

# Adsorption of Non-ionic Surface Active Agent on Fine Coal and Lignite

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The adsorption of Triton X-100 in aqueous solution on the less than 53  $\mu\text{m}$  size fractions of Tunçbilek lignite and Zonguldak bituminous coal was studied. The adsorption isotherms were formed for 5, 30 and 1,440 (equilibrium) minutes. The isotherms were evaluated using both Langmuir and Freundlich adsorption equations. Concentrations of the reagent in the monolayer after equilibrium adsorption were determined to be 8.17 and 7.27  $\mu\text{M/g}$  coal for the lignite and bituminous coal using the Langmuir adsorption equation. The specific adsorption capacity per unit area of Zonguldak bituminous coal was 5.3 times higher than that of Tunçbilek lignite. The adsorption kinetic tests were also conducted with the reagent and coal samples used in the study. The experimental data indicated that there were two very different adsorption rates, one being fast and the other very slow. A large amount of the reagent was adsorbed on the solid surface during the fast adsorption stage.

**Key Words:** Reagent adsorption, adsorption kinetics, coal-lignite

## Introduction

Adsorption is a technique that is used in many different fields. It involves the accumulation of solute molecules at an interface. The surface characteristics of coal may be altered significantly by the adsorption of a surface active agent on the coal surface.

Reagent usage and type of coal are important factors in coal cleaning processes, coal-liquid mixtures and the dewatering characteristics of slurries. The separation performance and rheological behaviour of coal-liquid mixtures are affected by reagent adsorption on the fine coal particles as well as the nature of solid particles. The degree and extent of adsorption may significantly affect the performance of the process.

The adsorption of chemical reagents on coal surfaces is markedly affected by the functionality of the solid surface, the molecular structure of the surfactant being adsorbed and the properties of the aqueous phase.

Much research has been conducted on the adsorption of chemical reagents on coal<sup>1-9</sup>, coal macerals<sup>9</sup>, peat<sup>10,11</sup> and lignite<sup>12</sup> surfaces. Anionic, cationic<sup>3-6,13</sup> and non-ionic<sup>1,7,8,14</sup> surfactants were used to show their adsorption behaviour. The effects of various parameters on the adsorption process such as the pH<sup>3,4,6,8</sup>, the presence of electrolytes<sup>14,15</sup>, the rank of coal<sup>16</sup> and temperature<sup>7</sup> were studied.

The results of several studies have shown that the adsorption equilibrium of surface active agents or chemicals are described by means of Freundlich- and Langmuir- type isotherms<sup>1,8,10-12</sup>.

The orientation of surfactant molecules<sup>1,2</sup> and their chain length<sup>3,4,7</sup> greatly influence the adsorption process. It has been indicated that the orientation of the surfactant on coal particles occurs in two ways: it either adsorbs on the non-polar surface of coal with the polar groups outward, or with the positively charged group of the reagent oriented towards the negatively charged sites on the coal surface<sup>16</sup>.

Recently, it has been observed that the adsorption of Triton X-100, which is a perfect dispersing agent for coal<sup>2</sup>, on Tunçbilek lignite and Zonguldak bituminous coal, has considerably changed the separation performance of solid particles in inorganic heavy media<sup>17</sup>. In the same study, it was found that the recovery of the final product obtained from heavy media separation decreased in the presence of Triton X-100. The present study therefore focused on understanding the adsorption behaviour of Triton X-100 on the lignite and bituminous coal used in the previous study<sup>17</sup>. The adsorption kinetics of lignite and bituminous coal were also examined using the same reagent.

## Theory

The experimental evaluation of the adsorption from solutions of surface active agents at the solid liquid interface usually involves the measurement of changes in its concentration in the bulk solution. At the solid-liquid interface, the specific amount of surfactant adsorbed per unit area or mass of solid is determined, also the reagent concentration in the liquid phase and the orientation of the adsorbed molecules relative to the surface and solution as well as the extent of the adsorption.

The Langmuir adsorption isotherm is a type of adsorption isotherm commonly observed in adsorption from solutions of reagents<sup>18</sup>, expressed as

$$\frac{C_s}{C_{s,m}} = \frac{K_L C_{e,l}}{K_L C_{e,l} + 1} \quad (1)$$

From Eq. 1, replacing  $1/K_L$  with  $k$  then the following equation may be written:

$$C_s = \frac{C_{s,m} C_{e,l}}{C_{e,l} + k} \quad (2)$$

where  $C_{e,l}$  is the equilibrium concentration of the reagent in the liquid phase,  $C_{s,m}$  is the surface concentration of the reagent at full monolayer adsorption,  $C_s$  is the reagent concentration adsorbed on the coal surface and  $K_L$  is the adsorption equilibrium constant, which is a measure of the partitioning of the surfactant and water between the surface and bulk solution. The linear form of Eq. 2 is given by

$$\frac{1}{C_s} = \frac{k}{C_{s,m} C_{e,l}} + \frac{1}{C_{s,m}} \quad (3)$$

A plot of  $1/C_s$  versus  $1/C_{e,l}$  should be a straight line with slope  $k/C_{s,m}$  and intercept  $1/C_{s,m}$ .

The Freundlich adsorption isotherm<sup>19</sup> is widely used, particularly in the low to intermediate concentration range. It is expressed as

$$C_s = K_F (C_{e,l})^n \quad (4)$$

where  $C_s$  is the reagent concentration adsorbed on the coal surface,  $C_{e,l}$  is the equilibrium concentration remaining in the solution corresponding to  $C_s$ , while  $K_F$  and  $n$  are the constants. The logarithmic form of Eq. 4 can be written as

$$\log C_s = \log K_F + n \log C_{e,l} \quad (5)$$

A plot of  $\log C_s$  versus  $\log C_{e,l}$  will yield a straight line with slope  $n$  (the intensity of adsorption) and an intercept equal to  $\log K_F$  ( $K_F$  is the capacity of adsorbent).

## Experimental

Both lignite and bituminous coal were used for the study, and were sampled from the Tunçbilek and Zonguldak collieries. The reagent used was polyethylene glycol tert-octylphenyl ether (Triton X-100), which is non-ionic.

The lignite and bituminous coal were first crushed in a crusher which produced material of less than 5 mm in diameter. The crushed coals were then milled in a ball mill for the desired particle size reduction. The milled coals were sieved and particles of less than 53  $\mu\text{m}$  diameter were collected and stored in sealed plastic bags.

Elemental and proximate analyses of the samples were determined according to ASTM Standards<sup>20,21</sup> and all related data are given in Table 1. The pH values of the slurries were measured using an Orion 960 Autochemistry System as the slurry was being continuously mixed.

**Table 1.** BET surface area, proximate and elemental analyses of the coal samples

|           | Surface area,<br>BET           | Moisture | Ash       | VM         | FC   | C    | H   | N   | S <sub>o</sub> | O    |
|-----------|--------------------------------|----------|-----------|------------|------|------|-----|-----|----------------|------|
| Coal      | m <sup>2</sup> g <sup>-1</sup> | wt. %    | db, wt. % | daf, wt. % |      |      |     |     |                |      |
| Tunçbilek | 39.5                           | 5.8      | 16.5      | 38.3       | 61.7 | 71.9 | 5.4 | 2.6 | 1.4            | 18.7 |
| Zonguldak | 6.5                            | 0.5      | 11.6      | 23.2       | 76.8 | 88.3 | 5.2 | 1.0 | 0.5            | 5.0  |

S<sub>o</sub>: organic sulphur, O: by difference, db: dry base

The particle size distributions of the fine coals were determined using a Malvern-MasterSizer particle sizer. The analysis is based on the principle of laser ensemble light scattering. The surface areas (BET) of the coals were determined using a Micromeritics ASAP 2000 instrument. The measurements were performed at the liquid nitrogen boiling point of 77 K. The BET<sup>22,23</sup> surface areas of the fine lignite and bituminous coal were determined from the adsorption isotherms for each of the degassed samples (Table 1). Pore volume distribution was calculated using a procedure developed by Barret et al.<sup>24</sup>. The Kelvin equation<sup>25</sup> was used to evaluate the apparent pore radius from the desorption isotherms.

### The adsorption of Triton X-100

The adsorption tests were conducted at room temperature (295 K) in glass vessels with a total volume of 100 ml. Magnetic followers were provided to agitate the slurries by means of a magnetic stirrer. The adsorption vessels were covered with Teflon lids to avoid the effects of air during the adsorption process. All tests were performed under natural pH conditions.

Blank adsorption tests were performed at room temperature to ascertain whether the reagent was being adsorbed on the walls, lid and magnetic follower of the adsorption vessel. The adsorption on these parts of the adsorption system was negligible.

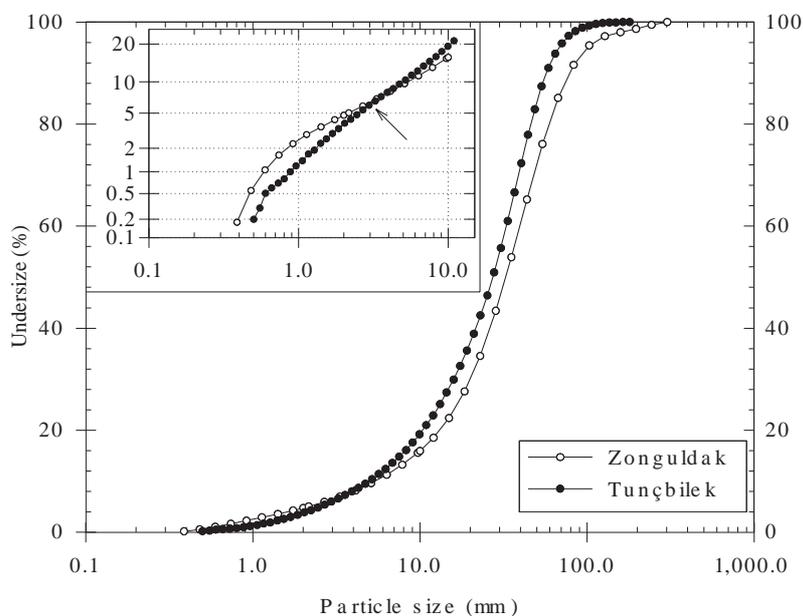
Dry coal samples (3.0 g) were mixed with 30 ml of distilled water in the adsorption vessel for 5 minutes, after which 17 ml of Triton X-100 solution at the desired concentration was added. The coal solution mixture had a solid content of 6% and was left to be conditioned for the required time period of 5, 30 and 1,440 minutes. At the end of the adsorption process, the conditioned sample was filtered using a vacuum pump. The filtrates containing Triton X-100 were analysed using a Shimadzu UV-160A Spectrophotometer.

### The adsorption kinetics of Triton X-100

The adsorption kinetic tests were performed as detailed above under the same slurry concentration (6% , wt./wt.), volume and mixing rate. The amount of reagent used in all the kinetic tests was 5 mg of reagent per gram of dry coal mass. As outlined above, the samples were taken while the adsorption was in progress. After filtration, the filtrates were collected in vials for UV analysis. Filtration took approximately 5-10 seconds, and so the amount of the reagent adsorbed on the solid particles during the filtration was assumed to be negligible over this time period.

## Results and Discussion

Particle size distributions of the samples are illustrated in Figure 1. As can be seen from the figure, the lignite particles are finer above 3.5  $\mu\text{m}$  particle size, and under this particle size (about 8% of the material in both coals), the particles of Zonguldak coal are finer than Tunçbilek lignite. Particle size distributions for the samples within the 0.1-10  $\mu\text{m}$  size range are given in the log-probability graph to the left of Figure 1.



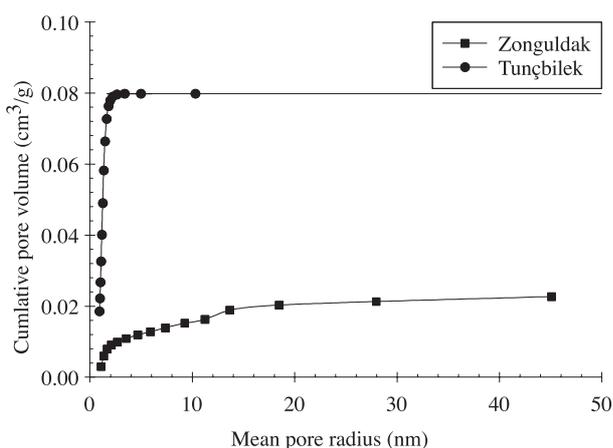
**Figure 1.** Particle size distributions of the coal samples

Variations in the cumulative pore volumes with the mean pore radius for the samples are shown in Figure 2. The total (external + internal) surface areas of the coals are given in Table 1 as reported in the

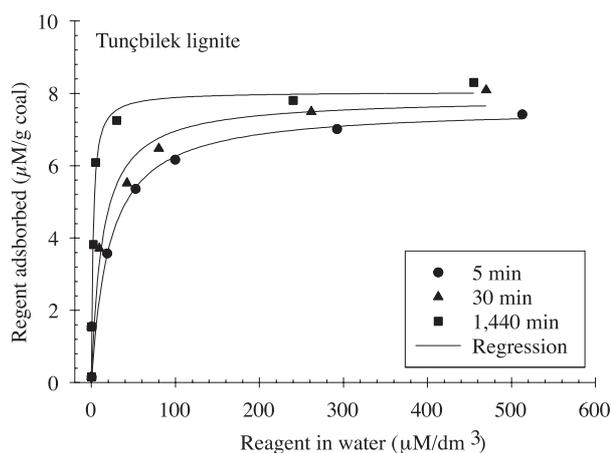
experimental section. The total surface areas of the lignite and bituminous coal, which were determined from the adsorption isotherms using the BET technique, are 39.5 and 6.5 m<sup>2</sup>/g coal respectively. The cumulative pore volume increases sharply to 0.08 cm<sup>3</sup>/g coal for the lignite. The corresponding mean pore radius for the cumulative pore volume is about 2.5 nm. After this point, the increase in the cumulative volume is very slight. This shows that the majority of pores are less than 2.5 nm. In the case of Zonguldak coal, the curve gradually increases towards 0.02 cm<sup>3</sup>/g coal. Clearly this coal has a wider distribution of pore sizes when compared with the lignite.

### The Adsorption of the Reagent on the Samples

Triton X-100 adsorbed on the lignite and bituminous coal was plotted as a function of residual unadsorbed reagent in water. Figures 3 and 4 show the amounts of the reagent adsorbed on the lignite and bituminous coal, respectively. The isotherms shown in the figures were obtained at the end of 5, 30 and 1,440 (24 h) minute adsorption periods. The curves for 1,440 minutes show the equilibrium adsorption isotherms. The curves for 5 and 30 minutes were only given to show how close these values were to the equilibrium values. Solutions containing Triton X-100 were not withdrawn from the coal slurries between 30 and 1,440 minutes for analyses. Therefore the adsorption may have reached the equilibrium level before 1,440 minutes.



**Figure 2.** Variation of the cumulative pore volume as a function of mean pore diameter



**Figure 3.** Adsorption isotherms for Tunçbilek lignite using Triton X-100

The equilibrium adsorption isotherms were described by means of the Langmuir and Freundlich adsorption isotherms. The parameters calculated from the linear forms of the Langmuir and Freundlich isotherms are tabulated in Table 2. Correlation coefficients, which exhibit deviation from linearity, and obtained linear forms of the Langmuir and Freundlich curves are given in the same table.

Table 3 shows the amounts of the reagent adsorbed at the equilibrium on the lignite and bituminous coal obtained from the experimental and calculated values using the Langmuir (Eq. 2) and Freundlich (Eq. 4) equations. The amounts of the reagent on the solid surfaces obtained from the experimental results are close to the data calculated from Eqs. 2 and 4. However, the values obtained from the Langmuir equations show better correlation to the experimental results than that of the Freundlich equation. Similar results have been found in a number of studies<sup>3,7-12</sup>.

**Table 2.** Langmuir and Freundlich isotherm constants for the coal samples

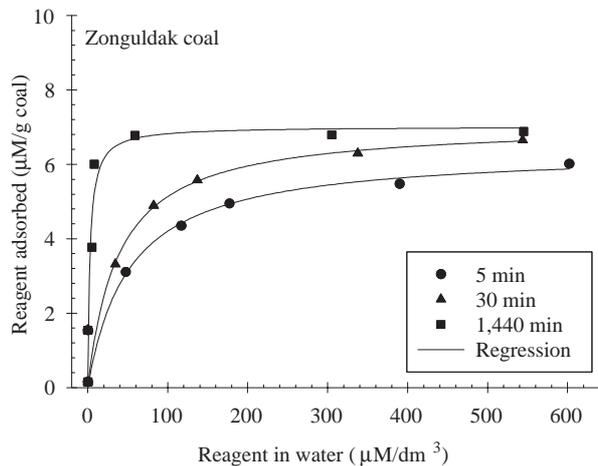
| Coal      | Time (equilibrium)<br>min | Langmuir constants |           |      |             | Freundlich constants |       |       |
|-----------|---------------------------|--------------------|-----------|------|-------------|----------------------|-------|-------|
|           |                           | $r^a$              | $C_{s,m}$ | k    | $K_L(=1/k)$ | $r^a$                | $K_F$ | n     |
| Tunçbilek | 1440                      | 0.99               | 8.17      | 2.20 | 0.45        | 0.88                 | 4.28  | 0.117 |
| Zonguldak | 1440                      | 0.95               | 7.27      | 4.13 | 0.24        | 0.79                 | 3.98  | 0.099 |

<sup>a</sup>correlation coefficient

**Table 3.** Comparison of adsorption data for the coal samples (contact time: 1,440 mins)

| Initial reagent loading |                     | Tunçbilek lignite                              |  |                       |                         | Zonguldak bituminous coal                      |  |                       |                         |
|-------------------------|---------------------|--|--|-----------------------|-------------------------|--|--|-----------------------|-------------------------|
| mg/g coal               | $\mu\text{ M/dm}^3$ | Reagent in water (exp.)<br>$\mu\text{ M/dm}^3$ | Reagent adsorbed, ( $C_s$ , $\mu\text{M/g coal}$ ) |                       |                         | Reagent in water (exp.)<br>$\mu\text{ M/dm}^3$ | Reagent adsorbed, ( $C_s$ , $\mu\text{M/g coal}$ ) |                       |                         |
|                         |                     |  | Experimental                                       | Langmuir (calculated) | Freundlich (calculated) |  | Experimental                                       | Langmuir (calculated) | Freundlich (calculated) |
| 0.1                     | 9.86                | 0.0  | 0.15   | -                     | -                       | 0.0  | 0.15   | -                     | -                       |
| 1.0                     | 98.62               | 0.0  | 1.54   | -                     | -                       | 0.0  | 1.54   | -                     | -                       |
| 2.5                     | 246.57              | 2.0  | 3.82   | 3.89                  | 4.64                    | 5.0  | 3.78   | 3.98                  | 4.67                    |
| 4.0                     | 394.50              | 5.0  | 6.10   | 5.67                  | 5.17                    | 14.0   | 5.96   | 5.61                  | 5.16                    |
| 5.0                     | 493.14              | 30.0   | 7.25   | 7.61                  | 6.37                    | 59.0   | 6.80   | 6.80                  | 5.95                    |
| 7.5                     | 739.71              | 240.0  | 7.83   | 8.09                  | 8.13                    | 305.0  | 6.81   | 7.17                  | 7.01                    |
| 10.0                    | 986.28              | 455.0  | 8.32   | 8.13                  | 8.76                    | 545.0  | 6.91   | 7.22                  | 7.42                    |

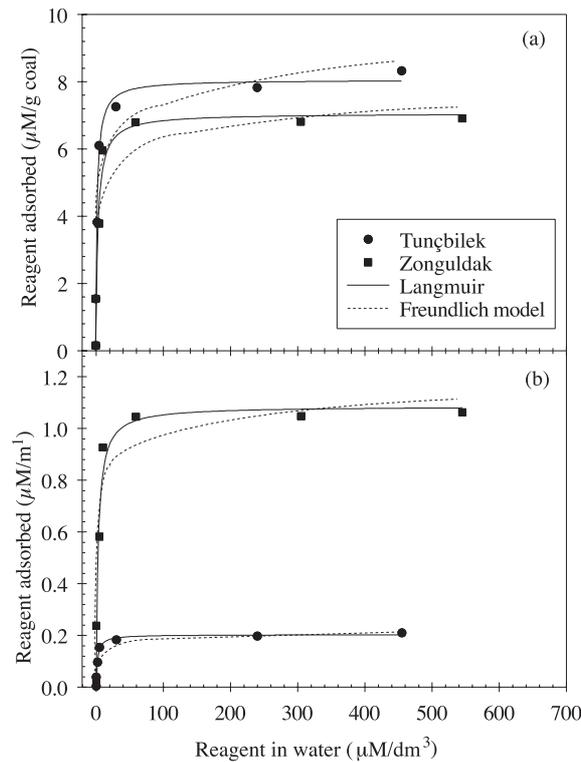
The trends of the curves shown in Figures 3 and 4 are quite similar. However, the amounts of the reagent adsorbed per gram of the solids are different. Figure 5 shows the equilibrium isotherms of the samples obtained from the 1,440 minute adsorption period. The figure is useful to show the amounts of the reagent adsorbed on the samples in terms of  $\mu\text{M/g coal}$  (Figure 5a) and  $\mu\text{M/m}^2$  (Figure 5b). As seen in the figure and also reported in Table 2, the amounts of the reagent adsorbed, calculated from the Langmuir model, on the lignite and bituminous coal, are 8.17 and 7.27  $\mu\text{M/g coal}$  at monolayer adsorption (Figure 5a). This shows that the reagent concentration per gram of Tunçbilek lignite is 1.12 times higher than that of Zonguldak coal.



**Figure 4.** Adsorption isotherms for Zonguldak bituminous coal using Triton X-100

In terms of the reagent adsorbed per unit area ( $\mu\text{M/m}^2$ ) of the coals, there is a significant difference (Figure 5b). The amounts of the reagent adsorbed on the samples are 0.21  $\mu\text{M/m}^2$  for Tunçbilek lignite and 1.11  $\mu\text{M/m}^2$  for Zonguldak bituminous coal at monolayer adsorption. This shows that the reagent concentration per  $\text{m}^2$  of Zonguldak bituminous coal is 5.3 times higher than that of Tunçbilek lignite. For

these calculations, it was assumed that the reagent concentration distribution on the total surface (BET) is the same throughout the surface. However, it should be noted that as the pores are very fine (nitrogen molecules may be adsorbed on their surface), the reagent molecule may not penetrate into them due to their size. Therefore, a considerable fraction of the internal surface may not contain the reagent molecules by virtue of very fine inaccessible pores. The difference of the surface concentrations of the reagent may be attributed to the molecular orientation of Triton X-100 molecules during the adsorption process and the high surface area of the lignite. The surface functionality of the coal is a key factor for the orientation of the reagent as well as the chemical structure of the reagent (functional groups in the reagent molecule). This fact may be expected, as it is well known that lignites and bituminous coal have markedly different origins and chemical structures. Therefore, the surface characteristics of low rank coals (i.e. lignites) and high rank coals are different. As bituminous coals are hydrophobic, lignites are hydrophilic due to their polar oxygen-containing functional groups<sup>26–30</sup>. The extent of the molecular orientation of the reagent during adsorption process may be controlled by the existing functional groups on the coal surface. Previous studies regarding Tunçbilek lignite and Zonguldak bituminous coal showed that the chemical structure of these coals was different<sup>31,32</sup>.



**Figure 5.** Comparison of the equilibrium adsorption isotherms (1,440 minutes) for Tunçbilek lignite and Zonguldak bituminous coal. a) in terms of  $\mu\text{M/g}$  coal b) in terms of  $\mu\text{M/m}^2$

The equilibrium concentration of Triton X-100 in the liquid phase ( $C_{e,l}$ ) can be calculated from the data obtained for the given values of  $C_s$  using the Langmuir isotherms for Tunçbilek lignite and Zonguldak bituminous coal:

$$\text{Tunçbilek lignite: } C_s = \frac{8.17C_{e,l}}{2.2 + C_{e,l}} \quad (6)$$

$$\text{Zonguldak coal: } C_s = \frac{7.27C_{e,1}}{4.13 + C_{e,1}} \tag{7}$$

similarly from the Freundlich isotherms:

$$\text{Tunçbilek lignite: } C_s = 4.28 (C_{e,1})^{0.117} \tag{8}$$

$$\text{Zonguldak coal: } C_s = 3.98 (C_{e,1})^{0.099} \tag{9}$$

### Adsorption Kinetics

The adsorption kinetics of the reagent on the lignite and bituminous coal were carried out over the period of 0-1,440 minutes (Table 4). The data were evaluated in terms of  $\mu\text{M/g}$  coal. Figure 6 shows the adsorption kinetic curves using Triton X-100 for Tunçbilek lignite and Zonguldak coal over the whole period.

**Table 4.** Adsorption kinetic data for the coal samples

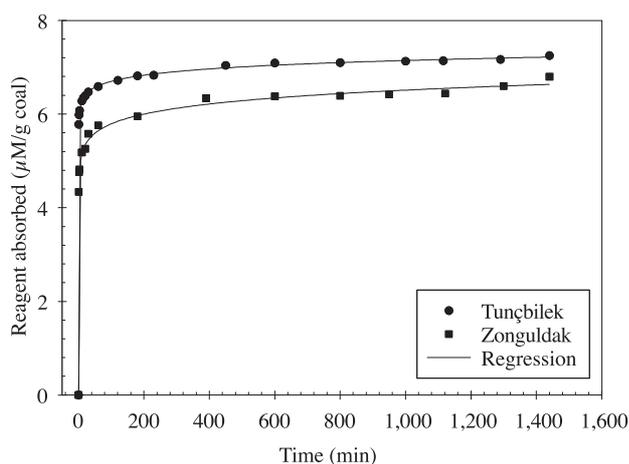
| Tunçbilek lignite |  |  |                    | Zonguldak bituminous coal |  |  |                    |
|-------------------|--|--|--------------------|---------------------------|--|--|--------------------|
| Time (min)        | Reagent in water $\mu\text{M}/\text{dm}^3$ | Reagent adsorbed $\mu\text{M}/\text{g}$ coal | Reagent adsorbed % | Time (min)                | Reagent in water $\mu\text{M}/\text{dm}^3$ | Reagent adsorbed $\mu\text{M}/\text{g}$ coal | Reagent adsorbed % |
| 0.0               | 493.0                                      | 0.00   | 0.00               | 0.0                       | 493.0                                      | 0.00   | 0.00               |
| 0.5               | 124.1                                      | 5.78   | 74.83              | 0.5                       | 216.0                                      | 4.34   | 56.20              |
| 1.5               | 111.0                                      | 5.98   | 77.49              | 1.5                       | 189.0                                      | 4.76   | 61.67              |
| 3.0               | 105.0                                      | 6.08   | 78.70              | 3.0                       | 185.0                                      | 4.82   | 62.48              |
| 10.0              | 92.0                                       | 6.28   | 81.34              | 10.0                      | 162.3                                      | 5.18   | 67.09              |
| 15.0              | 88.0                                       | 6.34   | 82.15              | 20.0                      | 157.0                                      | 5.26   | 67.55              |
| 20.0              | 85.2                                       | 6.39   | 83.27              | 30.0                      | 137.0                                      | 5.58   | 72.22              |
| 30.0              | 80.0                                       | 6.47   | 83.77              | 60.0                      | 125.0                                      | 5.76   | 74.65              |
| 60.0              | 72.0                                       | 6.59   | 85.40              | 180.0                     | 113.0                                      | 5.95   | 77.08              |
| 120.0             | 64.0                                       | 6.72   | 87.02              | 390.0                     | 88.0                                       | 6.34   | 82.15              |
| 180.0             | 58.0                                       | 6.81   | 88.24              | 600.0                     | 86.0                                       | 6.38   | 82.56              |
| 230.0             | 55.0                                       | 6.83   | 88.85              | 800.0                     | 85.0                                       | 6.39   | 82.76              |
| 450.0             | 43.6                                       | 7.04   | 91.12              | 950.0                     | 83.0                                       | 6.42   | 83.17              |
| 600.0             | 40.5                                       | 7.09   | 91.79              | 1,121.0                   | 82.2                                       | 6.44   | 83.32              |
| 800.0             | 39.6                                       | 7.10   | 91.97              | 1,300.0                   | 71.5                                       | 6.60   | 85.50              |
| 1,000.0           | 38.0                                       | 7.13   | 92.29              | 1,440.0                   | 59.0                                       | 6.80   | 88.03              |
| 1,115.0           | 37.1                                       | 7.14   | 92.48              |                           |  |  |                    |
| 1,290.0           | 35.5                                       | 7.17   | 92.79              |                           |  |  |                    |
| 1,440.0           | 30.0                                       | 7.25   | 93.92              |                           |  |  |                    |

As seen in the figure, both the lignite and bituminous coal adsorb the reagent very fast at the beginning of the adsorption process. The curves of both samples pass an inflection range, when the reagent adsorbed is about 5-5.4  $\mu\text{M}/\text{g}$  for Zonguldak coal and 6-6.6  $\mu\text{M}/\text{g}$  for Tunçbilek lignite. Adsorption proceeds to a saturation level over time for both samples. The amounts of Triton X-100 adsorbed on the solid particles increase only slightly for long adsorption periods. The amounts of the reagent per gram mass are slightly different for the samples. For example, the amount of the reagent the adsorbed per gram of Tunçbilek lignite is about 1.09 times higher than Zonguldak bituminous coal at the end of the adsorption kinetic period. When the reagent adsorbed on the surface of samples is compared, 85.40% of the reagent is adsorbed in 60 minutes

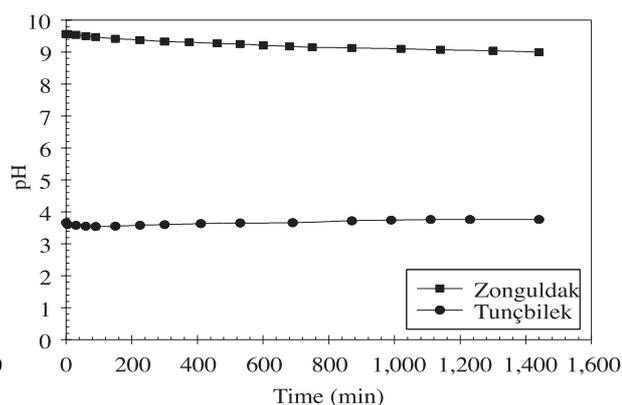
by Tunçbilek lignite, whereas 74.65% of the reagent is adsorbed over the same time by Zonguldak bituminous coal. This may be attributed to the higher surface area of the lignite.

The pH of the slurry is governed by the dissociation of ionogenic groups on the coal or lignite, such as those having carboxylic, phenolic and hydroxylic functionality and, to some extent, the level of soluble inorganic material present in the coal. An increase in the total concentration of the oxygen-containing functional groups results in a gradual increase in the surface acidity of the coal<sup>30,33</sup>. The total oxygen content of Tunçbilek lignite (18.7%) is higher than that of Zonguldak bituminous coal (5%), as reported in Table 1. The lower initial pH value (3.66) for Tunçbilek lignite may be due to a higher ratio of acidic functional groups on its surface.

The variation of pH over time for the lignite and bituminous coal water slurries is presented in Figure 7. The pH values of the lignite and bituminous coal water slurries were 3.66 (acidic) and 9.57 (basic) at the start of tests, respectively. There were no considerable changes in pH values during the course of the adsorption process. The pH value for the lignite water slurry increased slightly from 3.66 to 3.76. In the case of Zonguldak coal water slurry, the pH value dropped from 9.57 to 9.00. Slight changes in the pH values are due to functional groups present on the surfaces of the lignite and the bituminous coal. The nature of mineral matter in the bulk may also change the pH of the slurry.



**Figure 6.** Adsorption kinetics of the reagent based on per unit mass, over the whole period of the adsorption (0-1,440 minutes) and for the first 60 minutes



**Figure 7.** Variation of pH with time for the lignite and bituminous coal slurries

Slight changes in the pH did not significantly affect the amount of the reagent adsorbed on the solid surfaces. However, the natural pH values (for example, 3.66 and 9.57 for the lignite and bituminous coal) may affect the amount of reagent adsorbed.

## Conclusions

The amounts of the reagents adsorbed per unit area or mass greatly depended on the chemical structure of the coal surface and pore size. The organic and inorganic chemical structure of the coal should be considered during the adsorption process as well as the surface area of the solid particles.

The adsorption equilibrium isotherms were evaluated using both the Langmuir and Freundlich adsorption equations for the less than 53  $\mu\text{m}$  size fractions of both Tunçbilek lignite and Zonguldak bituminous

coal. The values obtained from the Langmuir and Freundlich models were fitted to the experimental results for both samples. The calculated values were found to be close to the experimental results. However, the values obtained from the Langmuir equation were closer to the experimental results than that of the Freundlich results.

The amount of Triton X-100 adsorbed per  $\text{m}^2$  of Tunçbilek lignite was significantly less than the amount adsorbed by Zonguldak bituminous coal.

The experimental data obtained in the work indicated that there were two different adsorption rates, one being fast and the other very slow. The fast adsorption occurs first at 2 and 10 minutes for the lignite and bituminous coal, respectively. Afterwards, the rates become very slow. A larger amount of the reagent is adsorbed on the solid surface during the course of fast adsorption stage.

## Acknowledgements

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## Nomenclature

|                |  |
|----------------|--|
| $C_{e,l}$      | : Equilibrium liquid phase solute concentration, $\mu\text{Mdm}^{-3}$      |
| $C_s$          | : Equilibrium solid-phase solute concentration, $\mu\text{Mg}^{-1}$        |
| $C_{s,m}$      | : Langmuir monolayer capacity, $\mu\text{Mg}^{-1}$                         |
| $K_F$          | : Freundlich isotherm constant, $\mu\text{Mg}^{-1}/(\mu\text{Mdm}^{-3})^n$ |
| $K_L$          | : Langmuir isotherm constant, $\text{dm}^3\text{g}^{-1}$                   |
| $k$            | : $=1/K_L$ , $\text{gdm}^{-3}$   |
| $n$            | : Freundlich isotherm constant   |
| $\mu\text{ m}$ | : Micrometer   |

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