorption processes, and the thermodynamic parameters indicated that sorption onto activated charcoal is endothermic, whereas sorption onto fly ash appears to be exothermic. Fly ash is a low-cost material that is often available on-site and offers an interesting alternative to high-cost advanced wastewater treatment systems for removing recalcitrant organic materials.

1. INTRODUCTION

In mechanical pulping, wood-derived organic substances are released into the process water. Discharging such material into the aquatic environment contributes to the consumption of dissolved oxygen in the recipient water body. Biological treatment of wastewater is therefore used to reduce the environmental impact of discharge. However, previous studies have demonstrated that lignin-related material in pulping wastewater persists despite biological treatment and substantially contributes to the residual amount of oxygen-consuming substances in treated wastewater.^{1–4}

The available techniques for removing recalcitrant material such as lignin include membrane filtration and various physicochemical treatments, such as precipitation and advanced oxidation processes (AOPs). These are all well-established and efficient methods for treating industrial effluents, although they suffer from disadvantages that increase the total cost for treatment such as fouling of membranes, generation of chemical sludge, or consumption of electrical energy or chemical reagents.^{5–8}

Another well-established and powerful technique for treating domestic and industrial effluents is adsorption, although it does not appear to have been adopted by the pulp and paper industry. Activated charcoal, the most widely and effectively used adsorbent, has a porous structure providing a large surface area and a good capacity for adsorbing organic molecules by a variety of physicochemical mechanisms and forces, for example, van der Waals forces, H-binding, dipole–dipole interactions, ion exchange, covalent bonding, cation bridging, and water bridging.⁹ The use of activated charcoal is limited by its high cost, and even if regeneration were possible, its use results in the generation of additional effluent and considerable adsorbent loss.⁹ Alternative low-cost materials, in particular ashes, have therefore become the subject of considerable interest for removing organic pollutants

such as phenolic and lignin-related compounds in pulping wastewaters. Sun et al.¹⁰ studied the treatment of papermaking wastewater using bottom ash from a power plant in batch experiments, and their results demonstrated the potential of ash for removing organic pollutants. Treatment of various effluents from agriculture-based small paper mills with bagasse fly ash was studied by Srivastava et al.;⁷ bagasse fly ash was found to be a good adsorbent for reducing chemical oxygen demand (COD) and removing color, and its removal efficiency was further enhanced by combining adsorption with coagulant pretreatment. Ugurlu et al.¹¹ studied the removal of lignin and phenolic compounds from bleached kraft mill effluent using a variety of adsorbents. Their results indicated that low-cost and high-availability fly ash offers good potential for removal of the investigated pollutants. In batch adsorption studies, Aksu and Yener⁹ compared fly ash from a power station with activated charcoal for the removal of monochlorinated phenols. They found that, although activated charcoal exhibited a much higher adsorption capacity, fly ash had potential as an inexpensive adsorbent with an intermediate adsorption capacity. Judging from these results, the use of fly ash for adsorption appears to offer a potentially simple and economical solution to the challenges posed by stringent discharge requirements. To the best of our knowledge, no studies have been reported on the treatment of wastewater generated by mechanical pulping using sorption processes with fly ash.

This study, therefore, investigated the potential of sorption for removing recalcitrant lignin-related material in pulping wastewater. Lignin-related material was isolated from wastewater

Received: February 24, 2011

Accepted: May 20, 2011

Revised: May 17, 2011

Published: May 20, 2011

samples using adsorption chromatography; fly ash and activated charcoal were used to study the adsorption of the isolated material. The two adsorbents were compared to investigate the potential of fly ash as an alternative to activated charcoal. Sorption mechanisms can be described by fitting experimental data to various isotherm models; the Langmuir, Freundlich, Redlich–Peterson, Temkin, and Dubinin–Radushkevich isotherm equations were used here. These models have been used to describe the adsorption of phenolic substances and various dyes with aromatic moieties by many other researchers.^{7,9–24} The sorption behavior of lignin was further studied in detail by quartz crystal microgravimetry with dissipation monitoring (QCM-D) using well-defined and nonporous substrates. The experimental data were also used for the calculation of thermodynamic parameters to predict the nature and spontaneity of the adsorption systems.

The fly ash used here was generated in a mill's steam-producing boiler fuelled with bark residues. The present use of fly ash is limited to land filling, and the potential use of this material in water purification operations adds value to a residue, often considered as a waste. Maximizing the utilization of resources does not necessarily stop here: further reuse of the material in road construction, brick manufacturing, or energy-recovery applications should be investigated to further extend the life cycle of fly ash.

2. MATERIALS AND METHODS

2.1. Sampling. Wastewater samples were collected at the integrated SCA Ortviken mill in Sundsvall, Sweden, which produces lightweight coated paper and newsprint from thermomechanical pulp (TMP). Approximately 55% of the produced TMP is bleached using alkali and hydrogen peroxide. The collected samples were mixed effluent from the TMP plant, bleaching plant, paper machines, and debarking and sludge dewatering processes. Samples were collected on two occasions for the experiments using activated charcoal and fly ash.

2.2. Wastewater Fractionation. The wastewater was fractionated to isolate the lignin-related material by adsorption chromatography using Amberlite XAD-8 resin (Fluka Chemie, Buchs, Switzerland), as described in detail by Pranovich et al.²⁵ It has previously been demonstrated that this method can be used to isolate pure and unaltered lignin-related material from wastewater.¹ The isolated material is henceforth referred to as lignin.

2.2.1. Absorptivity Coefficient by UV Absorption. The isolated lignin fractions from the two wastewater samples were characterized by absorption of UV radiation at 280 nm. The absorptivity coefficients varied between 0.0099 and 0.0114, with average values of 0.0105 and 0.0112 for the two samples. A previous chemical characterization of lignin isolated from wastewater collected at the same sampling point showed an absorptivity coefficient of 0.0129 L/(g cm).¹ The similarities in absorptivity suggest that the lignin samples were alike in character and that the characterization presented in Andersson et al.¹ can be applied to the lignin used here.

2.3. Adsorbents. Two different adsorbents were used: activated charcoal and fly ash. The activated charcoal (Merck, Darmstadt, Germany) was of analytical grade with 90% of the particles smaller than 100 μm . The fly ash was collected from one of the mill's steam-producing boilers fuelled with bark residues. The fly ash was sieved, and the <0.053-mm fraction was used in the experiments. The fly ash was dried for 24 h at 105 °C and stored in a desiccator until use. The adsorbents were characterized in terms of particle size, metal and nonmetal contents, and surface area.

2.4. Batch Adsorption Studies. Batch experiments were performed to study the effects of adsorbent dose, initial adsorbate concentration, and temperature and to obtain equilibrium data. For every experiment, fresh lignin solutions were prepared by dissolving the isolated lignin material in deionized water and measuring the concentration by UV absorption. The stability of the prepared lignin samples, with respect to experiment variables, was controlled using a 0.5 g/L lignin solution: The effect of pH was determined by varying the solution pH between 2 and 12 by addition of dilute HCl or NaOH. The samples were placed on a shaker for 90 min and filtered before the pH was readjusted to 6.8–7.2. The effect of temperature on the stability of the lignin solution was investigated by placing a sample in a water bath at 60 °C for 6 h before filtration. Any effects of stirring and reaction time were controlled by placing a sample of the lignin solution on a shaker for 6 h before filtration. Any change in lignin concentration by the different treatments was detected by UV absorption.

The adsorbents were added to the lignin solutions in 200 mL sample flasks mounted either on a shaker or in a water bath shaker at 200 rpm to keep the adsorbent suspended. The adsorption time for the equilibrium studies was set to 6 h: kinetic studies showed that there was no significant increase in lignin adsorption onto either of the two adsorbents after this time.²⁶ All samples were filtered using Whatman GF/A fiberglass filters (Schleicher and Schuell, Maidstone, U.K.) to remove the adsorbent. The removal of lignin from the aqueous samples was determined by UV absorption and calculated using the expression

$$Q_t = \frac{C_0 - C_t}{m} \quad (1)$$

where Q_t (mg/g) is the lignin removed at time t by a unit mass of the adsorbent, C_0 (mg/L) is the initial lignin concentration, C_t (mg/L) is the lignin concentration at time t , and m (g/L) is the amount of adsorbent added.

The effect of varying adsorbent dose on the removal of lignin was determined by adding 2–10 g/L activated charcoal or 5–300 g/L fly ash to a lignin solution with an initial lignin concentration of 0.5 g/L.

To observe the effect of the adsorbate concentration and to collect equilibrium isotherm data, parallel experiments were performed at room temperature (20 °C) and in a water bath at 60 °C. The initial lignin concentrations were 0.2, 0.5, 1.0, and 1.5 g/L, corresponding to relevant levels in wastewater from the production of peroxide-bleached thermomechanical pulp. The adsorbent doses used were 4 and 50 g/L for activated charcoal and fly ash, respectively.

The possible environmentally detrimental effects of using fly ash were assessed by means of leaching experiments. Samples containing 50 and 100 g/L fly ash suspended in deionized water were prepared. The samples were mounted on a shaker at 20 °C or in a water bath shaker at 60 °C for 6 h. The adsorbent was removed by filtration, and the inorganic element content of the filtrate was determined. The possible formation of complexes between lignin and leached elements was studied by mixing the leachate with a 1.0 g/L lignin solution in equal proportions. The samples were mounted on a shaker for 6 h to allow complexes to form and filtered to remove any formed complexes. Any changes in the lignin concentration or inorganic element content of the filtered samples were determined by UV absorption and ICP-OES (see sections 2.6.1 and 2.6.2).

2.5. Quartz Crystal Microgravimetry with Dissipation Monitoring (QCM-D). Adsorption experiments were also performed

Table 1. Equilibrium Model Equations; Transferred y and x Values, Slope (b) and Intercept (c) for the Isotherm Equations; and Dimensions and Meanings of Equation Constants

Langmuir Isotherm ^{33,35,37,41}				
$Q_{eq} = q_m K_L C_{eq} / (1 + K_L C_{eq})$	$y = C_{eq} / Q_{eq}$	$x = C_{eq}$	$b = 1/q_m$	$c = 1/(q_m K_L)$
q_m (mg/g) signifies the adsorption capacity K_L (L/mg) is related to the energy of adsorption and the affinity between adsorbent and adsorbate; the higher the value of K_L , the higher the affinity $R_L = 1/(1 + K_L C_0)$ (dimensionless) is a special feature where $R_L < 1$ indicates a favorable adsorption process, $R_L = 1$ indicates a linear isotherm, and $R_L = 0$ indicates an irreversible isotherm				
Freundlich Isotherm ^{20,33,42,43}				
$Q_{eq} = K_F C_{eq}^{1/n}$	$y = \ln Q_{eq}$	$x = \ln C_{eq}$	$b = 1/n$	$c = \ln K_F$
K_F (L/g) represents the adsorption capacity $1/n$ (dimensionless) indicates the heterogeneity of the adsorbent sites and the affinity between the adsorbate and the adsorbent; the higher the value of $1/n$, the higher the heterogeneity and affinity				
Temkin Model ^{14,41,43,44}				
$Q_{eq} = (RT/b_T) \ln(K_T C_{eq})$	$y = Q_{eq}$	$x = \ln C_{eq}$	$b = RT/b_T$	$c = (RT \ln K_T)/b_T$
K_T (L/g) is the equilibrium binding constant b_T (J/mol) is related to the heat of adsorption				
Redlich–Peterson Model ^{33,41,43}				
$Q_{eq} = K_R C_{eq} / (1 + \alpha C_{eq}^\beta)$	$y = \ln(K_R C_{eq} / Q_{eq}) - 1$	$x = \ln C_{eq}$	$b = \beta$	$c = \ln \alpha$
K_R (L/g) is constant that is varied to maximize the linear correlation coefficient R^2 α (L/g) is an equation constant β (dimensionless) is a constant in the range of 0–1; if $\beta = 1$, the equation reduces to the Langmuir equation, whereas if αC_{eq}^β is much larger than 1, the equation can be approximated by a Freundlich equation				
Dubinin–Radushkevich Model ^{14,33,41}				
$Q_{eq} = Q_m \exp(-K_{DR} \varepsilon^2)$	$y = \ln Q_{eq}$	$x = \varepsilon^2$	$b = K_{DR}$	$m = \ln Q_m$
K_{DR} (mol/kJ) ² is related to the energy of sorption, E $E = 1/(2K_{DR})^{1/2}$ (kJ/mol) is the mean free energy of sorption, which determines the type of sorption process Q_m (mg/g) is a model constant $\varepsilon = RT \ln(1 + 1/C_{eq})$				

using a Q-Sense D300 instrument (Q-Sense AB, Västra Frölunda, Sweden), which simultaneously measures both frequency and dissipation; 5 MHz-AT cut sensor crystals with SiO₂ coatings were used with and without spin-coated lignin films.^{27,28} In all measurements, the cell was initially filled with Milli-Q water and rinsed until a stable baseline was established. Data were collected using Q-Soft at the fundamental frequency (5 MHz) and at the third and fifth overtones (15 and 25 MHz, respectively). The temperature in the QCM-D measuring chamber during the adsorption experiments was carefully controlled at 23 °C. The third overtone was used to determine the adsorbed mass as the data collected from the fundamental frequency of this instrument were somewhat unstable because of energy trapping by the O-ring.

2.5.1. Spin-Coating of Lignin Thin Films. The dehydrogenated polymer from coniferylaldehyde (DHP-coniferylaldehyde) used in this study was described earlier by Holmgren et al.²⁹ The DHP-coniferylaldehyde was dissolved to a concentration of 2.0 wt % in pyridine (p.A.). A Chemat Technology KW-4A spin-coater (Chemat Technology, Amersham, Bucks, U.K.) was used to coat the QCM crystals. Before the spin-coating, the QCM crystals were rinsed with ethanol (99.5%) and copious Milli-Q water and dried in a stream of nitrogen gas. Immediately before the spin-coating, the silicon wafers were exposed to 0.1 M NaOH for 20 s to hydroxylate the SiO₂ layer, rinsed with plenty of

Milli-Q water, and finally dried with a stream of nitrogen gas. During the spin-coating, a rotation speed of 3500 rpm was used for 1 min.

2.6. Analyses. **2.6.1. Lignin Content.** The lignin contents of aqueous samples were determined by the absorption of UV radiation at 280 nm measured on a Cary 100 UV–vis spectrophotometer (Varian, Palo Alto, CA). The absorptivity coefficients were calculated from prepared lignin solutions of known concentrations, as described by Lin,³⁰ and used to calculate the lignin concentration of the treated samples. The UV absorption was measured on filtered samples (GF/A) at pH 6.8–7.2 to ensure consistent absorptivity coefficients. The light-scattering disturbance caused by residues of activated charcoal was subtracted from the measured absorption at 280 nm in the samples. No disturbance caused by fly ash residues was detected in the filtered samples.

2.6.2. Adsorbent Characterization. The particle sizes of the activated charcoal and of the sieved fraction of the fly ash were determined using laser diffraction particle size analysis (Malvern MasterSizer, Malvern, U.K.). The adsorbents were suspended in deionized water for the analysis. Samples were analyzed both immediately and after 6 h on a shaker to determine whether the particles agglomerated with time.

The surface area of activated charcoal and fly ash was measured by Swerea IVF (Mölndal, Sweden) using adsorption of nitrogen gas (Gemini 2360, Micromeritics, Norcross, GA) and multipoint Brunauer–Emmett–Teller (BET) analysis. The samples were dried for 24 h at 350 °C in nitrogen gas prior to the analyses.

The fly ash and leachate samples were analyzed for the typically most abundant metals and nonmetals found in this type of samples. The analyses were performed on a TJA-IRIS-Advantage spectrometer (Thermo Jarrell Ash Corporation, Franklin, MA) using inductively coupled plasma optical emission spectrometry (ICP-OES). The samples were prepared by digestion with H₂O₂ and HNO₃, evaporation, redissolution in deionized water, and finally filtration. Internal standards were used for quantification. The fly ash was further analyzed for carbon and oxygen content by Ljunga Lab AB (Ljungaverk, Sweden) using LECO CS444 and TCH600 instruments (Leco, St Joseph, MI). The carbon in the sample was detected as carbon dioxide, and the oxygen was detected as carbon dioxide and carbon monoxide after inductive combustion of the sample.

2.7. Adsorption Modeling. As a prerequisite for the design of an appropriate sorption treatment system, the driving force of adsorption and the capacity of the adsorbent need to be predicted. Isotherm models describe the equilibrium relationship of the adsorbate in the solid and liquid phases of the system. The Langmuir model, developed for ideal gas-phase physisorption, is one of the most widely applied sorption isotherms.³¹ Most systems, however, are neither ideal nor apply to gas-phase physisorption; other models, such as the Freundlich equation developed for nonideal sorption, should therefore be analyzed for comparison.³¹ In addition to the frequently applied Langmuir and Freundlich models, the Temkin, Redlich–Peterson, and Dubinin–Radushkevich equations are used by many authors in reported sorption systems.^{15,16,19,32–39} Ugurlu et al.¹¹ suggested that the removal of lignin from bleached kraft mill effluent by adsorption onto fly ash is best described by the Langmuir equation. The adsorption of lignin onto activated charcoal was described using the Langmuir model by Mohan and Karthikeyan.¹⁷ Badmus and Audu¹³ found that both the Langmuir and Freundlich models adequately fit experimental data concerning the removal of organic material from industrial wastewater by adsorption onto periwinkle-shell-based activated charcoal. Singh et al.²² found that both the Freundlich and Langmuir models adequately fit experimental data concerning phenol adsorption onto activated charcoal. The Freundlich model provided the best fit to experimental data concerning the removal of COD from pulp and paper mill wastewater using bagasse fly ash as reported by Srivastava et al.⁷ Aksu and Yener⁹ found that the Langmuir and Freundlich models and the Redlich–Peterson equation could be used to describe the adsorption of chlorinated phenol onto fly ash and activated charcoal. Basar¹⁴ used the Dubinin–Radushkevich equation to elucidate the type of process responsible for the adsorption of dyes onto activated charcoal. In this study, all of the above-mentioned models were applied to data from equilibrium experiments to find the best match.

The heat of adsorption can be used to determine the type of sorption process taking place, namely, physical or chemical adsorption.⁴⁰ Physical adsorption, or physisorption, is principally the effect of relatively weak van der Waals forces, whereas chemical sorption, or chemisorption, is caused by strong chemical bonds between the surface of the adsorbent and the adsorbate.⁴⁰

2.7.1. Equilibrium Models. The Langmuir, Freundlich, Redlich–Peterson, Temkin, and Dubinin–Radushkevich models all express the relationship between the amount of adsorbate on the adsorbent at equilibrium, Q_{eq} , and the equilibrium adsorbate

concentration in the surrounding liquid, C_{eq} . The isotherm equations and the dimensions and meanings of the equation constants are listed in Table 1. The Langmuir equation is valid for homogeneous surfaces and assumes ideal monolayer formation,^{35,41} whereas the Freundlich isotherm equation predicts nonideal sorption on heterogeneous surfaces and multilayer sorption systems.³³ The Redlich–Peterson isotherm combines the features of the Langmuir and Freundlich isotherms and applies to both homogeneous and heterogeneous systems.^{31,33,41} The Temkin equation suggests that the fall in heat of sorption is linear, in contrast to the Freundlich model, which assumes that it is logarithmic.³³ Special features of the adsorption isotherms include the Langmuir equilibrium parameter indicating the favorability of the sorption process³⁷ and the Dubinin–Radushkevich constant related to the mean free energy of sorption.^{33,41} The simplest method to determine isotherm constants for two-parameter isotherms is to transform the isotherm variables so that the equation can be converted to a linear form and then to apply linear regression.³³ Although a linear analysis is impossible for the three-parameter Redlich–Peterson isotherm, a trial-and-error procedure can be applied to a pseudolinear form of the isotherm.³³ The transferred y and x values, slope, and intercept for the linear equations are included in Table 1.

2.8. Adsorption Thermodynamics. The transfer of solute from the solution to the solid/liquid interface will affect the thermodynamic properties of the system. The free energy change of the adsorption process, ΔG° (kJ/mol), is related to the equilibrium constant, K_0 , according to

$$\Delta G^\circ = -RT \ln K_0 \quad (2)$$

where R is the universal gas constant [8.314 J/(mol K)] and T (K) is the temperature. The free energy change is also related to the entropy change, ΔS° [kJ/(mol K)], and heat of adsorption, ΔH° (kJ/mol), by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

Combining eqs 2 and 3 yields

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

The value of the equilibrium constant, K_0 , varies depending on the choice of isotherm equation, and such a variation would lead to inadequate estimates of ΔG° , ΔH° , and ΔS° .³⁶ Khan and Singh⁴⁵ suggested that $\ln K_0$ can be obtained from the intercept of $\ln(Q_{eq}/C_{eq})$ plotted versus Q_{eq} , regardless of what isotherm model provides the best fit to the experimental data. This method seems to be widely adopted and was therefore used for calculating the equilibrium constant in this work.^{21,44,46–50}

As mentioned earlier, the thermodynamic characteristics can be used to distinguish between physisorption and chemisorption. Although the distinction between the two types of sorption might be difficult, it was proposed in Jaycock and Parfitt⁴⁰ that the heat of adsorption ranges from 0 to 20 kJ/mol in the case of physisorption and from 80 to 400 kJ/mol in the case of chemisorption.

3. RESULTS AND DISCUSSION

3.1. Factors Influencing Adsorption. **3.1.1. Adsorbent.** According to laser diffraction measurements, the mean particle diameter ($D[4,3]$) of fly ash was 23 μm and increased to 29 μm after 6 h in suspension in deionized water. The particle diameter

of the activated charcoal was 57 μm and did not increase with time. The surface area of activated charcoal was 840 m^2/g , and that of fly ash was 28.6 m^2/g , according to analyses using adsorption of nitrogen gas. The main components of the fly ash were found to be oxygen and carbon; the weight percentages of the contributing inorganic elements are reported in Table 2.

3.1.2. Lignin Solution Stability. Experiments where the pH of aqueous lignin samples was varied showed that a change in the aqueous lignin concentration occurred only at very low pH, below 2, likely as a result of self-aggregation. It is therefore reasonable to assume that the removal of lignin in the adsorption experiments was not an effect of increasing the pH. No changes in lignin concentration due to stirring, reaction time, increased temperature, or filtration were detected in aqueous samples without added adsorbent.

3.1.3. Adsorbent Dose. Experiments with varying adsorbent dose (m) indicated that lignin adsorption increased with increasing adsorbent dose, whereas the adsorbent efficiency (i.e., the amount of lignin adsorbed per unit mass of adsorbent in mg/g) decreased (Figure 1). At $m < 4 \text{ g}/\text{L}$ for activated charcoal and $m < 50 \text{ g}/\text{L}$ for fly ash, the adsorbent surface became saturated with lignin, and the residual concentration in the solution was high. At $m = 6 \text{ g}/\text{L}$ for activated charcoal and $m = 100 \text{ g}/\text{L}$ for fly ash, the adsorption efficiency became almost constant. For the isotherm batch experiments, 4 g/L for activated charcoal and 50 g/L for fly ash were chosen as appropriate adsorbent doses.

3.1.4. Aqueous Adsorbate Concentration. Experimental results indicated that the amount of lignin adsorbed per unit mass of adsorbent increased with increasing initial aqueous adsorbate concentration (Figure 2). The driving force to overcome the resistance to mass transfer of the adsorbate between the aqueous and the solid phases thus appears to be provided by the lignin concentration. At initial lignin concentrations of 1.5 and 0.2 g/L , the equilibrium amounts of lignin adsorbed onto activated

charcoal were 211 and 46 mg/g , corresponding to 57% and 90% removals, respectively. For the same initial concentrations using fly ash, the adsorption amounts were 13 and 3.6 mg/g , corresponding to 41% and 91% removals, respectively.

3.2. Equilibrium Modeling. Isotherm constants were obtained from the experimental data using linear regression analysis to the linear forms of the isotherm expressions and are listed together with the correlation coefficients in Table 3. The Dubinin–Radushkevich model failed to provide an adequate fit to the experimental data and is not discussed further. The correlation coefficients indicate that the Redlich–Peterson model best described all sorption systems except adsorption to fly ash at 60 $^{\circ}\text{C}$, which was best described by the Langmuir expression. It should, however, be noted that the good fit of the former model might be deceptive because of the parameter K_R , which was varied to maximize the correlation coefficient R^2 . In Figure 3, the various models and the obtained constants are used to plot the calculated equilibrium amount of adsorbate on the solid surface (Q_{eq}) versus the amount in solution (C_{eq}). It can be seen that all models displayed similar relationships between Q_{eq} and C_{eq} , which correlated rather well to the experimental data. Within the range of solute concentrations used in these experiments, the Redlich–Peterson model coincided with the Freundlich model in all systems.

Considering the high correlation coefficients of the Langmuir and Freundlich models (varying between 0.9818 and 0.9981), both equations appear to produce reasonable models of sorption in all systems; it can therefore be assumed that the equation parameters R_L , q_m , and $1/n$ can be used to describe the process favorability and adsorption capacity of both adsorbents. The R_L values from the Langmuir equation were all between 0 and 1, indicating a favorable sorption process. This was supported by the $1/n$ values less than 1 obtained for the Freundlich model. The Langmuir values of q_m , signifying adsorption capacity, were 270 and 256 mg/g for activated charcoal at 20 and 60 $^{\circ}\text{C}$, respectively; the values for fly ash were 13 and 17 mg/g at 20 and 60 $^{\circ}\text{C}$, respectively. The adsorption capacity of activated charcoal thus seems to decrease with increasing temperature, whereas the capacity of fly ash increased with increasing temperature.

Mohan and Karthikeyan¹⁷ reported q_m values of 0.42 mg/g for lignin adsorption on activated charcoal: both adsorbents used here thus yielded substantially higher adsorption capacities according to the Langmuir equation. Aksu and Yener⁹ studied the adsorption of chlorophenol onto fly ash and reported experimental values of

Table 2. Composition of Fly Ash (wt %)^a

component	wt %	component	wt %	component	wt %
O	37	S	6.1	Al	1.0
Ca	31	Mn	3.7	Fe	0.9
C	9.2	Mg	2.1	others	5.8
K	6.1	P	2.0		

^a All elements analyzed by ICP-OES except oxygen and carbon, which were analyzed by inductive combustion and IR detection.

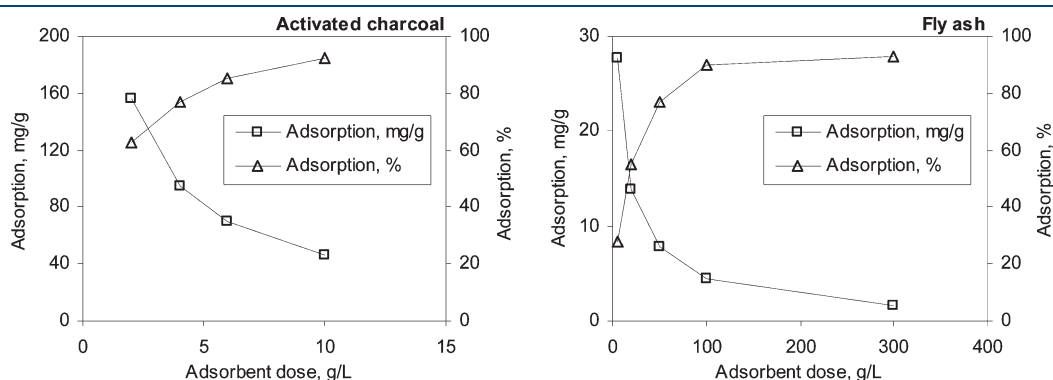


Figure 1. Lignin adsorption onto activated charcoal and fly ash with increasing doses of added adsorbent, in units of mg/g and as a percentage of the initial lignin concentration. Experimental parameters: initial lignin concentration, 0.5 g/L ; adsorbent dose, 2–10 g/L for activated charcoal and 5–300 g/L for fly ash; reaction time, 6 h. All samples were filtered, and the pH was adjusted to 6.8–7.2 before UV analysis.

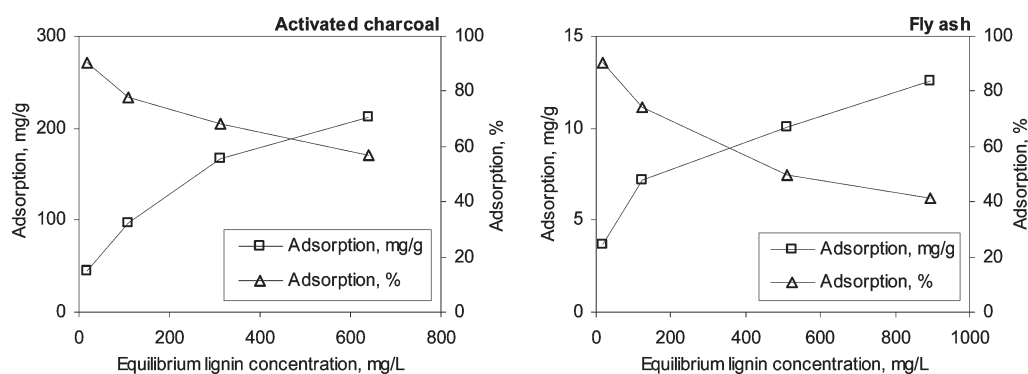


Figure 2. Lignin adsorption onto activated charcoal and fly ash with increasing equilibrium lignin concentration, in units of mg/g and as a percentage of the initial lignin concentration. Experimental parameters: initial lignin concentration, 0.2, 0.5, 1.0, and 1.5 g/L; adsorbent dose, 4 g/L for activated charcoal and 50 g/L for fly ash; reaction time, 6 h. All samples were filtered, and the pH was adjusted to 6.8–7.2 before UV analysis.

Table 3. Constants and Correlation Coefficients Obtained by Linear Regression for the Langmuir, Freundlich, Redlich–Peterson, and Temkin Isotherm Models of Lignin Adsorption onto Activated Charcoal and Fly Ash

	Langmuir Isotherm				
	T (°C)	K_L (L/mg)	q_m (mg/g)	R_L^a	R^2
activated charcoal	20	0.0060	270	0.25	0.9852
	60	0.0084	256	0.19	0.9848
fly ash	20	0.0108	13	0.16	0.9818
	60	0.0101	17	0.17	0.9976

	Freundlich Isotherm			
	T (°C)	K_F (mg/g)/(mg/L)	$1/n$	R^2
activated charcoal	20	9.0	0.50	0.9966
	60	13.5	0.44	0.9981
fly ash	20	1.5	0.31	0.9931
	60	1.3	0.39	0.9831

	Redlich–Peterson Model				
	T (°C)	K_R (L/g)	α (L/mg)	β	R^2
activated charcoal	20	5.609	0.320	0.60	0.9985
	60	11.641	0.565	0.63	0.9997
fly ash	20	5.123	3.2	0.70	0.9988
	60	4.205	3.0	0.62	0.9940

	Temkin Model			
	T (°C)	K_T (L/mg)	b_T (kJ/mol)	R^2
activated charcoal	20	0.08	45	0.9708
	60	0.12	58	0.9721
fly ash	20	0.25	1107	0.9767
	60	0.13	816	0.9957

^a Calculated for $C_0 = 500$ mg/L.

q_m equal to 98.7 and 118.6 mg/g for *o*- and *p*-chlorophenol, respectively. These findings are similar to the values obtained in the present study.

The b_T parameter of the Temkin model, related to heat of adsorption, suggested that the sorption onto activated charcoal was endothermic whereas sorption onto fly ash was exothermic.

However, the poor fit of the model to the experimental data limits the reliability of the calculated parameters.

3.3. Adsorption onto Silica and DHP-Coniferylaldehyde Thin Films Monitored Using QCM-D. Quartz crystal microgravimetry with dissipation monitoring (QCM-D) was used to investigate the adsorption of lignin onto nonporous substrates, namely, silica and spin-coated synthetic lignin thin films based on coniferylaldehyde. QCM-D entails precisely measuring the resonance frequency of a piezoelectric crystal. In the simple Sauerbrey model of mass determination, the adsorbed mass, Δm , is proportional to the change in resonance frequency, Δf as⁵¹

$$\Delta m = C \frac{\Delta f}{n_f} \quad (5)$$

where n_f is the number of the overtone and C is a sensitivity constant. Equation 5 is assumed to yield quantitatively correct values if the adsorbed layers are thin and rigidly attached to the surface. This adsorbed mass is composed of both the adsorbed amount of polymer and the liquid immobilized in the adsorbed layer. For thicker layers that are less rigid, the direct proportionality in eq 5 breaks down, resulting in an underestimation of the adsorbed mass.⁵² The dissipation factor, D , is experimentally determined by measuring the time constant, τ , for the exponential decay in the amplitude of the piezoelectric crystal when the driving voltage is turned off and is calculated as

$$D = \frac{1}{\pi f \tau} \quad (6)$$

For a studied system, an increase in D can be interpreted as indicating increased viscoelasticity of the adsorbed layer due to swelling (i.e., incorporation of water in the adsorbing substance).

Figure 4 shows the outcome of two of the experiments reflecting the lignin adsorption onto silica at pH 2.0 and synthetic lignin made from coniferylaldehyde (DHP-coniferylaldehyde) at pH 7.0. The results indicate that lignin adsorbed onto the silica surface only at relatively low pH values, likely because lignin self-aggregates at low pH and the formed aggregates interact with the silica surface.

To model the possibility of interaction between lignin-resembling structures attached to a surface and lignin isolated from the wastewater, QCM-D crystals with spin-coated DHP-coniferylaldehyde thin films were used in the experiments. It can be seen from the outcome presented in Figure 4 that, unlike with pure

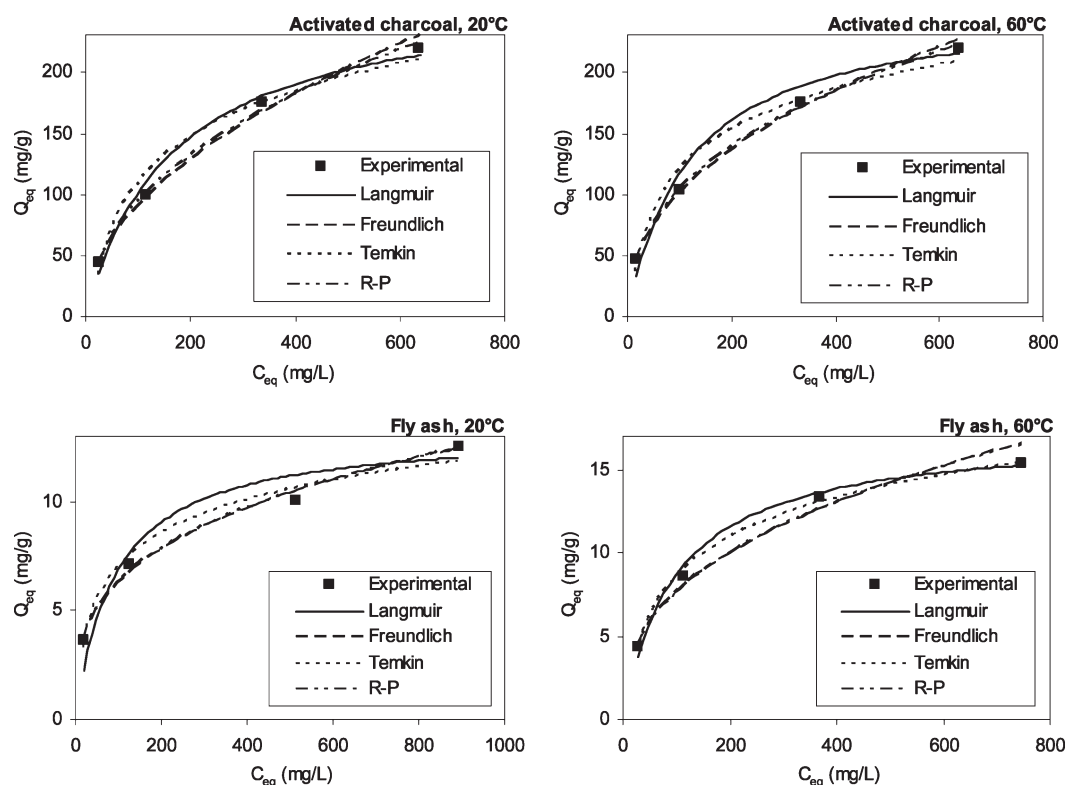


Figure 3. Equilibrium amount of lignin adsorbed on the adsorbent (Q_{eq}) at increasing equilibrium lignin concentrations (C_{eq}) expressed by the Langmuir, Freundlich, Temkin, and Redlich–Peterson (R–P) isotherm models. Experimental parameters: initial lignin concentration, 0.2, 0.5, 1.0, and 1.5 g/L; adsorbent dose, 4 g/L for activated charcoal and 50 g/L for fly ash; temperature, 20 and 60 °C; reaction time, 6 h.

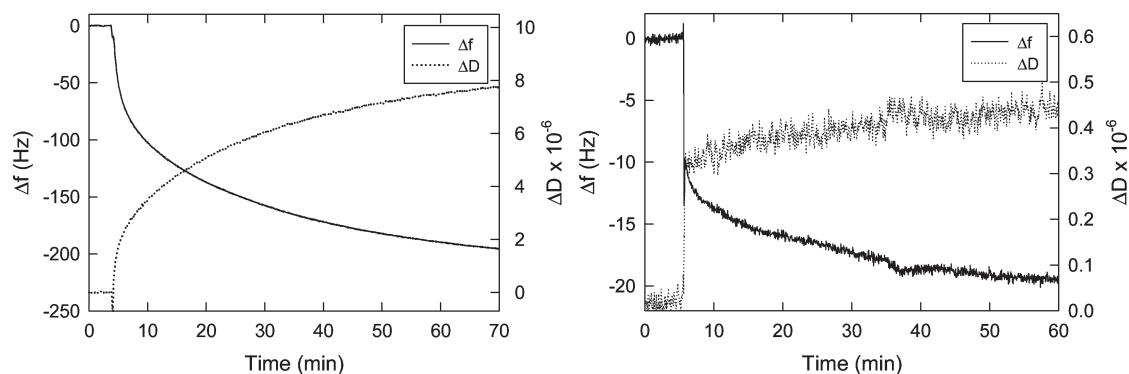


Figure 4. Lignin adsorption onto a silica surface at pH 2.0 and onto a spin-coated DHP-confiferylaldehyde film at pH 7.0, monitored using QCM-D measurements, where Δf is the change in resonance frequency and ΔD is the dissipation factor. Experimental parameter: Lignin concentration, 1.0 g/L. The frequency value of the third overtone is given.

silica as the adsorbent surface at pH 7.0, there is an interaction between DHP-confiferylaldehyde and lignin: $\Delta f = -20$ Hz and 0.45×10^{-6} . The fairly low dissipation indicates a relatively rigid adsorbed layer, and the use of the Saubrey equation to estimate the lignin coverage could be possible. By assuming a sensitivity constant, C , of $-0.177 \text{ mg}/(\text{m}^2 \text{ Hz})$,⁵³ the lignin adsorption was calculated to $1.2 \text{ mg}/\text{m}^2$. This indicates that adsorption could occur at least to a second layer when a lignin-containing adsorbent surface is exposed. However, the interactions governing the adsorption were found to be relatively weak, indicating physisorption to be the dominating reaction, because after five rinsing

cycles with Milli-Q water, almost complete desorption of the lignin was observed after 250 min (not shown).

3.4. Thermodynamics. The values of $\ln K_0$ for thermodynamic calculations were obtained from the intercept of the plots of $\ln(Q_{eq}/C_{eq})$ versus Q_{eq} (Figure 5) and are presented in Table 4.

The changes in enthalpy and entropy, ΔH° and ΔS° , from the transfer of adsorbate from the solution onto the solid surface of the adsorbent were obtained from the plot of $\ln K_0$ versus $1/T$ (Figure 6) according to eq 4: ΔH° was obtained from the slope, and ΔS° was obtained from the intercept, and both are presented in Table 4. The values of ΔG° can be determined using either

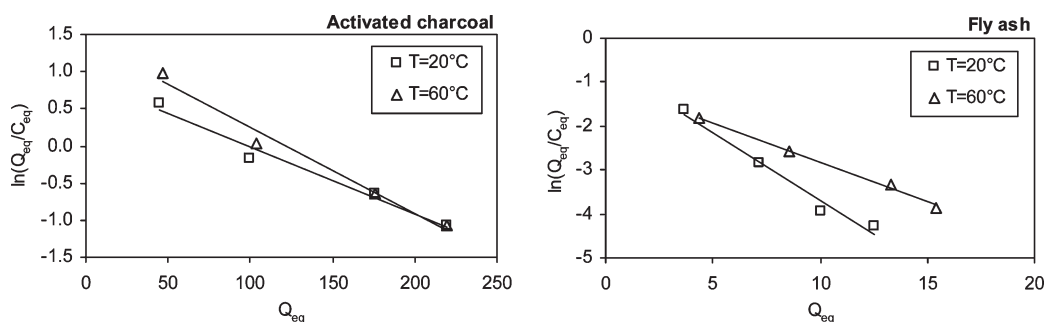


Figure 5. Plots of $\ln(Q_{eq}/C_{eq})$ as a function of Q_{eq} to determine K_0 for lignin adsorption on activated charcoal and fly ash. Q_{eq} (mg/g) and C_{eq} (mg/L) represent the lignin removal and the lignin concentration in the solution, respectively, at equilibrium ($t = 360$ min), and T ($^{\circ}\text{C}$) is the temperature. Experimental parameters: initial lignin concentration, 0.2, 0.5, 1.0, and 1.5 g/L; adsorbent dose, 4 g/L for activated charcoal and 50 g/L for fly ash; temperature, 20 and 60 $^{\circ}\text{C}$; reaction time, 6 h.

Table 4. Obtained Values of $\ln K_0$, ΔH° , and ΔS° for the Adsorption of Lignin on Activated Charcoal and Fly Ash and Calculated ΔG° Values

activated charcoal					fly ash			
T ($^{\circ}\text{C}$)	$\ln K_0$	ΔH° (kJ/mol)	ΔS° [kJ/(mol K)]	ΔG° (kJ/mol)	$\ln K_0$	ΔH° (kJ/mol)	ΔS° [kJ/(mol K)]	ΔG° (kJ/mol)
20	0.88	10.5	0.0429	−2.1	−0.62	−7.98	−0.0324	1.5
60	1.39			−3.8	−1.02			2.8

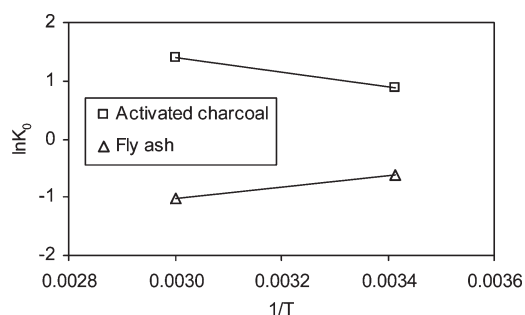


Figure 6. Plot of $\ln K_0$ versus $1/T$ for lignin adsorption to activated charcoal and fly ash. ΔH° and ΔS° were determined from the slope and intercept, respectively.

eq 2 or eq 3 and are presented in Table 4. The negative values of ΔG° (−2.1 and −3.8 kJ/mol) for the adsorption of lignin onto activated charcoal were obtained by an increase in entropy (0.0429 kJ/mol). The sorption onto activated charcoal thus seems to be spontaneous. The positive value of ΔH° (10.5 kJ/mol) is indicative of an endothermic adsorption reaction, in accordance with the obtained values of b_T , and is in the range of physisorption. For the adsorption of lignin on fly ash, the obtained ΔH° value is negative (−7.98 kJ/mol), which indicates an exothermic reaction and is in the range of physisorption. The change in entropy was negative, yielding positive values of ΔG° (1.5 and 2.8 kJ/mol), which suggest that the process was not spontaneous. It should, however, be mentioned that the adsorption reaction is not an isolated process, and even though the entropy of the system is reduced, the entropy of the universe (including the system and the surroundings) might increase.

As mentioned previously, the choice of K_0 will likely influence the results of thermodynamic calculations; here, the method of Khan and Singh⁴⁵ was used. As a comparison, the equilibrium

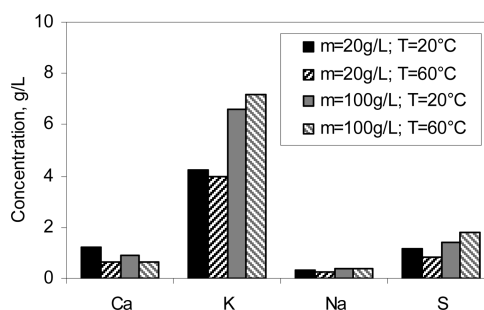


Figure 7. Dominant elements of leaching filtrate from fly ash at different doses. Experimental parameter: adsorbent dose (m), 20 and 100 g/L. Parallel samples were mounted on a shaker (20 $^{\circ}\text{C}$) or in a water bath (60 $^{\circ}\text{C}$) for 6 h and filtered before ICP-OES analysis.

constants obtained from the Freundlich model, K_F , can be used to calculate values of ΔG° . Using eq 2, ΔG° amounts to −5.3 and −7.2 kJ/mol for activated charcoal and to −1.0 and −0.7 kJ/mol for fly ash at 20 and 60 $^{\circ}\text{C}$, respectively. The Freundlich equation yielded high correlation coefficients when applied to the experimental data, and the obtained values of ΔG° are within the same range as those presented in Table 4. However, using the equilibrium constant of the Langmuir expression, K_L , eq 2 yields values of ΔG° between 11 and 13 kJ/mol for the two adsorbents at 20 and 60 $^{\circ}\text{C}$, deviating from the values obtained using the method of Khan and Singh.⁴⁵ Consequently, care must be taken to ensure that the same procedure is used to obtain K_0 for thermodynamic calculations when comparing the results of various sorption studies.

3.5. Leaching from Fly Ash. Leaching experiments with fly ash indicated that the dominant elements in filtrates from ash suspensions were potassium, calcium, sulfur, and sodium. Figure 7 shows the leached amounts in filtrates from suspensions of 50

and 100 g/L fly ash at 20 and 60 °C analyzed by ICP-OES. Of course, the salt content of the effluent must be considered relative to the salinity and size of the recipient water body.

The filtrate from leaching of $m = 100$ g/L and 60 °C was mixed with a lignin solution of 1.0 g/L to investigate complex formation between lignin and leached metals. The ICP-OES analysis indicated no significant change in the content of metals or nonmetals. These findings imply that no major formation of lignin and metal complexes occurred in the samples and that the lignin removal in the adsorption experiments was, in fact, due to sorption rather than the formation of complexes large enough to be removed by filtration. These results concur with the UV analysis of the samples, which indicated no reduction of lignin concentration due to mixing with leachate.

4. CONCLUSIONS

In this work, both activated charcoal and fly ash exhibited potential for lignin adsorption. The removal efficiencies increased with increasing adsorbate concentration and increasing adsorbent dose. Adsorption onto both adsorbents was best described by the Redlich–Peterson isotherm model; however, it should be noted that this three-parameter equation might yield deceptively high correlation coefficients because of the trial-and-error procedure used to obtain the pseudolinear form of the equation. The experimental data also correlated well with the Freundlich and Langmuir equations, yielding satisfying correlation coefficients: the best fit for adsorption onto activated charcoal at 20 and 60 °C and fly ash at 20 °C was provided by the Freundlich model, whereas the Langmuir model provided a slightly better fit for sorption onto fly ash at 60 °C. The adsorbent capacities, q_m , obtained from the Langmuir equation were 256 mg/g for activated charcoal and 17 mg/g for fly ash at 60 °C. From the QCM-D measurements, it was determined that sorption in at least two layers might be possible, although the interactions between the lignin adsorbate and the lignin surface used were relatively weak. The experimental data were also used to calculate the thermodynamic parameters, which suggested that adsorption of lignin onto activated charcoal is an endothermic and spontaneous process, whereas adsorption onto fly ash can be described as exothermic and a nonspontaneous reaction. The experimental results underline the potential of fly ash for the removal of organic pollutants from wastewaters. Although the adsorption capacity of activated charcoal greatly exceeded that of fly ash, the latter has the important qualities of being a low-cost material and being available on-site. Further investigations using column operations and process water should be made to assess the practical utility of the fly ash adsorption system in large-scale applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kerstin.andersson.x@sca.com.

ACKNOWLEDGMENT

This work was financed by the Knowledge Foundation through the FSCN Industrial Research College for Mechanical Pulp Technology at Mid Sweden University. We thank Ingrid Nylander at SCA R&D Centre for laboratory assistance.

NOMENCLATURE

adsorbate = lignin
 adsorbent = activated charcoal and fly ash
 b_T = Temkin constant related to the heat of adsorption (J/mol)
 C_0 = initial adsorbate concentration (mg/L or g/L)
 C_{eq} = adsorbate concentration at equilibrium (mg/L)
 C_t = adsorbate concentration at time t (mg/L)
 E = energy of sorption (kJ/mol)
 K_{DR} = Dubinin–Radushkevich constant (mol/kJ)², related to energy of sorption, E
 K_F = Freundlich constant related to adsorption capacity (mg/g)/(mg/L)
 K_L = Langmuir energy of adsorption (L/mg)
 K_R = Redlich–Peterson isotherm parameter (L/g)
 K_T = Temkin constant (L/g)
 m = adsorbent dose (g/L)
 $1/n$ = Freundlich adsorption intensity or heterogeneity factor
 Q_{eq} = amount of adsorbate removed per unit mass of added adsorbent at equilibrium (mg/g)
 $Q_{eq(calc)}$ = calculated Q_{eq} value (mg/g)
 $Q_{eq(exp)}$ = experimental Q_{eq} value (mg/g)
 q_m = Langmuir adsorption capacity (mg/g)
 Q_m = Dubinin–Radushkevich constant (mg/g)
 Q_t = amount of adsorbate removed per unit mass of added adsorbent at time t (mg/g)
 R = universal gas constant [8.314 J/(mol K)]
 R^2 = correlation coefficient
 R_L = Langmuir equilibrium parameter
 t = reaction time (min)
 T = absolute temperature (K)
 α = Redlich–Peterson constant (L/mg)
 β = Redlich–Peterson constant
 ΔG° = free energy change (kJ/mol)
 ΔH° = enthalpy change (kJ/mol)
 ΔS° = entropy change [kJ/(mol K)]
 ε = variable in the Dubinin–Radushkevich equation, equal to $RT \ln(1 + 1/C_{eq})$

REFERENCES

- (1) Andersson, K. I.; Pranovich, A. V.; Norgren, M.; Holmbom, B.; Eriksson, M. Effects of biological treatment on the chemical structure of dissolved lignin-related substances in effluent from thermomechanical pulping. *Nord. Pulp Pap. Res. J.* **2008**, 23 (2), 164–171.
- (2) Helmreich, B.; Schiegl, C.; Wilderer, P. A. Fate of lignin in the process of aerobic biological treatment of paper mill wastewater. *Acta Hydrochim. Hydrobiol.* **2001**, 29 (5), 296–300.
- (3) Magnus, E.; Carlberg, G. E.; Hoel, H. TMP wastewater treatment, including a biological high-efficiency compact reactor: Removal and characterisation of organic components. *Nord. Pulp Pap. Res. J.* **2000**, 15 (1), 29–36.
- (4) Widsten, P.; Laine, J. E. Seasonal variations in the composition and behaviour in biological treatment of an effluent from an integrated pulp and paper mill. *Nord. Pulp Pap. Res. J.* **2003**, 18 (2), 151–161.
- (5) Pérez, M.; Torrades, F.; Domènech, X.; Peral, J. Removal of organic contaminants in paper pulp effluents by AOPs: An economic study. *J. Chem. Technol. Biotechnol.* **2002**, 77 (5), 525–532.
- (6) Pokhrel, D.; Viraraghavan, T. Treatment of pulp and paper mill wastewater: A review. *Sci. Total Environ.* **2004**, 333 (1–3), 37–58.
- (7) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Treatment of pulp and paper mill wastewaters with poly aluminium chloride and bagasse fly ash. *Colloids Surf. A* **2005**, 260 (1–3), 17–28.

- (8) Thompson, G.; Swain, J.; Kay, M.; Forster, C. F. The treatment of pulp and paper mill effluent: A review. *Bioresour. Technol.* **2001**, *77* (3), 275–286.
- (9) Aksu, Z.; Yener, J. A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents. *Waste Manage.* **2001**, *21* (8), 695–702.
- (10) Sun, W. L.; Qu, Y. Z.; Yu, Q.; Ni, J. R. Adsorption of organic pollutants from coking and papermaking wastewaters by bottom ash. *J. Hazard. Mater.* **2008**, *154* (1–3), 595–601.
- (11) Ugurlu, M.; Gurses, A.; Yalcin, M. Removal of phenolic and lignin compounds from bleached kraft mill effluent by fly ash and sepiolite. *Adsorption* **2005**, *11* (1), 87–97.
- (12) Aravindhnan, R.; Rao, J. R.; Nair, B. U. Application of a chemically modified green macro alga as a biosorbent for phenol removal. *J. Environ. Manage.* **2009**, *90* (5), 1877–1883.
- (13) Badmus, M. A. O.; Audu, T. O. K. Periwinkle shell-based granular activated carbon for treatment of chemical oxygen demand (COD) in industrial wastewater. *Can. J. Chem. Eng.* **2009**, *87* (1), p69–77.
- (14) Basar, C. A. Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot. *J. Hazard. Mater. B* **2006**, *135* (1–3), 232–241.
- (15) Karagozoglu, B.; Tasdemir, M.; Demirbas, E.; Kobya, M. The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: Kinetic and equilibrium studies. *J. Hazard. Mater.* **2007**, *147* (1–2), 297–306.
- (16) Lin, J. X.; Zhan, S. L.; Fang, M. H.; Qian, X. Q.; Yang, H. Adsorption of basic dye from aqueous solution onto fly ash. *J. Environ. Manage.* **2008**, *87* (1), 193–200.
- (17) Mohan, S. V.; Karthikeyan, J. Removal of lignin and tannin colour from aqueous solutions by adsorption onto activated charcoal. *Environ. Pollut.* **1997**, *97* (1–2), 183–187.
- (18) Önal, Y. Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. *J. Hazard. Mater. B* **2006**, *137* (3), 1719–1728.
- (19) Rodriguez, A.; Garcia, J.; Ovejero, G.; Mestanza, M. Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: Equilibrium and kinetics. *J. Hazard. Mater.* **2009**, *172* (2–3), 1311–1320.
- (20) Sahu, A. K.; Mall, I. D.; Srivastava, V. C. Studies on the adsorption of furfural from aqueous solutions onto low-cost bagasse fly ash. *Chem. Eng. Commun.* **2008**, *195* (3), 316–335.
- (21) Sahu, A. K.; Srivastava, V. C.; Mall, I. D.; Lataye, D. H. Adsorption of furfural from aqueous solution onto activated carbon: Kinetic, equilibrium and thermodynamic study. *Sep. Sci. Technol.* **2008**, *43* (5), 1239–1259.
- (22) Singh, K. P.; Malik, A.; Sinha, S.; Ojha, P. Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material. *J. Hazard. Mater.* **2008**, *150* (3), 626–641.
- (23) Tutem, E.; Apak, R.; Unal, C. F. Adsorptive removal of chlorophenols from water by bituminous shale. *Water Res.* **1998**, *32* (8), 2315–2324.
- (24) Wu, J.; Yu, H.-Q. Biosorption of 2,4-dichlorophenol from aqueous solution by *Phanerochaete chrysosporium* biomass: Isotherms, kinetics and thermodynamics. *J. Hazard. Mater.* **2006**, *137* (3), 498–508.
- (25) Pranovich, A. V.; Reunanen, M.; Sjöholm, R.; Holmbom, B. Dissolved lignin and other aromatic substances in thermomechanical pulp waters. *J. Wood Chem. Technol.* **2005**, *25* (3), 109–132.
- (26) Andersson, K. I.; Eriksson, M.; Norgren, M. Removal of Lignin from Wastewater Generated by Mechanical Pulping Using Activated Charcoal and Fly Ash: Adsorption Kinetics. *Ind. Eng. Chem. Res.* **2011**, *50*, doi: 10.1021/ie200379p.
- (27) Notley, S. M.; Norgren, M. Adsorption of a strong polyelectrolyte to model lignin surfaces. *Biomacromolecules* **2008**, *9* (7), 2081–2086.
- (28) Norgren, M.; Gärdlund, L.; Notley, S. M.; Htun, M.; Wågberg, L. Smooth model surfaces from lignin derivatives. II. Adsorption of polyelectrolytes and PECs monitored by QCM-D. *Langmuir* **2007**, *23* (7), 3737–3743.
- (29) Holmgren, A.; Norgren, M.; Zhang, L.; Henriksson, G. On the role of the monolignol gamma-carbon functionality in lignin biopolymerization. *Phytochemistry* **2009**, *70* (1), 147–155.
- (30) Lin, S. Y. Ultraviolet spectrophotometry. In *Methods in Lignin Chemistry*; Lin, S. Y., Dence, W. C., Eds.; Springer-Verlag: Berlin, 1992; pp 217–232.
- (31) Gerente, C.; Lee, V. K. C.; Le Cloirec, P.; McKay, G. Application of chitosan for the removal of metals from wastewaters by adsorption: Mechanisms and models review. *Crit. Rev. Environ. Sci. Technol.* **2007**, *37* (2), 41–127.
- (32) Gupta, V. K.; Ali, I.; Saini, V. K. Defluoridation of wastewaters using waste carbon slurry. *Water Res.* **2007**, *41* (15), 3307–3316.
- (33) Ho, Y. S.; Porter, J. F.; McKay, G. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water Air Soil Pollut.* **2002**, *141* (1–4), 1–33.
- (34) Ho, Y. S.; McKay, G. The sorption of lead(II) ions on peat. *Water Res.* **1999**, *33* (2), 578–584.
- (35) Hu, H.; Trejo, M.; Nicho, M. E.; Saniger, J. M.; Garcia-Valenzuela, A. Adsorption kinetics of optochemical NH₃ gas sensing with semiconductor polyaniline films. *Sens. Actuators* **2002**, *82* (1), 14–23.
- (36) Liu, Y.; Liu, Y.-J. Biosorption isotherms, kinetics and thermodynamics. *Sep. Purif. Technol.* **2008**, *61* (3), 229–242.
- (37) Poots, V. J. P.; McKay, G.; Healy, J. J. Removal of basic dye from effluent using wood as an adsorbent. *J. Water Pollut. Control Fed.* **1978**, *50* (5), 926–935.
- (38) Sarkar, M.; Banerjee, A.; Pramanick, P. P. Kinetics and mechanisms of fluoride removal using laterite. *Ind. Eng. Chem. Res.* **2006**, *45* (17), 5920–5927.
- (39) Sarkar, M.; Sarkar, A. R.; Goswami, J. L. Mathematical modeling for the evaluation of zinc removal efficiency on clay sorbent. *J. Hazard. Mater.* **2007**, *149* (3), 666–674.
- (40) Jaycock, M. J.; Parfitt, G. D. *Chemistry of Interfaces*; Ellis Horwood: Chichester, U.K., 1981.
- (41) Mall, I. D.; Srivastava, V. C.; Agarwal, N. K.; Mishra, I. M. Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses. *Colloids Surf. A* **2005**, *264* (1–3), 17–28.
- (42) Cicek, F.; Özer, D.; Özer, A. Low cost removal of reactive dyes using wheat bran. *J. Hazard. Mater.* **2007**, *146* (1–2), 408–416.
- (43) Vijayaraghavan, K.; Padmesh, T. V. N.; Palanivelu, K.; Velan, M. Biosorption of nickel (II) ions onto *Saragassum wightii*: Application of two-parameter and three-parameter isotherm models. *J. Hazard. Mater. B* **2006**, *133* (1–3), 304–308.
- (44) Gunay, A.; Arslankaya, E.; Tosun, I. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *J. Hazard. Mater.* **2007**, *146* (1–2), 362–371.
- (45) Khan, A. A.; Singh, R. P. Adsorption thermodynamics of carbofuran on Sn(IV) arsenosilicate in H⁺, Na⁺, and Ca²⁺ forms. *Colloids Surf.* **1987**, *24* (1), 33–42.
- (46) Gupta, V. K.; Singh, P.; Rahman, N. Adsorption behavior of Hg(II), Pb(II), and Cd(II) from aqueous solution on Duolite C-433: A synthetic resin. *J. Colloid Interface Sci.* **2004**, *275* (2), 398–402.
- (47) Manju, G. N.; Raji, C.; Anirudhan, T. S. Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Res.* **1998**, *32* (10), 3062–3070.
- (48) Raji, C.; Anirudhan, T. S. Batch Cr(VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. *Water Res.* **1998**, *32* (12), 3772–3780.
- (49) Varshney, K. G.; Gupta, A.; Singhal, K. C. The adsorption of carbofuran on the surface of antimony(V) arsenosilicate: A thermodynamic study. *Colloids Surf. A* **1995**, *104* (1), 7–10.
- (50) Watkins, R.; Weiss, D.; Dubbin, W.; Peel, K.; Coles, B.; Arnold, T. Investigations into the kinetics and thermodynamics of Sb(III) adsorption on goethite (α-FeOOH). *J. Colloid Interface Sci.* **2006**, *303* (2), 639–646.
- (51) Sauerbrey, G. Verwendung von Schwingquarzen zur wagung dünner Schichten und zur Mikrowagung. *Z. Phys.* **1959**, *155* (2), 206–222.

(52) Voinova, M. V.; Jonsson, M.; Kasemo, B. 'Missing mass' effects in biosensor's QCM applications. *Biosens. Bioelectron.* **2002**, *17* (10), 835–841.

(53) Edvardsson, M.; Rodahl, M.; Kasemo, B.; Höök, F. A dual-frequency QCM-D setup operating at elevated oscillation amplitudes. *Anal. Chem.* **2005**, *77* (15), 4918–4962.