

## Full length article

# Plasma activation on natural mordenite-clinoptilolite zeolite for water vapor adsorption enhancement



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## ABSTRACT

Water vapor is one of the crucial impurities in biogas which have to be removed for optimal performance. Utilization of natural zeolites as water vapor adsorbents is one of the proposed solutions. However, the small specific surface area of natural zeolite needs to be improved to increase the material adsorption capacity, one of the methods being physicochemical treatment. The consequences of the increased specific surface area by physicochemical treatment are the Si/Al ratio and hydrophobicity enhancement which counterbalance the benefits of the increased specific surface area. In this work, plasma activation treatment was applied successfully to increase the water adsorption capacity of natural zeolites after dealumination. The transformations of the chemical and physical properties of the material after plasma treatment are discussed. Our results point that the certain intrinsic properties on the zeolites in terms of Si/Al ratio and specific surface area are prerequisite to benefit from plasma activation. This work offers a new perspective on improving porous silica-based materials water adsorption characteristics which could lead to improved adsorbents in the future.

## 1. Introduction

Biogas is one of the promising renewable energy sources. It can be produced in small or large capacities by processing organic waste. Some studies claim that biogas is the most efficient production of biomass conversion [1–4]. The World Bank announced biogas as a modern fuel for cooking [5]. Biogas contains methane as the fuel gas and various other impurities. These impurities limit biogas utilization beyond heating source for cooking [6–8].

The methane enrichment of biogas is needed to increase energy level utilization, particularly for electricity production. One of the gas impurities which need to be removed is water vapor since it decreases the heating value and accelerates the corrosion of the equipment for electricity generation [8,9]. Various biogas purification technologies have been utilized to reduce the water vapor content in biogas, one of these is based on natural zeolites as a molecular sieve. Also, several studies have reported that natural zeolites have excellent capacity to adsorb water vapor in various other application such as in agricultural product drying [10], diesel/biodiesel dehydration [11], and bioethanol dehydration [12,13]. The drawback of natural zeolites is their small

specific surface area, typically in the range of 14–30 m<sup>2</sup>/g [11,12,14,15].

Increasing natural zeolites specific surface area can substantially improve their adsorption capacity. Physicochemical modification of Gunungkidul natural zeolite has been demonstrated to significantly increase the material surface area [16–18]. However, the treatment led to a decrease in the hydrophilic properties of the zeolite which is in line with the increase in the Si/Al ratio [19–23]. As a consequence, the benefits of the increased surface area are canceled by the increased hydrophobicity and could not positively affect the adsorption of water vapor.

Plasma treatment offers potential pathways for improvement of the wetting properties of natural zeolites. This hypothesis is substantiated by published studies of plasma activation employed on plane surfaces of silicon, silica oxide, and glass, where water contact angle was substantially reduced [24,25]. Other published studies also reported that plasma charging creates a hydrophilic surface which is caused by oxide layer constructions [26,27], porous surface diffusivity [28], and silanol groups bonding [29,30]. A technology for plasma treatment of particulate materials using customized plasma reactor that we reported

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recently provides opportunities to improve the water adsorption properties of zeolite microparticles [31–36].

The goal of this study is to investigate the potential of air plasma treatment to improve the hydrophilicity of natural zeolites, which had undergone physicochemical treatment for increasing their surface area. Ultimately, this work aims to demonstrate that plasma treatment can be a viable technology to produce high surface area, natural zeolite based water adsorbents.

## 2. Materials and methods

### 2.1. Materials

Natural zeolite powder from Gunungkidul, Yogyakarta, Indonesia was obtained from CV Mountain Stone, the local mining supplier company, and was assigned as the A0 zeolite in the text. This natural zeolite represents the mordenite-clinoptilolite structure [37,38]. HCl was supplied in the purity of 37–38% by Merck.

The zeolite powder was prepared with size under 40 mesh (425  $\mu\text{m}$ ). For increasing the material surface area and Si/Al ratio, it was dealuminated by soaking in 1 M and 12 M HCl for 24 h and assigned as A1 and A5 zeolites, respectively. The post-dealuminated zeolite was washed to clean and neutralize the material. Afterward, the zeolite was heated at 400 °C for 3 h. The A0, A1, and A5 zeolites were utilized as the base adsorbent materials and then treated by air plasma for water vapor adsorbent applications.

### 2.2. Plasma activation

The air plasma activation treatment was executed in the cylindrical chamber of the custom-built plasma reactor, with a top U-shaped and a bottom round-shaped electrode. It was powered by plasma generator (13.56 MHz RF) and equipped by agitation platform for continuously moving the powders or particulate materials [33–35,39].

For optimization purposes, plasma activation was conducted on the highest Si/Al ratio natural zeolite at a pressure of 16 Pa, power of 50 W, and treatment time of 20 min. The conditions of treatment of the different material used through this study and their assigned codes are shown in Table 1. All of the samples were stored in the closed vials for two months before characterization of the treated material and water vapor adsorption measurement.

### 2.3. Characterization of the materials after plasma activation

The morphology of the zeolite particles was captured by a Hitachi SU3500 Scanning Electron Microscope (SEM). Si/Al and O/Si ratio of bulk material were determined by elemental composition measurement by Energy Dispersive X-ray spectroscopy (EDX) attached to the SEM. For preparation, the samples were dried in the oven at 105 °C for overnight. Afterward, the sample was splashed in small quantities on carbon tape surface. No metallisation was used in the SEM

**Table 1**

Code of the natural zeolites in the various treatment of plasma activation.

Natural zeolite	Plasma activation power (W)	Activation time (min)	Code
A0	0	0	A0
	50	20	A0520
A1	0	0	A1
	50	20	A1520
A5	0	0	A5
	50	20	A5520
		10	A5510
		5	A5505
	30	20	A5320
	10		A5120

measurements.

Micromeritics ASAP 2420 analyzer was used for determining the specific surface area (BET Model) and porosity (BJH Model). Isotherm nitrogen adsorption-desorption at  $-196\text{ }^{\circ}\text{C}$  was used for this measurement. For preparation, the sample was degassed for 24 h at 120 °C (A0 zeolite) or 350 °C (A1 and A5 zeolites) for removing water and other impurities from the pores [40]. The A0 zeolite was degassed at a lower temperature than others to avoid the structural decomposition of calcite [41–44], which is known to be part of in this natural zeolite structure [34]. A1 and A5 zeolites were degassed at 350 °C since calcinated at 400 °C conducted during earlier treatment have already changed the calcite structure into anorthite [38].

XPS analysis was conducted to investigate the surface composition and typical element bonding of plasma activation treatment. Specs SAGE XPS spectrometer (SPECS GmbH, Germany) was operated on 10 kV and 20 mA of Mg K $\alpha$  radiation source ( $h\nu = 1253.6\text{ eV}$ ). It was equipped the hemispherical analyzer of Phoibos 150 with MCD-9 detector. CasaXPS software was used to fit the survey spectra with an energy range of 0–1000 eV at the resolution of 0.5 eV and the pass energy of 30 eV. The high-resolution spectra of the element were also obtained from the analysis to determine the typical bonding. The C1s neutral carbon peak of 285 eV was used to calibrate the surface charging effect for all the binding energies.

The FTIR spectra were recorded by a Thermo Nicolet Magna 750 FTIR instrument equipped with an MTEC model 300 photo-acoustic detector (GMI, US) and supported the 'Omnic' software. The powder samples were put directly into the aluminium pan as the sample holder, then loaded directly to the instrument for analysis. The measurement was operated using the mirror velocity of 0.1581 cm/s which is appropriate with a sampling depth of 22.4  $\mu\text{m}$ . The measurement was carried out at a resolution of 8  $\text{cm}^{-1}$  with the default setting of 256 scans on the range of 4000–400  $\text{cm}^{-1}$ .

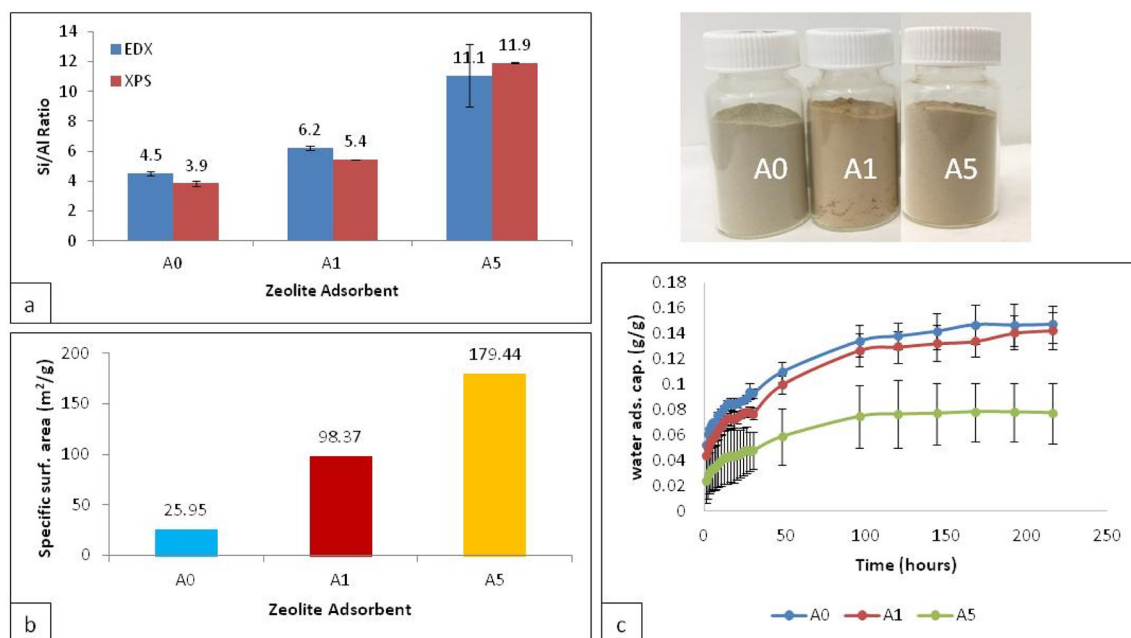
### 2.4. Water adsorption capacity measurements

After two months storage, the activated plasma zeolite was utilized to determine water vapor adsorption capacity. For the preparation, the materials were dried in an oven at 105 °C overnight. One gram of zeolite was placed in an open container and then inserted in a desiccator containing water and stored at room temperature. All experiments were carried out in triplicates. The amount of water vapor adsorbed by zeolite was measured by weighing the zeolite at certain time intervals. The weighing was conducted until the zeolite weight is stable. Furthermore, the normalized specific surface area of water vapor adsorption capacity of the various natural zeolite was also calculated to determine the water adsorption affinity.

## 3. Results and discussions

### 3.1. Characterization and water vapor adsorption capacity of physiochemically modified natural zeolites

Three types of natural zeolites were utilized in this experiment assigned as A0, A1, and A5 zeolites. The material was in the form of a powder of identical particles size of under 425  $\mu\text{m}$ , shown in the images in the top right-hand side of Fig. 1. The Si/Al ratios (Fig. 1(a)) in A0, A1, and A5 zeolites were 4.5, 6.2, and 11.1 determined by EDX measurement, while XPS resulted in 3.9, 5.4, and 11.9, respectively. As expected, the Si/Al ratio increased with the higher acid concentration used in the preparation process [38]. The Si/Al transformation of the zeolites also resulted in changes in their surface area. The specific surface areas of A0, A1, and A5 zeolites were 25.95, 98.37, and 179.44  $\text{m}^2/\text{g}$ , respectively (Fig. 1(b)). This was an increase of nearly four times for A1 zeolite and seven times for A5 zeolite relative to A0 zeolite. However, the increased surface area did not result in greater water vapor adsorption capacity (Fig. 1(c)). The water adsorption



**Fig. 1.** Properties of zeolites before and after dealumination: (a) Si/Al ratio determined from EDX and XPS measurements; (b) Specific surface area; (c) water adsorption capacity.

capacity of A0, A1, and A5 zeolites were 0.148, 0.143, and 0.078 gH<sub>2</sub>O/g, respectively. Strikingly, the A5 zeolite had the highest surface area but the lowest water vapor adsorption capacity. This is consistent with published studies which report that increased Si/Al ratio adversely affects the hydrophilicity of the material and thus its water adsorption properties [19–23].

### 3.2. Plasma activation

Plasma activation was carried out in a custom build system equipped with a platform for continuous agitation of particles [33–35,39]. The condition for air plasma treatment was plasma power of 50 W, the pressure of 16 Pa and treatment time of 20 min. The activated zeolites were stored in closed vials to avoid air contamination before being used as water vapor adsorbent. During this period of storage, the surface aging processes are expected to have occurred since the plasma activated surface very reactive particularly in the initial period after activation. Published studies have reported periods of 10–20 days post plasma treatment required for the surface to reach stable reactivity and wetting characteristics. [45,46] Therefore, we expect that storage time of two months that was selected for this study was sufficient to acquire balanced surface characteristics.

The XPS survey spectra of the A5 zeolite before and after plasma treatment (assigned as A5520) are shown in Fig. 2(a) and (b). The spectra show the presence of oxygen (O 1s), silicon (Si 2p) and aluminium (Al 2p) at binding energies of 532 eV, 99 eV, and 73 eV, respectively. Quantification of the oxygen content of all zeolite samples before and after air plasma treatment is shown in Fig. 2(c). Overall the plasma process increased the oxygen content in all samples. The most significant increase was observed in A1 and A5 zeolites of 1.4% and 3.3%, while the increase in oxygen content in the original A0 zeolite was insignificant and within the measurement error. The increased oxygen concentration suggests that the oxygen from the air that was present during plasma treatment has triggered oxidation reactions on the surface of the zeolites, a phenomenon that has also been observed by others [24].

Table 2 presents the O/Si ratio in all three zeolites before and after plasma treatment determined from XPS and EDX measurements. XPS is sensitive to the outermost 10 nm of the material surface while EDX

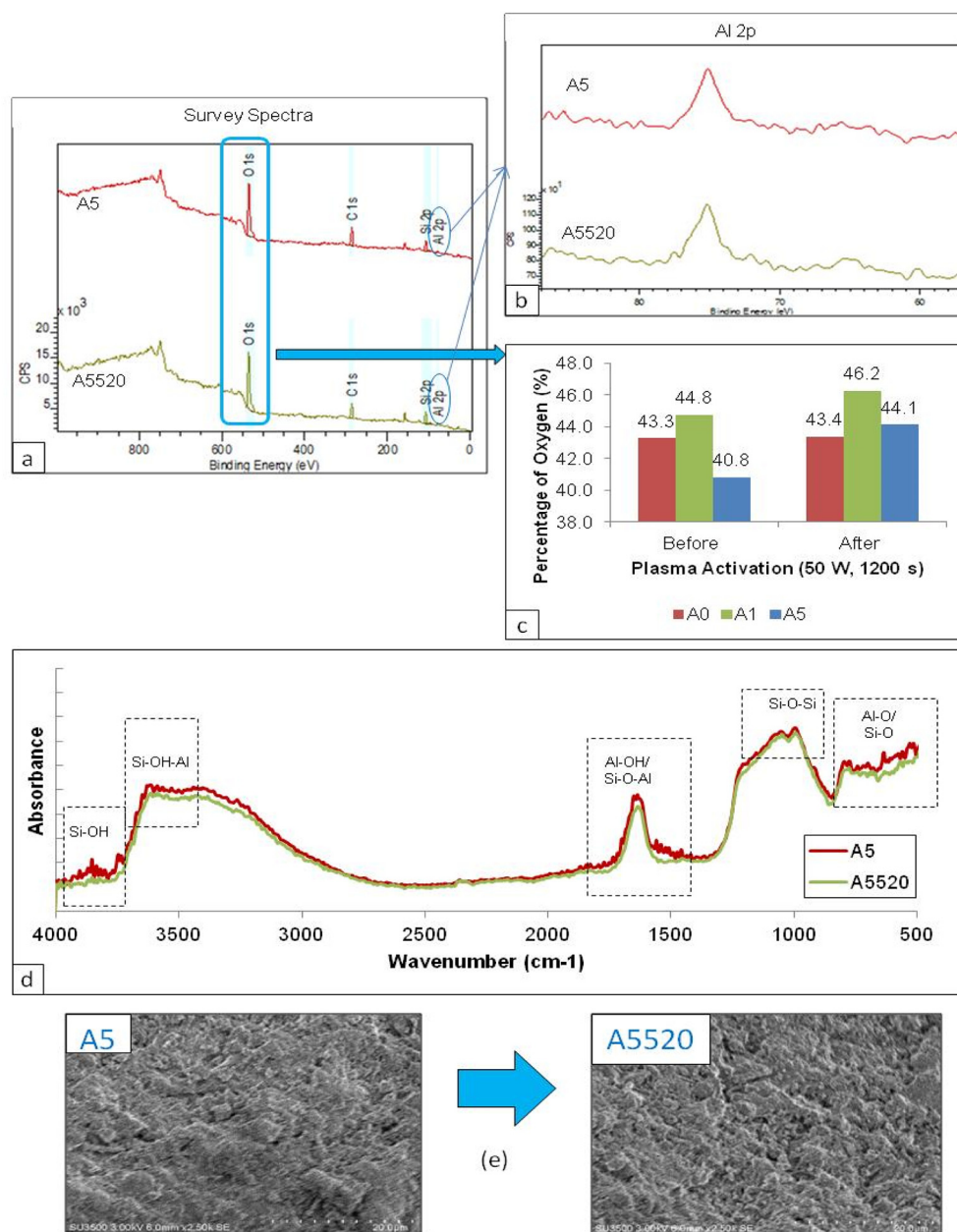
allows probing the entire structure of the zeolites. In the case of A1 and A5 zeolites, which had undergone dealumination, the O/Si ratio increased after plasma treatment. Interestingly, there was no change in the O/Si ratio in the A0 zeolite when measured by XPS and even smaller decrease according to EDX. The changes in surface area after plasma treatment are also shown in Table 2. In the case of A0 zeolite, the surface area slightly increased which could be explained by the removal of impurities from the original materials. In contrast, there was a decrease in surface area in the cases of A1 and A5 zeolites which could be attributed to the build-up of an oxide layer of SiO<sub>x</sub> in the pores of the zeolites when the Si/Al ratio is high. These results are consistent with published studies on different silica surfaces supporting the build-up of a silica layer by plasma charging [26,27].

Further studies were conducted by FTIR. The spectra of A5 zeolite before and after air plasma treatment are shown in Fig. 2(d). The FTIR spectra of both zeolites are almost similar as shown in published study of treated plasma zeolite [47]; but there are some vibration peak at oxygen bonds. The spectra show peaks associated with Al–O/Si–O (500–800 cm<sup>−1</sup>), Si–O–Si (1000 cm<sup>−1</sup>), Al–OH/Si–O–Al (1500–1800 cm<sup>−1</sup>), Si–OH–Al (3500–3600 cm<sup>−1</sup>), and Si–OH (3700–3900 cm<sup>−1</sup>) bonds. It is interesting to note the disappearance some peak of the Si–OH bond (3700–3900 cm<sup>−1</sup>) and Al–OH/Si–O–Al bond (1500–1800 cm<sup>−1</sup>) after plasma activation. This may create dangling bonds important for water vapor adsorption since the structure will tend to attempt for regenerating [30,48,49].

Finally, changes in the morphology of the zeolites were studied by SEM (Fig. 2(e)). The images of A5 zeolite before and after air plasma treatment do not show any significant morphological changes on the surface of the material. While the measurement of the specific surface area by BET showed a slight decrease in this parameter, the changes do not appear to be significant enough to be detected by SEM.

### 3.3. The water vapor adsorption capacity of natural zeolite after plasma activation at 50 W and 20 min

Plasma activation had only a small impact on the water vapor adsorption capacity of A0 zeolite as shown in Fig. 3(a). The adsorption capacity of A0 and A0520 zeolites were 0.148 and 0.142 g H<sub>2</sub>O/g, respectively. The low Si/Al and O/Si ratios in this material, combined



**Fig. 2.** (a) XPS Survey spectra of A5 zeolite before and after plasma treatment; (b) Al 2p region zoom; (c) Oxygen percentage of A0, A1 and A5 zeolites as determined by XPS before and after plasma treatment; (d) FTIR spectra of A5 zeolite and; (e) SEM images of A5 zeolite before and after plasma treatment.

**Table 2**

O/Si ratio and specific surface area of the natural zeolites before and after plasma activation.

Code	Plasma activation power (W)	Activation time (min)	O/Si		Specific surface area (m <sup>2</sup> /g)
			XPS	EDX	
A0	0	0	1.6	1.5	25.95
A0520	50	20	1.6	1.4	29.81
A1	0	0	1.6	1.3	98.37
A1520	50	20	1.7	1.5	48.40
A5	0	0	1.6	1.2	179.44
A5520	50	20	1.7	1.3	153.15

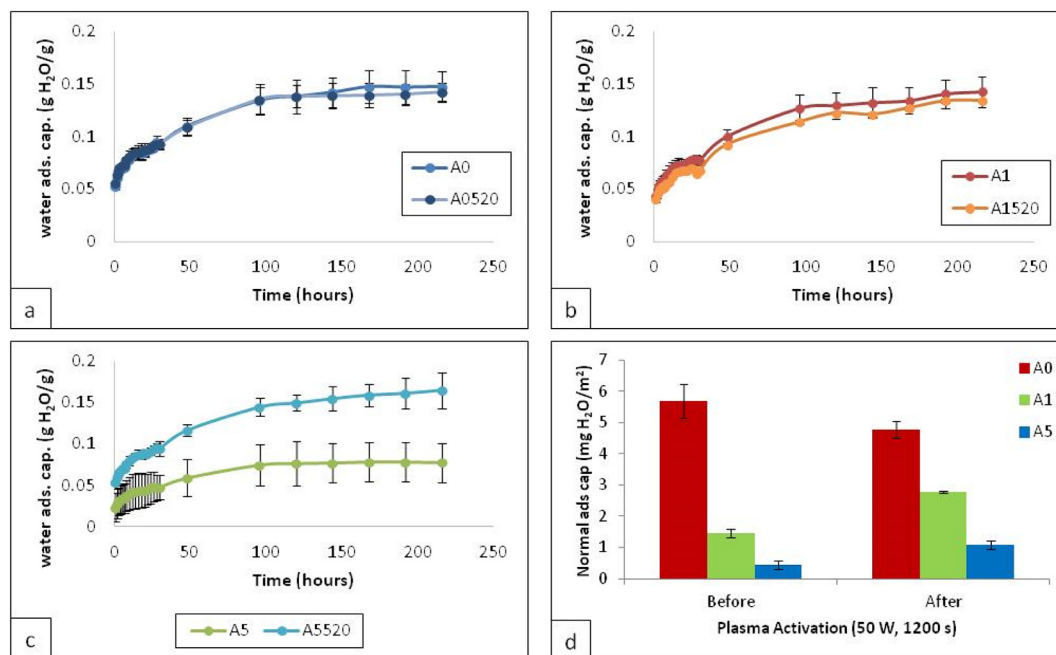
with its low surface area, do not appear to favor significant water vapor adsorption even after plasma treatment.

Air plasma treatment adversely affected the A1 zeolite (Fig. 3(b)). The adsorption capacity of A1 and A1520 zeolites were 0.143 and

0.134 g H<sub>2</sub>O/g, respectively. Although the O/Si ratio increased for A1 zeolite treatment, the surface area of this material significantly decreased. The later counterbalanced the increased oxidation of the A1 zeolite caused by plasma treatment. However, the A5 zeolite showed the opposite trend (Fig. 3(c)). The water adsorption capacity of A5 zeolite increased from 0.078 to 0.165 g H<sub>2</sub>O/g. This is a significant increase that exceeded the water adsorption capacity of the other two zeolites being considered in this study. This could be attributed to the high Si content of this material which is oxidized after air plasma treatment. Our finding is supported by published studies showing that plasma activation improves Si surface reactivity and hydrophilicity [30,48,50].

Further, in order to determine the affinity to water vapor, we looked at the normalized specific surface area as a function of the water vapor adsorption capacity of the material. Two different trends are shown in Fig. 3(d). The normalized water vapor adsorption capacity was reduced for the A0 zeolite after plasma activation, while the affinities for water





**Fig. 3.** Water adsorption capacity before and after plasma activation for (a) A0 zeolite; (b) A1 zeolite; (c) A5 zeolite; and (d) water adsorption capacity normalized to the zeolites specific surface area.

vapor of A1 and A5 zeolites showed the vice versa. These trends can be correlated with the increased oxygen content and O/Si ratios for A1 and A5 zeolites, as reported in Table 2.

### 3.4. Effect of plasma power and time of treatment on the water adsorption of A5 zeolites

Since A5 zeolite has shown to be most favorably affected by the air plasma treatment process, we carried out further studies to determine the influence of plasma power and time of treatment on the water vapor adsorption of this material. The studied durations of treatment were 5 min (A5505), 10 min (A5510) and 20 min (A5520). All durations of material activation increase the water vapor adsorption significantly than untreated material, but there is no significant effect for each different treatment time. The maximum adsorption capacity of 0.167 gH<sub>2</sub>O/g was reached even at the shortest time (Fig. 4(a)). The effect of plasma power used for treatment was also insignificant. Fig. 4(b) shows that plasma powers of 10, 30, 50 W led to materials with water adsorption capacities of 0.164, 0.160, 0.165 gH<sub>2</sub>O/g respectively. The only significant effect of plasma power and time was on the specific surface area which increased with plasma power, as shown in Table 3. However, this effect did not benefit the water adsorption capacity since the affinity to water vapor remained unchanged when different plasma

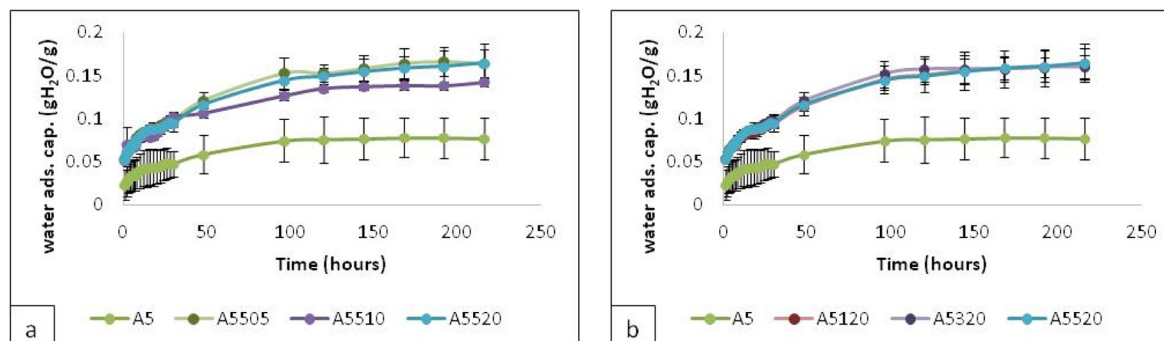
**Table 3**

O/Si ratio, specific surface area, and adsorption affinity of the A5 zeolites after treatment using different plasma power and duration.

Code	Plasma activation power (W)	Activation time (min)	O/Si (XPS)	Specific surface area (m <sup>2</sup> /g)	Adsorption affinity (mgH <sub>2</sub> O/m <sup>2</sup> )
A5	0	0	1.6	179.44	0.43 ± 0.13
A5505	50	5	1.7	148.48	1.11 ± 0.11
A5120	10	20	1.7	146.87	1.12 ± 0.12
A5520	50	20	1.7	153.15	1.08 ± 0.14

powers were applied.

The results from the last section indicate the plasma power and time of treatment in the range used in this study had the almost negligible effect of the material water adsorption capacity. However, these findings may have important process design consequences. The lowest power used and the shortest time of treatment was sufficient to obtain optimal outcomes in terms of water adsorption which can be converted into economic and environmental benefits due to time, costs and electrical energy savings.



**Fig. 4.** Water adsorption capacity of A5 zeolite as a function of the conditions of plasma activation used: (a) duration of plasma activation and (b) plasma power.

#### 4. Conclusions

In this work, plasma activation was implemented to improve the water vapor capacity of natural zeolites. The original material (A0 zeolite) was treated with HCl to investigate the influence of air plasma treatment on zeolites with different specific surface areas and Si/Al ratios. Plasma activation resulted in notable oxidation of the A1 and A5 zeolites which had high Si content. However, the treatment resulted in a significant reduction of the specific surface area of A1 zeolite. Plasma treatment did not affect the water adsorption capacity of A0 and A1 zeolites. This can be explained by the low O/Si ratio in the original A0 zeolite and the reduced specific surface area of A1 zeolite after plasma treatment. However, the activation by plasma had a significant positive effect on A5 zeolite, where a 2.5-time increase in water absorption capacity was observed. Overall, we showed that plasma activation had caused significant transformation of the chemical and physical properties of zeolites. However, careful consideration of the intrinsic properties of the starting material is required to achieve desired benefits in terms of water adsorption capacity. This work offers a new perspective on improving porous silica-based materials water adsorption characteristics which could lead to adsorbents with superior properties in the future. From application point of view, detailed studies concerned with adsorbents aging, appropriate storage conditions, and shelf life of material need to be carried out in next steps.

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