Improved flotation of heat treated lignite with saline solutions containing mono and multivalent ions

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Abstract: Flotation of lignites is inherently difficult. However, pre-heat treatment of coal is also known to make coal surfaces more hydrophobic possibly through removal of water entrapped in the structure of coal. In this context, the objective of this study was, therefore, to determine changes in the hydrophobicity of some lignites under moderately controlled heat treatment, and correlate the flotation response of lignites in different salt solutions of NaCl, KCl, CaCl₂, and MgCl₂ without using any reagent. The results of flotation tests suggested that, under the present test conditions, it was possible to float thermally pre-treated lignite samples of partially hydrophobic character in salt solutions in the absence of collector and frother. In addition, the effect of heat treatment on hydrophobicity, and in turn flotation was explained by a theoretical model based on extended DLVO interactions to quantify the effects of both heat treatment and salt concentration on bubble-particle interactions. The results of theoretical modeling suggested that the removal of hydrogen containing groups from coal surfaces significantly contributed to the electrical double layer and hydrophobic forces that governed the magnitude of energetic barrier and also the extent of bubble-particle attachment.

Keywords: heat-treatment, lignite, saline solutions, flotation, DLVO

1. Introduction

It is well known that coals with higher ranks generally possess a natural floatability whereas lower rank coals are more hydrophilic due to the considerable amount of oxygen functional groups like carboxyl, phenolic, and carbonyl functionalities on lignite surfaces, which increase the bonding with water molecules, and creates difficult-to-float lignite surface (Cebeci, 2002). According to their hydrophilic character, lignites are difficult to float even at high dosages of oily collectors such as kerosene. It is not uncommon for several tens of kilograms of fuel oil consumption per ton of feed to float sub-bituminous coal or lignite (Cinar, 2009). This is not only uneconomic but also deteriorates the selectivity of separation due to adverse effect on particle aggregation (Celik and Seyhan, 1995).

Colloidal interactions between bubbles and particles affect the floatability of minerals (Li and Somasundaran, 1993; Laskowski et al., 2013; Ozdemir et al., 2013; Quinn et al., 2014). There are a number of studies in the literature indicating that dissolved ions in flotation pulps induce important effects on the flotation of minerals such as potash, trona, and borax (soluble minerals) in brine solutions (Ozdemir, 2013). These studies have advanced some mechanisms to explain flotation of coal and other minerals in inorganic electrolyte solutions. Among them, bubble coalescence in salt solutions seems to be a significant factor for coal flotation in saline water (Ozdemir, 2013).

Although many studies involving the effect of various conditions as surfactant type, pH, particle size, and that of heat treatment on coal flotation were available in literature (Cinar, 2009; Ye, 2017), however the combined effect of heat treatment together with the use of electrolytes on coal flotation has

not been thoroughly investigated. Therefore, the objective of this study was to investigate the flotation behaviour of a low rank lignitic coal after heat treatment in different salt solutions without frother and collector. Four inorganic electrolytes, namely, NaCl, KCl, CaCl$_2$, and MgCl$_2$, were purposely chosen and used in the experimental program to clarify the mechanism of enhancement in lignite flotation at modestly controlled heat treatment. Several methods such as Fourier Transform Infrared Spectroscopy (FTIR), zeta potential, and contact angle measurements were also used to correlate the flotation response and quantify hydrophobic and hydrophilic groups in coal. Additionally, although there have been recent publications on modelling colloidal interactions between particles in salt solutions (Guven et al., 2015), none of them has analyzed the effect of heat treatment on floatability of fine coals leading to the interaction between particles. Therefore, in this study, in addition to the flotation characteristics of fine coals in the presence of different electrolytes, another powerful theoretical tool the extended-DLVO model was utilized to explain the effect of heat treatment and electrolyte addition on flotation recoveries.

2. Materials and methods

2.1. Materials

The lignite sample used in this study was obtained from Turkish Coal Enterprise Coal deposit, Kutahya, Turkey. Prior to flotation tests, raw sample with -15+4 mm size was enriched by a dry jigging process using pneumatic All-air jig to obtain a clean coal for flotation tests. The enriched low-ash lignite sample (Clean Coal) was first crushed using a series of jaw, cone, and roll crushers to reduce the particle size under 1 mm. The particle size distribution and ash content of the lignite sample used in flotation tests are shown in Fig. 1. Following the crushing process, the sample size was reduced to 212 μm by grinding in a ceramic ball mill. The sample was finally sieved through a 38 μm sieve due to the presence of higher ash content under 38 μm, which would deteriorate the flotation conditions; size fraction of 212×38 μm sample was used for the flotation experiments. On the other hand, in order to investigate the effect of heat treatment on the wettability characteristics of lignite samples, different types of electrolytes of technical grades (98% purity) sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl$_2$), and magnesium chloride (MgCl$_2$) were used. The concentrations of salt solutions as 0.1 mol/dm^3, 0.5 mol/dm^3, 1 mol/dm^3, and 2 mol/dm^3 were prepared with mono-distilled water (GFL, Germany).
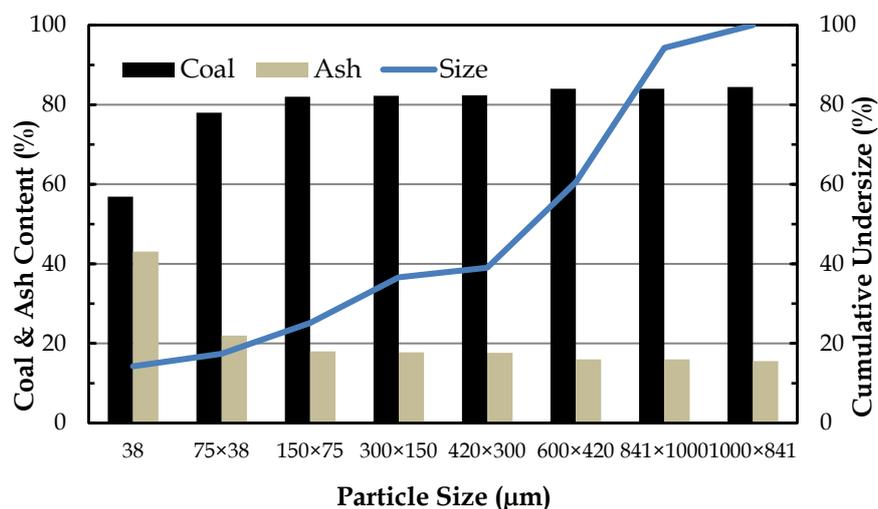

Fig. 1. Particle size distribution, and coal and ash contents of lignite sample

2.2. Methods

2.2.1. Heat treatment and FTIR analysis

Functional groups such as carboxyl and hydroxyl species in coal have major influence on floatability of coal (Aplan et al., 1976; Fuerstenau et al., 1988). It is well known that Fourier Transform Infrared

Spectroscopy (hereafter FTIR) analysis provides useful information on the composition of functional groups like aliphatic and aromatic groups in coal structure. Thus, the low floatability of low rank coals can be attributed to the higher content of oxygen containing groups in their structure. Therefore, any attempt to decrease their content will improve the floatability of coal (Ye et al., 1988; Celik and Seyhan, 1995; Cinar, 2009; Xia et al., 2013; Niu et al., 2017).

In this study, spectral analysis namely, FTIR was carried out to quantitatively determine these groups, and also calculate the hydrophilicity index (*HI*) of samples treated at different temperatures through measuring areas under the specific FTIR peaks. The absorption intensities of the peaks together with the areas under the peaks for carboxyl, hydroxyl, aliphatic CH, and aromatic CH groups were used to quantify the extent of these species. Since coal rank is mainly classified by its carbon content, the value of this index can be used to evaluate the degree of hydrophobicity rather than its rank or carbon content (Ye et al., 1988; Celik et al., 1995). *HI* is also a good indicator of the balance of hydrophilic/ hydrophobic groups at a coal surface which can be proven by contact angle data, flotation recovery and etc. (Jin et al., 1987). The *HI* is given by Eq. 1:

$$\text{Hydrophilicity Index } (HI) = (-\text{COOM}) + 2(-\text{OH})/(\text{RH}) + (\text{Ar} - \text{H}) \tag{1}$$

where (–COOM), (–OH), and (Ar–H) are the adsorption intensity values as expressed by the Kubelka–Munk function.

The effect of heat treatment on the flotation of low ash lignite samples of 212×38 μm in size was investigated in an oven at 105 °C for periods of 0.5, 1, 1.5, 2, and 4 h. FTIR spectrum of each sample upon heat treatment was obtained to follow the changes in floatability and HI index of the lignite samples.

2.2.2. Zeta potential measurements

The zeta potential measurements of both original and heat-treated lignite particles were conducted using ZetaPlus Zeta Potential Analyzer (Brookhaven Instrument Corporation, Holtsville, New York, U.S.A) to determine the electrophoretic mobility of charged particles. At least 10 g of sample was dry ground for 15 min using a mortar and pestle. The sample upon grinding was screened through a 38 μm sieve, and the undersize fraction was conditioned in deionized water (DI, Milli Q, Millipore Corp., 18 MΩ × cm) for 15 min using a magnetic stirrer at 500 rpm. The suspension pH was adjusted by adding the desired amount of 0.1 mol/dm³ HCl or 0.1 mol/dm³ NaOH (analytical grade, Merck KGaA, Darmstadt, Germany), and allowed mixing for 5 min to reach a stable condition. Before each experiment, the suspensions were kept for 5 min to let the coarse particles to settle down. A small amount of suspension was then taken from the top of the suspension, and transferred into the cell. Finally, twenty measurements at each pH value were performed, and their average was recorded for each lignite sample. An average error of these measurements was about 3%. The experiments were carried out at room temperature (23°C).

2.2.3. Contact angle measurements

Contact angle measurements of lignite samples were performed with capillary rise method. In this method, the mass of liquids with different surface energy values in a 0.8 cm diameter glass tube filled with coal particles was measured vs. time. Thus, the increase of the penetrating liquid in terms of mass was recorded every 5 sec until constant values were obtained. Eq. 2 given below was used to calculate the contact angle as follows:

$$\frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma} \tag{2}$$

where m^2 is the square of the mass variation, t is the time, γ is the surface tension, ρ is the density of liquids, and η is the viscosity. The properties of the penetrating liquids are presented in Table 1.

2.2.4. Flotation experiments and analysis

The flotation experiments were carried out with heat-treated samples in a laboratory scale Denver Flotation Cell of 1 dm³ in order to investigate the effect of both heat treatment and salt concentration on the floatability of lignite coals. The parameters such as solids concentration and impeller speed were respectively taken constant at 10 wt. % and 1200 rpm in all tests.

For each flotation experiment, a 100 g of sample was added to the flotation cell and conditioned with the salt solutions for 3 min without any flotation reagent addition. The air (10 dm³/min) was introduced to the cell, and froth was collected for 1, 3, 5, 7, and 15 min in order to determine the flotation kinetics. All products, i.e. concentrates and tailings were collected at pre-determined times, filtered, weighed, and upon drying at 60 °C analysed for ash content and calorific value. The ash analysis was carried out according to ASTM D 3174-73 standards. The flotation tests were evaluated with their cumulative combustible recovery (CR) values, which were calculated by Eq. 3 as follows:

$$CR(\%) = \frac{C(t).(1-X_C(t))}{F.(1-X_F)}) \cdot 100 \tag{3}$$

where F is the feed mass (%), and X_F, $X_C(t)$ are the mass fractions of ash in the feed and products, respectively.

Table 1. Properties of liquids used for capillary rise measurements

Wetting Liquid	Density (kg/m³)	Viscosity (mPa.s)	Surface Tension mJ/m²
Water	997	1.01	72.8
Heptane	684	0.41	20.3

3. Results and discussion

3.1. Effect of heat treatment

As mentioned in the methods section, *HI* index based on the measurement of areas under specific FTIR peaks provided very useful knowledge about the degree of wettability and also the rank of coal. The representative FTIR results for the original sample at ambient temperature and treated at 105 °C for 90 min are shown in Fig. 2. Of these, the areas under the FTIR peaks of 1440 cm⁻¹, 1620 cm⁻¹, 1430, and 3030 cm⁻¹ corresponding to OH⁻, COOH, R-H, and aromatic hydrogen groups were used for the *HI* calculations. The areas under these peaks were calculated by counting the number of squares per 1 mm² area. The *HI* values of the coal samples treated at different times calculated by Eq. 3, are presented in Table 2. The *HI* of the coal demonstrated a substantial decrease as a function of heating time.

Table 2. *HI* values before and after heat treatment of lignite samples

Heat treatment time (min)	Hydrophilicity Index (*HI*)
Original	8.65
30	5.54
90	2.67

As evident in Table 2, while the *HI* index of original sample was 8.65, it gradually decreased to 5.54 and then to 2.67 upon 30 and 90 min of heat treatment, respectively. This in turn showed that removal of oxygen containing groups on the coal surfaces lead to more hydrophobic surfaces, and hence higher flotatabilities. In literature, similar trends were reported to confirm the effect of heat treatment on lignite floatability. Cinar (2009) showed that while the *HI* value of Malkara lignites was 17.25, it decreased to 2.87 after heat treatment at 105 °C for 4 h. On the other hand, the pre-treated coals above 450 °C were found to reduce their both pyritic and organic sulphur in coal which then increased both the carbonization and separation efficiency of coal by a dry permanent magnetic roll separator (Celik and Yildirim, 2000). On the other hand, in another study of the same research group, it was found that upon increasing the microwave pre-treatment time to 200 s, while the moisture content followed a descending trend, the combustible matter recovery significantly increased. In other words, the flotation of coal particles increased by the microwave treatment (Xia et al., 2013). In a recent paper, the effect of pyrolysis pre-treatment (500-600 °C) of coal samples was investigated (Yu, 2017). In another study, a low-temperature pyrolysis for sub-bituminous coal samples showed that while hydrophobic groups increased after the heat-treatment, a significant decrease was obtained for hydrophilic functional groups (Niu et al., 2017).
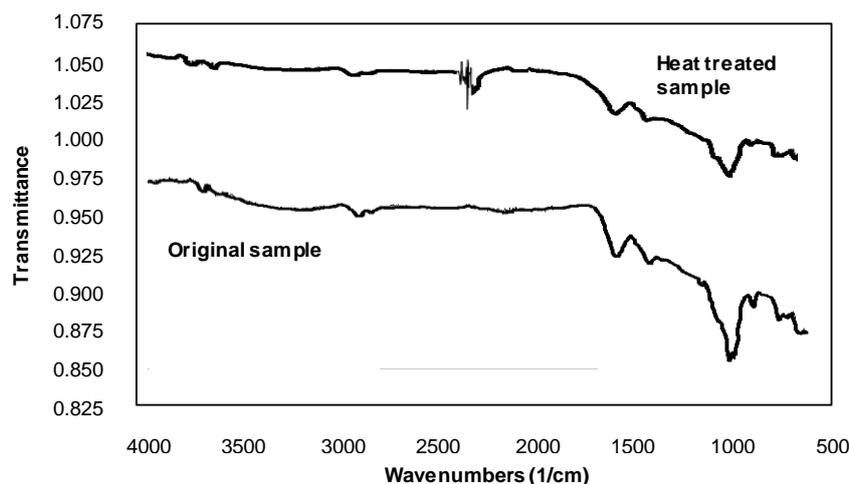
Fig. 2. FTIR spectrums of the lignite sample at room temperature (22±2°C) and 105°C for 90 min

3.2. Zeta potential measurements

Zeta potential measurement is one of the most important indicators for determining the extent of charge on a mineral, the dependence of pH on charge, and adsorption of any reagent on the surface as a function of concentration. On the other hand, the surface charge of coal also depends on the temperature, pH, and the presence of phenolic and carboxylic groups. By the way, as temperature increases and pH decreases, the released protons (H^+) interact with the surface functional groups and ionize them. At that point, the surface of the coal becomes more positive upon increasing the temperature and accordingly the zeta potential increases. Thus, series of measurement was carried out for both original lignite at ambient temperature and heat treated samples for different times of 30, 60, 90, and 120 min. In these series of tests, the suspension was prepared at 0.5% solid ratio, and the measurements were carried out at 8 different pH values. As shown in Fig. 3, while the zeta potential values reached -35 mV at pH 10, they decreased to -10 mV at pH 3 for the untreated coal. However, after the heat treatment for 120 min, it decreased to -27 mV from +10 mV in the respective pH region.

Similar findings were also reported for Saray lignite (Celik and Seyhan, 1995). It was shown that while the zeta potential value of original sample was over -100 mV at pH 10, it decreased over twofold to -40 at pH 3. However, after low-heat treatment for 120 min, these values decreased fivefold, with the slope of the zeta potential vs. pH curve became more linear upon treatment. More interestingly, there is a consistent shift of zeta potential curves towards higher pH values upon heat treatment. Similarly, the iep values shifted from no iep value in the absence of heat treatment to an iep range of 3.9-4.5 with heat treatment time of 30 to 120 min.

In a recent study, Arif et al. (2017) studied the effects of heat treatment at lower temperatures between the range of 20- 40 °C on the surface characteristics of coal samples. Similarly, they found that the zeta potential values of low rank coals changed to a positive trend from -35 to -15 mV as a function of temperature. At that point, the findings reported in literature, and in this study clearly indicated that the removal of oxygen containing functional groups followed the similar trend upon low-heat treatment. In other words, the pre-heat treatment of lignite was found to enhance the hydrophobicity degree through removal of entrapped water in the pores of coal and those oxygen containing groups in the coal matrix.

From another view, it was also shown that the zeta potential of coal particles became more positive upon increasing the heat treatment time, likewise, the measurements performed in different salt solutions (Arif et al., 2017). The effect of electrolyte addition is well known to compress the electrical double layer, and thus reduce the absolute value of zeta potential; the higher the valence, the more this depression occurs. Coal treated with multivalent ions may even undergo charge reversal above a certain salt concentration (Çelik and Somasundaran, 1986). The same is true for coal as coal suspensions are

governed by the potential determining ions (pdi) of H^+ and OH^-. Any change in pH is reflected in significant changes in the charge profile of coal.
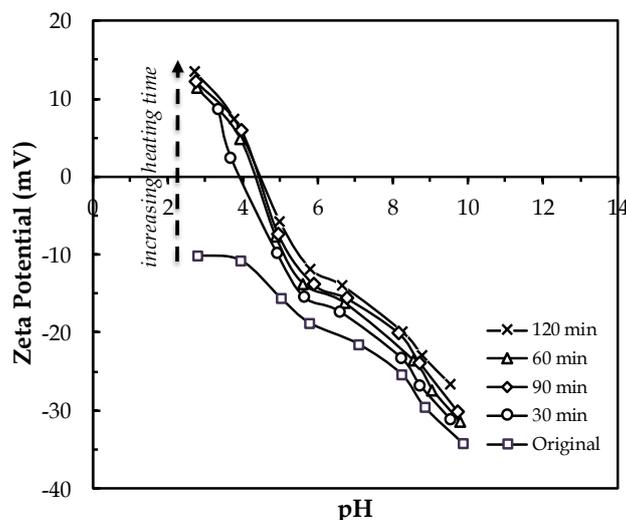

Fig. 3. Zeta potential-pH profile for the coal samples as a function of heat treatment time

3.3. Contact angle measurements

Contact angle measurements were adapted along with FTIR and zeta potential analysis in order to show the effect of heat treatment on the hydrophobicity modified of lignite samples. The results are presented in Table 3.

Table 3. Contact angles of lignite after heat treatment

Heat Treatment Time (min)	Contact angle (θ)
Original	56.0
30	75.4
60	76.8
90	77.0
120	77.5

As can be seen from Table 3, there is a proportional increase in the contact angles of lignite samples upon the heat treatment yielding higher hydrophobicities; this is in line with the calculated *HI* values obtained from FTIR spectra. Although temperature increase is known to increase the surface oxidation of coal samples, the increase on the contact angle values of lignite samples can be explained by the requirement of sufficient exposure time, which is well beyond the time scale of surface exposure during contact angle measurement (Arif et al., 2017).

3.4. Flotation experiments

The floatability of naturally hydrophobic particles has been reported to increase significantly upon addition of inorganic electrolytes (Klassen et al., 1963; Yoon and Sabey, 1989; Li and Somasundaran, 1991, 1993; Pugh et al., 1997; Harvey et al., 2002; Ozdemir et al., 2009; Ozdemir, 2013). This salt effect has been shown particularly with bituminous coals (Yoon, 1982; Ozdemir, 2013). The results from these studies exhibited the ion specific effect and also optimum concentrations for obtaining clean coal in salt solutions. On the other hand, some fundamental research showed that while the hydrophobicity of bituminous coal samples can be controlled at low salt concentrations (in this case NaCl), the hydrophobicities gradually decrease over a certain concentration range (Li and Somasundaran, 1993). In addition, some studies are also available on the effect of heat treatment on the hydrophobicity of

lignitic coals (Celik and Seyhan, 1995; Cinar, 2009; Xia et al., 2013; Niu et al., 2017). To our knowledge, the combined effect of heat treatment with electrolyte addition has not been systematically studied. Towards this aim, the effects of different salts on the floatability of heat treated lignite samples were investigated.

3.4.1. *Effect of heat treatment time on floatability of lignite*

In the first series of flotation tests, the optimum heat treatment time was determined in terms of maximum cumulative combustible recoveries at fixed salt type and concentration of 1 mol/dm³ NaCl. Fig. 4 presents the combustible recovery versus heat treatment time at 105 ºC. Fig. 4 clearly shows that while the recovery was around 32.5% for the untreated sample, it gradually increased to 66.1% after 60 min heating time remained constant up to 90 min , and then slightly decreased to 60% with further heat-treatment. It should be noted that lignite is not floatable without heat treatment in the absence and presence of salt addition. These results clearly show that heat treatment is a prerequisite in the improved floatability lignitic coal in salt solutions as also confirmed by *HI* values obtained from FTIR results. It appears that there are two opposing phenomena that control the hydrophobic/hydrophilic balance at the coal surface: i) while thermal treatment gradually breaks up the oxygen-containing groups such as carboxyl, which increases the hydrophobicity of the coals, ii) the oxidation of some hydrocarbon chains at the coal surface produces new phenol and carboxyl groups, which in turn make coal surfaces more hydrophilic (Fuerstenau et al., 1988). The decrease in the flotation recovery after 90 min proved that the flotation results are all in agreement with the contact angle data.

3.4.2. *Effect of salt concentration*

Although the maximum cumulative combustible recovery was obtained at 60 min (Fig. 4), 90 min were chosen as an optimum heating time based on the kinetics of flotation. Therefore, the flotation experiments were performed with lignite samples pre-treated for 90 min at 105 ºC in the presence of chloride halide solution concentrations. The results are shown in Fig. 5. The cumulative combustible recoveries in Fig. 5 increased to 45% and 66.6% at 0.5 mol/dm³ and 1 mol/dm³ NaCl concentrations, respectively. The recoveries after 1 mol/dm³ NaCl concentration slowed down. Interestingly, the ash content of the products also increased with increasing the salt concentration. These results clearly indicated that the salt concentration plays an important role in the lignite coal flotation in saline solutions.

Following the determination of optimum salt concentration in NaCl solutions further tests were continued with the other salts in order to compare the effect of different salts on flotation recovery of treated lignite samples.
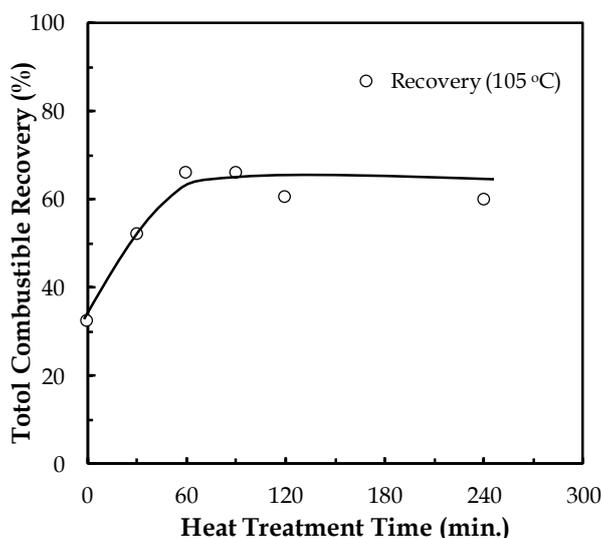

Fig. 4. Effect of heat treatment (105ºC) on maximum cumulative combustible recovery as a function of treatment time at 1 mol/dm³ NaCl solution

3.4.3. Effect of salt type

In this series of tests, different salt types as KCl, $MgCl_2$, and $CaCl_2$ were used keeping the salt concentration constant at 0.1 mol/dm^3 and 1 mol/dm^3 in flotation suspensions. Cumulative combustible flotation recoveries versus salt type illustrated in Fig. 6 indicated that $MgCl_2$ produced the highest cumulative combustible recovery while NaCl gave the lowest cumulative combustible recovery. Based on these results, the following order of floatability can be written:

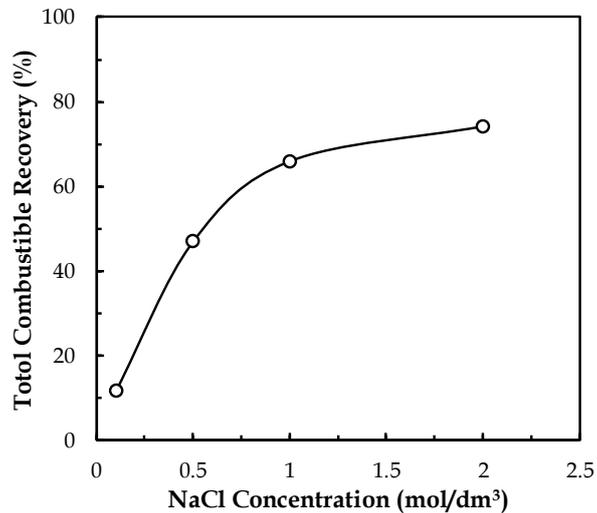$$MgCl_2 \geq CaCl_2 \geq KCl > NaCl.$$

Fig. 5. Flotation behaviour of heat treated (105 ^{o}C, 90 min) lignite sample in NaCl solution as a function of salt concentration
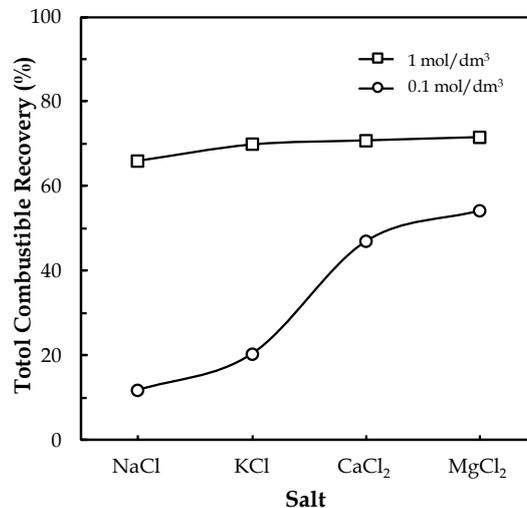

Fig. 6. Flotation behaviour of heat treated lignite sample in as a function of salt type (0.1 mol/dm^3 and 1 mol/dm^3 salt concentrations; 105 ^{o}C and 90 min. heat treatment)

The increase in the flotation recovery of mono and multivalent ions at 0.1 mol/dm^3 NaCl to $MgCl_2$ given in Fig. 6 can be easily attributed to the decrease in bubble coalescence. Craig et al. (1993) showed that there is a definite correlation between the valency of the electrolytes and the transition concentration, where bubble coalescence is reduced by 50% (Craig et al., 1993). Accordingly, the bubble coalescence was inhibited in the presence of some salts such as NaCl, KCl, $MgCl_2$ etc. For example, the salt transition concentration of $MgCl_2$ and $CaCl_2$ is 0.02 mol/dm^3 whereas that of NaCl and KCl is 0.08 and 0.1 mol/dm^3, respectively. The previous studies also showed that the high number of the bubbles in the system increased the flotation efficiency of coal particles in salt solutions (Kurniawan et al., 2011).

On the other hand, NaCl and MgCl$_2$ presented in Fig. 6 showed the similar results for the coal flotation recoveries at high concentration of 1 mol/dm^3, which leads to the assumption that the transition concentration of MgCl$_2$ would be closer to that value of NaCl. At salt concentrations higher than the transition concentration, bubble coalescence decreased, and eventually ceased at 1 mol/dm^3 for all salts where no significant variation in the flotation recovery was observed. These results show the importance of the effect of ion specificity (size and polarizability) at high salt concentrations on bubble coalescence. Similar results were also reported for the flotation of bituminous coal in salt solutions (Ozdemir, 2013). These results clearly showed that Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} ions have a strong ion specific effect on the flotation recovery of the lignite particles, divalent ions in salt flotation being more effective than monovalent ions.

3.4.4. Energy barrier analysis

In classical DLVO theory, the total DLVO energy includes only the electrostatic energy (V_E) and van der Waals energy (V_{vdW}), and generally fails when the surfaces are very hydrophilic or hydrophobic (Yao et al., 2016). In most of the systems, the total force is dominated by the repulsive long-ranged electrical double layer forces while the addition of attractive short-ranged forces change the characteristics of energy barriers, especially at short separation distances. However, the addition of hydrophobic forces with respect to polar interfacial interactions (Yoon and Mao, 1996; Guven et al., 2015) may provide a better explanation for the interactions between particles at different chemical media.

As mentioned in literature, the stability of an aqueous film and its associated energy barrier hinders the particle from attachment to the surface of a gas bubble which then dictate the outcome flotation recovery (Laskowski et al., 1991). Besides the effects of different parameters on the energy barrier calculations between particles, the interactions between heat treated coal surfaces has not been studied in detail. The aim was to show the extent of interactions in order to offer an explanation to the mechanism of improved lignite flotation.

Van der Waals, electrical double layer, and hydrophobic forces which were used in our theoretical treatment were calculated according to a derivative of DLVO model specifically developed for explaining the interactions between polystyrene and quartz surfaces (Suresh and Walz, 1996). The interactions were calculated via Eq. 4:

$$V_{vdW} = 2\pi RA \left[\frac{-2.45\lambda}{120\pi^2 h^2} + \frac{2.17\lambda^2}{720\pi^3 h^3} - \frac{0.59\lambda^3}{3360\pi^4 h^4} \right] \tag{4}$$

where *A* is the Hamaker constant, *R* is the radius of the spherical particle (μm), *λ* is the characteristic wavelength, *h* is the separation distance (nm) as measured from the coal particle surface. Eq. 5 given below describes the electrical double layer forces:

$$E_{EDL-SS} = 16R(4\pi\epsilon\epsilon_0) \left(\frac{kT}{e}\right)^2 \tanh\left(\frac{e\psi_1}{4kT}\right) \tanh\left(\frac{e\psi_2}{4kT}\right) e^{-\kappa h} \tag{5}$$

where ψ_1 and ψ_2 are the surface potentials of gas bubble and coal particle, respectively, *k* is the Boltzmann constant (1.38×10^{-23} m^2 kg s^{-2}K^{-1}), *e* is the charge of a proton (1.602×10^{-19} C), *T* is the temperature (298 K), κ^{-1} is the Debye length, *ε* is the bulk dielectric constant (80), ε_0 is the permittivity of free space (8.85×10^{-12} C^{2}J^{-1}m^{-1}). Hydrophobic forces were calculated with an equation similar to the classical van der Waals theory as given below in Eq. 6:

$$V_{hydrophobic} = \frac{K_H R}{12h} \tag{6}$$

where K_H represents the hydrophobic constant between bubble and particle which can be calculated using Eq. 7 below:

$$K_H = ae^{b_K\theta} \tag{7}$$

where *a* and b_K are constants which vary with the contact angle, θ (Pazhianur and Yoon, 2003).

Fig. 7 illustrates the calculated XDLVO forces between lignite particles and bubbles against distance of separation. A negative trend was obtained with the energy barrier height for heat-treated lignite as a function of treatment time in salt solutions. This also confirms the more hydrophobic nature of heat-treated time dependent samples. Indeed, the theoretical calculations were found in line with the zeta potential measurements of particles, which exhibited zeta potentials closer to zero leading to the decreased height of the energy barrier. Thus, it was found that energy barrier heights followed a

negative trend upon heat-treatment which resulted in higher flotation recoveries, as shown in Fig. 8. Thus, when we consider the required conditions for flotation, it is well-known that flotation recovery will increase in accordance with the hydrophobicity of particles. At that point, if the hydrophilicity index and only hydrophobic force were shown in the same graph (Fig. 9), it was found that hydrophobic force increases in reverse proportion with the hydrophilicity index value as expected.
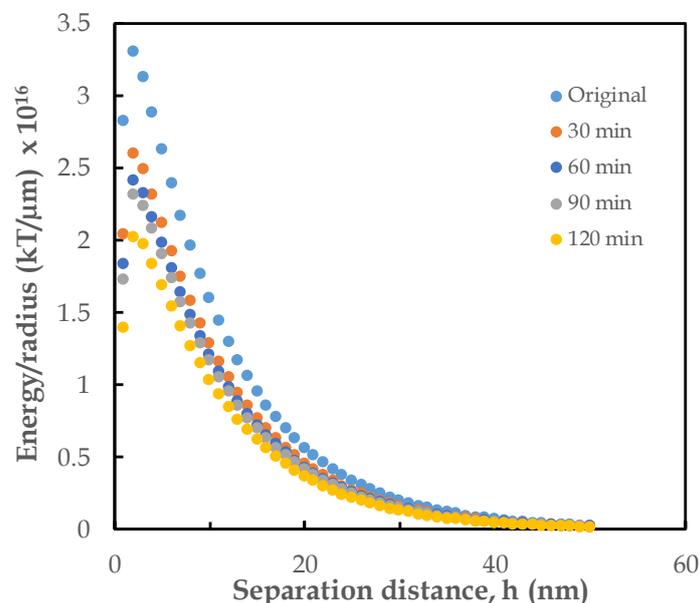
Fig. 7. XDLVO calculations between lignite particles and bubbles (Surface charges of coal particles were taken from Fig. 3 while the ψb (surface charge of bubble) was taken as -25 mV (Elmahdy et al. 2008), contact angle values were taken from Table 3)
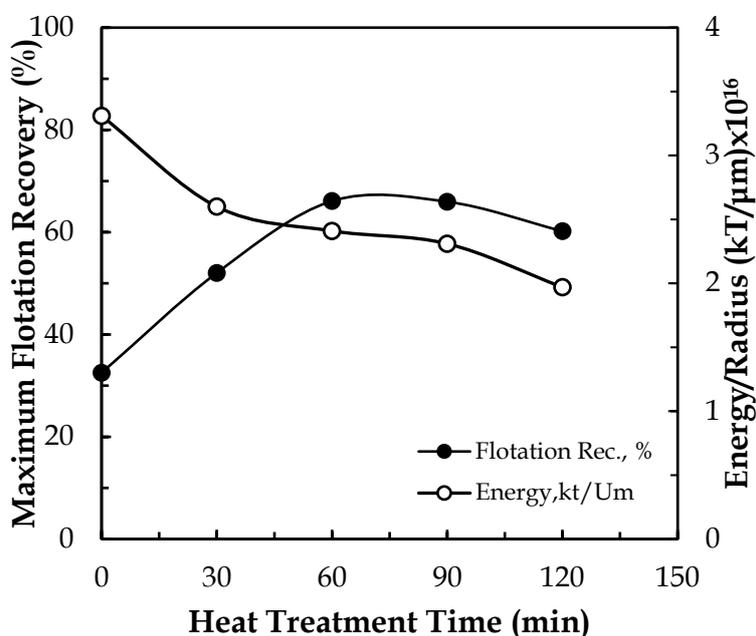
Fig. 8. Evaluation of flotation recovery with calculated energy barrier heights between bubble and particle

3.5. Discussion

The flotation results showed that the heat treatment of low rank coals increases the floatability and consequently hydrophobicity of coal. As stated in literature (Ye at al., 1988; Celik and Seyhan, 1995), the low-temperature heating removes the trapped water molecules within the pores and at the coal surface,

and in turn brings coal to a more hydrophobic state. In addition, there are two opposing phenomena, which control the hydrophobic/hydrophilic balance at the coal surface. While thermal treatment gradually breaks up the oxygen containing groups such as carboxyl, which bring coal to a more hydrophobic state, oxidation of some hydrocarbon chains at the coal surface creates new phenol and carboxyl groups that will make coal more hydrophilic. Thus, thermal treatment affects the hydrophobic/hydrophilic balance at the coal surface, and therefore, alters the floatability of coal positively or negatively depending on the final state. In the present study, the thermal treatment favorably affects the floatability of lignite coal, which is found in a good correlation with the *HI* values obtained from FTIR data (Fig. 4). On the other hand, depending on the removal of oxygen functional groups from lignite coal surfaces upon the thermal treatment process, the negative zeta potential values were significantly reduced, and the iep of lignite samples shifted to higher pH values (Fig. 3). The results of zeta potential tests are also consistent with literature data (Celik and Seyhan, 1995; Cinar, 2009). In addition, the use of various salts in lignite flotation also resulted in products of higher combustible recoveries which also show that the lignite sample can be recovered in chloride salts without using any frother or collector after the heat treatment. These results were also in line with the literature data (Celik and Seyhan, 1995; Cinar, 2009; Kurniawan et al., 2011; Ozdemir, 2013).
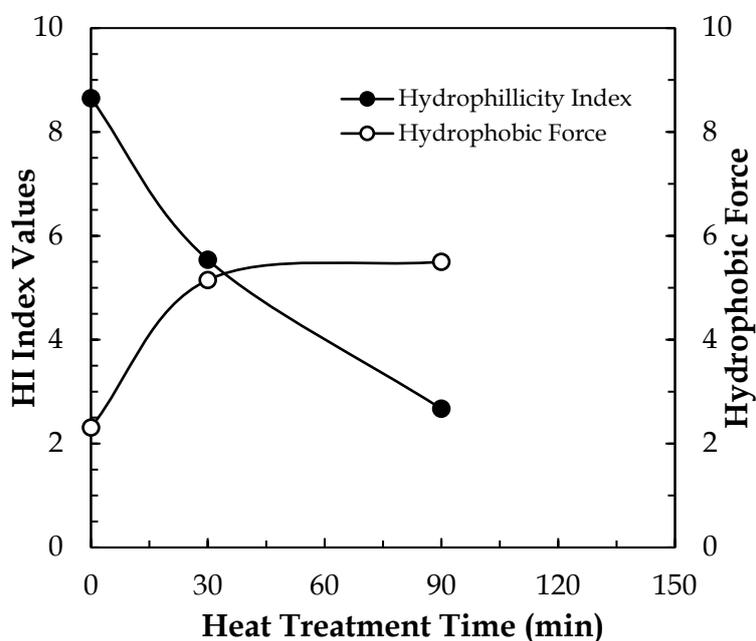

Fig. 9. Comparison of hydrophilicity index and hydrophobic force occurred

4. Conclusions

The combined effect involving heat treatment and use of electrolytes on the floatability of lower rank coals can be summarized as follows;

1) The improvement in the floatability of lignite coals upon low temperature heat treatment was ascribed to the removal of trapped water molecules within the pores and at the coal surface and to that of oxygen containing groups. It was the net effect of these two groups, as described by a hydrophilicity index that dictated whether a particular coal was amenable to thermal treatment or not. The FTIR measurements also demonstrated a direct correlation between the flotation recoveries and the hydrophobic and hydrophilic peaks in coal.

2) The effects of chloride salts as $MgCl_2$, $CaCl_2$, NaCl, and KCl on the flotation of heat treated lignitic coals were found to increase the combustible recovery at natural pH; the highest combustible recoveries were obtained with $MgCl_2$, and the lowest recoveries with NaCl. These findings also indicated that divalent ions were more effective than monovalent ions in the flotation of heat treated coals in salt solutions.

3) The results of theoretical modelling showed that increasing the heat-treatment time led to considerable decrease on energy barrier heights which is in reverse trend with the flotation experiments.

4) These results clearly suggest that a clean coal product with relatively high combustible recoveries may be produced with an appropriate salt type and its concentration.

Acknowledgments

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