Hindawi
International Journal of Chemical Engineering
Volume 2019, Article ID 6036479, 11 pages
https://doi.org/10.1155/2019/6036479

Research Article

Structured Polyvinyl Alcohol/Zeolite/Carbon Composites Prepared Using Supercritical Fluid Extraction Techniques as Adsorbent for Bioethanol Dehydration

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Received 13 August 2018; Revised 5 December 2018; Accepted 16 December 2018; Published 16 January 2019

Academic Editor: Sébastien Déon

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Introduction. Adsorption is a purification process with a more efficient energy level than others. Adsorption performance is strongly influenced by the ability of the adsorbent to be used; therefore, the modification of the adsorbent becomes a very important key for the purification process that occurs. *Methods*. In this study, the preparation of composite adsorbents was carried out by combining polyvinyl alcohol (PVA), zeolite (Zeo), and activated carbon (AC) as precursors. The crosslinking process was fulfilled by adding glutaraldehyde to the precursor mixtures followed by a supercritical fluid CO_2 extraction (SFE) technique to create conditions for the crosslinking process. The composites were analyzed using Braunner–Emmet–Teller (BET) surface area analysis, Fourier-transform infrared (FTIR), differential scanning calorimetry (DSC), and scanning electron microscopy with energy dispersive X-ray (SEM/EDX-mapping), while individual and composite adsorbents were evaluated for their ability in bioethanol dehydration at various initial concentrations of ethanol and temperature. *Results*. The BET characterization shows that composite preparation under supercritical CO_2 conditions provides reasonable surface areas, which are proportional to the content of activated carbon. The crosslinking process has been described by FTIR data interpretation, showing that PVA and glutaraldehyde were properly distributed on Zeo and AC precursors. The DSC characterization results give information that PVA successfully forms hydrophilic composites within Zeo and AC. The SEM micrograph analysis shows the formation of pores on the surface and cross section in structured adsorbents. The experimental adsorption shows that an increasing amount of AC in the composites increases the capacity of water adsorption (i.e., 0.80 gram of water/gram of adsorbent for PVA/Zeo/AC = 1 : 1 : 1 at 22°C). However, the effect is not significant when the ratio of AC is less than 0.5. As expected, the lower temperature increases the adsorption capacity. Further, by using approximately 4.5 gram adsorbents composite in 30 ml of water-ethanol mixtures, high concentration of bioethanol (>99%) can be achieved at various temperatures from 22°C to 40°C and bioethanol initial concentration from 88% to 96%. *Conclusion*. The SFE technique provides distinguished adsorbents composite properties. Further, the new composites provide about four times better adsorption capacity than that showed in the individual adsorbents test. The addition of AC influences on increasing the capacity and adsorption kinetics value.

1. Introduction

Environmental sustainability factors have become the main reason for the use of suitable alternative fuel types [1]. Fossil fuels have continued to decline, causing subsequent price increases, particularly in the developing countries. On the other hand, alternative renewable fuels provide eco-friendly, inexpensive, and pollution-free options that increase energy security [2]. In this case, bioethanol production is becoming more attractive for the scientific community [3]. Currently,

bioethanol production has increased by 4,959 kilotons in 2007, to 97,280 kilotons in 2017, which significantly contributes to the wholesale of biofuels in the world with a value of approximately 58 billion dollars per year [4, 5].

Bioethanol can be produced from a variety of raw materials. Bioethanol from lignocellulosic can be considered second-generation biofuel production technology, which has the advantage of not competing with food needs [6]. The production of second-generation bioethanol generally consists of the following steps: pretreatment, hydrolysis/saccharification, fermentation, and distillation to purify the bioethanol to meet a fuel grade [7]. Bioethanol fuel grade follows the standards such as ASTM D4806 to fulfill the maximum water content contained in products, i.e., 1% v/v [8]. Unfortunately, the purification process of bioethanol cannot be achieved using ordinary distillation, considering the azeotropic conditions (95.63% vol.; 78.15°C; 1.013 bar) [9] occurring in the water-ethanol system [10]. Researchers have reviewed several techniques for breaking down azeotropes in water-ethanol systems, such as pervaporation, permeation, adsorption, extraction, pressure-swing distillation, extractive distillation, azeotropic distillation, adsorption-distillation complexes, and pervaporation distillation complexes [11, 12]. Energy consumption in the purification process is a major concern considering the large energy utilization; moreover, there is an ongoing effort to achieve energy and economic efficiency [13]. According to Wang et al., the energy consumption of the adsorption process is 32 KJ/m^3 while the azeotropic distillation is 88 KJ/m^3; therefore, the adsorption process is a technique which provides higher energy efficiency compared to others [14–16].

Previous researchers have investigated the types of adsorbents related to the dehydration process of bioethanol, which includes zeolitic-based, carbon-based, polymer-based, bio-based, and composite-based. Several studies on the use of zeolitic adsorbent compounds have been published. Sowerby and Crittenden investigated the effect of type A zeolites, such as 3A, 4A, 5A, and 10A, which are used for bioethanol purification adsorption [17]. Meanwhile, Wang et al. compared type 3A zeolites with bio-based adsorbents [18]. In addition, some researchers conducted an investigation using NaZSM-5 type zeolites [19], silicalite [20], natural clinoptilolite [21], and several types of Linde type A (LTA), faujasite (FAU), and mordenite (MOR) [14]. Other studies explored the process of dehydration of bioethanol using carbon-based adsorbents [22–26]. In addition, the application of polymeric and composite adsorbents has been accomplished previously with polymeric resin Sepabead 207® [27], poly([1-vinyl-3-hexylimidazolium] [bis (trifluoromethyl sulfonyl) imide]), a polymeric ionic liquid [28], polyvinyl alcohol and zeolite 3A mixed matrix composite [29], and a carbon-natural zeolite composite [30] as an adsorbent for bioethanol purification regarding the fuel grade.

PVA is selected in the dehydration process because of its biodegradability, water solubility, and its bulk hydroxyl group on the surface, which can form a chemical bond between the PVA and water molecules [31]. PVA is a hydrophilic semicrystalline synthetic polymer [32]; therefore, in the appropriate conditions, the PVA can form composites with other materials, especially using CO_2 at a supercritical condition [12]. The molecular structure of certain liquids, especially CO_2 in supercritical conditions ($SCCO_2$), plays an essential role in the processing of composite polymers. It is important to realize that the specific interactions found between CO_2 and polymer also explains the high solubility of CO_2 in many of the glass polymers used in this composite preparation. It can be explored that the increased concentration of active polymer groups results in an appropriate increase in CO_2 solubility relative to hydroxy groups in PVA, creating specific interactions with functional groups in zeolite and activated carbon structures. In this case, PVA utilizes $SCCO_2$ properties (high diffusivity, low surface tension, and solvent recovery ease) to prepare the polymer composite materials. In other words, $SCCO_2$ dissolved in the composite preparation process significantly affects the mass transport properties of zeolites and activated carbon in the polymer matrix [33].

Zeolite 3A type is a rigid aluminosilicate compound which is highly selective to water, considering its pore size of 3 Å, while the molecular size of water is 2.8 Å. It has stable mechanical properties, regular micropore distribution, and a high adsorption capacity; however, it has a moderate internal surface and pore volume [34].

Activated carbon has microcrystals arranged randomly as a high surface area and a high pore volume; however, it has an unequal pore size distribution and low water selectivity under ambient conditions near azeotropic conditions. Hence, external improvement with other materials is necessary for the water adsorbent criteria [26, 35].

Considering the advantages and disadvantages of the three material properties, the preparation of excellent performance adsorbents for bioethanol dehydration will be conducted in this study. Observing and conducting adsorption studies on the three types of individual adsorbents has been performed in previous studies [10, 13]. The results will be used as the basis for choosing the precursor, the variation of the ratio of each precursor, and the adsorption performance using the composite adsorbent. In other words, the purpose of this study is to develop PVA/Zeo/AC as an adsorbent composite material that provides excellent physiochemical properties for the bioethanol dehydration process performance.

2. Materials and Methods

2.1. Materials. Bioethanol was obtained from the bioethanol's pilot plant, RCChem-LIPI. Meanwhile, the ethanol technical grade (±95%) was obtained from a local market and repurified using simple distillation to ensure a constant concentration and measurement using the densitometer Kyoto KEM density/specific gravity meter DA-640. Aquadest was obtained by a local water reverse osmosis process using NESCA YDO 6800. AC was purchased from Ajax Chemicals, in the Netherlands. Natural Zeo was obtained from research units from the Natural Product Technology (BPTBA)-LIPI, Yogyakarta, Indonesia. The

obtained natural Zeo was then characterized using X-ray diffraction (XRD), where data processing was performed using Match software. The characterization results revealed that the natural Zeo used was clinoptilolite-k monoclinic type ($Al_{3.4}8Ba_{0.16}Ca_{0.22}H_{2.58}K_{1.06}Na_{0.42}O_{38.58}Si_{14.52}$) [36]. Meanwhile, glutaraldehyde as a crosslinker was purchased from the Emerck Milipore Corp. Glutaraldehyde was used without pretreatment.

2.2. Methods

2.2.1. Material Preparation. The redistilled ethanol was diluted with aquadest to provide several initial concentrations (C_0) 96%, 94%, 92%, 90%, and 88% by volume, which were then analyzed using Kyoto KEM density/specific gravity meter DA-640. The substances were stored in dark glass bottles for the adsorption process. Adsorbent materials such as PVA, Zeo, and AC were pretreated; the particle size was reduced by using ball mill into 40 meshes, which was sieved by stainless steel mesh sieving vibrator Laboratory Test Sieve Retsch ASTM E11. The water content in PVA and AC was removed by heating in the oven Thermo Scientific Precision 652 at 105°C until the weight was constant, and the water content was measured using Ohaus. The PVA was then stored in the desiccator. AC was heated gradually using a Thermolyne 46200 high-temperature furnace employing a heat rate at 10°C/min to raise 150°C and detained for 2 hours to remove its water content. Afterward, it was cooled down simultaneously to room temperature in the desiccator.

A natural Zeo was washed using redistilled water, and it was activated using 1 M hydrochloric acid (HCl). In this case, 100 g Zeo was put into a beaker glass while 1000 mL of HCl 1 M was put dropwise approximately 2 ml/min; then, the mixture was stirred continuously for 24 hours. The Zeo was then washed using distilled water until pH 7 was achieved, and then filtered using the Whatman filter paper. The Zeo was further activated by heating the furnace to reach a temperature of 150°C with a rate of 10°C/min and detained for 2 hours; the temperature was then increased to 800°C and detained for 4 hours. Subsequently, the cooling process was carried out until the temperature reached 100°C with a rate of 10°C/min; then, AC was cooled down to room temperature in the desiccator.

2.2.2. Composites Preparation. 10% of the PVA solution in water was prepared by dissolving a certain amount of PVA in boiled redistilled water in a 1 L beaker glass and stirred using a mixing apparatus. Meanwhile, the Zeo and AC powder were mixed using a laboratory scale ball mill. The ratio of Zeo to AC was varied at 1 : 1, 1 : 0.75, 1 : 0.5, 1 : 0.25, and 1 : 0. Afterward, the PVA solution was mixed with Zeo and AC so that the ratio of PVA to Zeo was 1 : 1 for each composite adsorbent prepared. The mixture was then stirred. As much as 4% wt. (of the total mixture) of glutaraldehyde as a crosslinker was then added into the mixture. This mixing process was continuously carried out at 80°C for 2 hours.

After thoroughly mixed, the mixture was formed into granules with a diameter of approximately 3-4 mm using a granulator apparatus. The granules were incorporated into the stainless steel basket contained in the supercritical fluid extraction (SFE) reactor. The composite granular adsorbent production was performed at 2,500 psi with the temperature of 60°C for 4 hours. The dried sample was stored in the desiccator.

2.2.3. Material Characterizations. The physical properties of the adsorbent material, such as surface area, pore volume, pore size, and nanoparticle size, were characterized using BET Micromeritics TriStar II. In order to examine the availability of crosslinking in the produced composites, the functional group characterization was performed using FTIR Shimadzu IR Prestige-21. FTIR spectra were obtained using transmittance mode in the range of wavenumber from 4,000 to 550 cm^{-1}. The FTIR spectra were normalized, and major vibration bands were associated with the chemical group. Meanwhile, the thermal characterization of adsorbents was analyzed using the DSC Linseis Simultaneously Thermal Analysis Platinum Series STA PT 1600 with the following procedure: the composite sample was prepared into small pieces and it was weighed as 3 mg and fed into the crucible. The analysis was carried out exothermically from 30°C to 250°C with a heating rate of 10°C/min, and N_2 was used as a purge gas at 10 mL/min rate. The morphology and cross-section analysis of the adsorbent composite were characterized using SEM Hitachi. The sample was coated using Pt for 55 seconds with 30 mA current. Scanning electron microscopy with energy dispersive X-ray (SEM/EDX-mapping) analysis was determined on the 20 kV accelerated voltage. In addition, the mapping of the major elements of each constituent of the adsorbent was determined to characterize the position of the layer and the homogeneity of the formed composite. The hydroxyl and iodine value procedure has been described in the previous paper [10, 13].

2.2.4. Adsorption Test. The adsorption test for individual adsorbents has been described in the previous paper [10, 13] for temperatures of 20, 30, and 40°C. The adsorption process using composite adsorbents involves the ratio of PVA : zeolite is 1 : 1, where the value varies the AC: 1, 0.75, 0.5, 0.25, and 0; accordingly, five variations of composite PVA/Zeo/AC were obtained. The ethanol solution was prepared in various initial concentrations (88%, 90%, 92%, 94%, and 96%). The granular composite adsorbents used are 15% (approximately, 4.5 gram) in 30 mL of the water-ethanol mixture, which was put in the 100 mL laboratory glass. 10 samples were prepared to be taken for measurement at a different time (2 minutes difference for each sample). All samples were inserted into the New Brunswick shaker incubator for an adsorption process. The samples were taken and filtered using a Minisart syringe filter Sartorius Stedim; and then, the ethanol concentration of adsorption was measured using Kyoto KEM density/specific gravity meter DA-640. The same process was undertaken for each

temperature varied from 20, 30, and 40°C, the ethanol solution initial concentration, and the composite adsorbent variations. Thorough evaluation on experimental uncertainties following this method reveals that the level of uncertainties of the experimental results will be about 5%.

The calculation of adsorption capacity (q_e) was carried out based on the experimental results in accordance with mass balance, as typically the adsorption process reaches the equilibrium state. Calculation for adsorption capacity has been explained in the previous paper [10].

3. Results and Discussion

3.1. Adsorbents Characterization. Table 1 presents the characterization results for each adsorbent, which will be used as the precursor for the adsorbent composite preparation. AC as an individual adsorbent has a higher surface area and pore volume compared to PVA and Zeo. PVA has a lower surface area and pore volume compared to zeolite and activated carbon, but PVA has a higher hydroxy number compared to others. The iodine value of the AC is almost double compared to other individual adsorbents. These values indicate the ability to adsorb an adsorbate. In most cases, the higher surface area results in the higher value of iodine number.

Characterizations of the produced composites show that the less AC in the composites, in general, reduces the surface area and the pore volume. Meanwhile, the pore sizes and the iodine numbers do not change significantly to the variation of composition. The hydroxy number is higher when the composition of PVA is higher. However, the numbers are decreasing significantly compared to the original number of individual PVA. In this case, the PVA used in adsorbent composites acts more as a binder of Zeo and AC than other functions, so that the hydroxyl group in the original PVA is used mostly to form the composites.

The preparation process of the composite adsorbent was undertaken by employing the crosslink mechanism, utilizing the glutaraldehyde compound as a crosslinker. In addition, conditions in supercritical fluids also play an essential role in the composite preparation and drying process. The crosslinking process can be represented by the results of the analysis using FTIR, as shown in Figure 1. In the FTIR spectrum of PVA, all significant peaks associated with the hydroxyl and acetate groups were observed. Compared to pure PVA in the composites spectra, there is a strong peak formation in ca. 1670 cm^{-1}. This shows a strong interaction between the hydroxyl groups in PVA and the aldehyde groups found in glutaraldehyde to form acetal during crosslinked network formation [36–38].

The peaks of the Zeo and the AC presence in the composite have been identified. Two firm peaks occur at the wavelengths of 1054 cm^{-1} resulting from asymmetric stretch and bend of the Si-O or Al-O bonds, respectively, within the Zeo structure [38]. The peak occurring at 580 cm^{-1} indicates the presence of an interaction between PVA and Zeo. The intensity of this peak is increased by the composition of PVA and Zeo. The presence of carbon is identified in the two strong peaks at 1590 cm^{-1} and 1300 cm^{-1} representing the AC absorption band. This peak is associated with the asymmetrical C-C stretching mode or C-O stretching from a portion of the chain, in which intramolecular hydrogen bonds are formed between two adjacent OH groups [30, 39]. As indicated in Figure 1, the O-H stretch vibration peak (ν = 3330–3350 cm^{-1}) is relatively increased when compared with pure PVA. This indicates the formation of cross linking between PVA, GA, AC, and Zeo to create a solid composite through the hydrogen bonds mechanism [37, 40]. This FTIR characterization also confirms the results of hydroxy number analysis, where the numbers in all composites were significantly decreased compared to that of the original PVA.

Thermal characterization using the DSC of PVA, and one of the composites, is presented in Table 2. As depicted in the table, the value of temperature glass (T_g) does not change between PVA and the composite while the melting temperature (T_m) of the PVA is lower than that of the composite (232.7°C compared to 265.4°C). The same temperature glass between the two substances indicates that the crystallinity of both substances is unchanged. The increasing of T_m in the composite is due to the presence of hydrogen bonds [41].

The SEM image of the composite sample is presented in Figure 2. The figures show that many pore cavities have been created. The mapping figures indicate that PVA can be distributed among Zeo and AC particles while a thin layer of PVA is located on the top layer. The existence of pore cavities indicates that the formation of pores through supercritical conditions works optimally. The formation of these pores has a significant effect on the adsorption process by providing an entrance to the pore cavity.

3.2. Adsorption Analysis. The adsorption capacity equilibrium for each experiment is presented in Table 3 and Figure 3. The q_e calculations were carried out for each variation of composite adsorbents at various initial concentrations of ethanol and other temperatures. As appeared in Figure 3, the increase in water concentration, the q_e value, will increase. This is related to mass transfer, with the initial concentrations of water leading to the greater driving mass transfer force, which results in increasing q_e values. The experimental data fit quite well within 5% deviation with the Langmuir model.

At the same temperature, the decreasing of AC composition in the composite results in the decreasing capacity of adsorption. This result can be correlated with the physical-chemical properties of each adsorbent, where the increasing AC content in the adsorbents will increase their surface area and pore volume, which, in turn, will result in increasing q_e values. Further, as expected, the increasing adsorption temperature will decrease the q_e value, as shown in Figure 4. This shows that the adsorption follows the exothermic process. In our previous studies for the same solution system on individual adsorbent, the activated carbon has the highest adsorption capacity compared to PVA and zeolite, and the maximum adsorption capacity achieved was 0.2 g of water/g adsorbent [10]. In this study, at a temperature of 22°C, PVA/

Table 1: Physicochemical properties for individual and composite adsorbents.

Characterization	Adsorbents							
	PVA	Zeolite (Zeo)	Activated carbon (AC)	PVA/Zeo/AC 1 : 1 : 1	PVA/Zeo/AC 1 : 1 : 0.75	PVA/Zeo/AC 1 : 1 : 0.5	PVA/Zeo/AC 1 : 1 : 0.25	PVA/Zeo/AC 1 : 1 : 0
Surface area (m^2/g)	1.49	18.64	454.72	379.42	177.08	154.93	119.79	72.15
Pore volume (cm^3/g)	0.000434	0.019092	0.14	0.0841	0.071	0.0576	0.0621	0.0498
Pore size (nm)	2.0802	2.0903	2.0521	2.0521	1.8643	2.0206	1.9215	3.4433
Hydroxy number (mg KOH/g sample)	1,220.85	162.55	255.36	18.11	20.75	22.35	23.75	23.96
Iodine number (mg Iod/g sample)	1,281.17	1,281.45	2,209.67	1,331.16	1,298.49	1,296.51	1,286.36	1,232.98

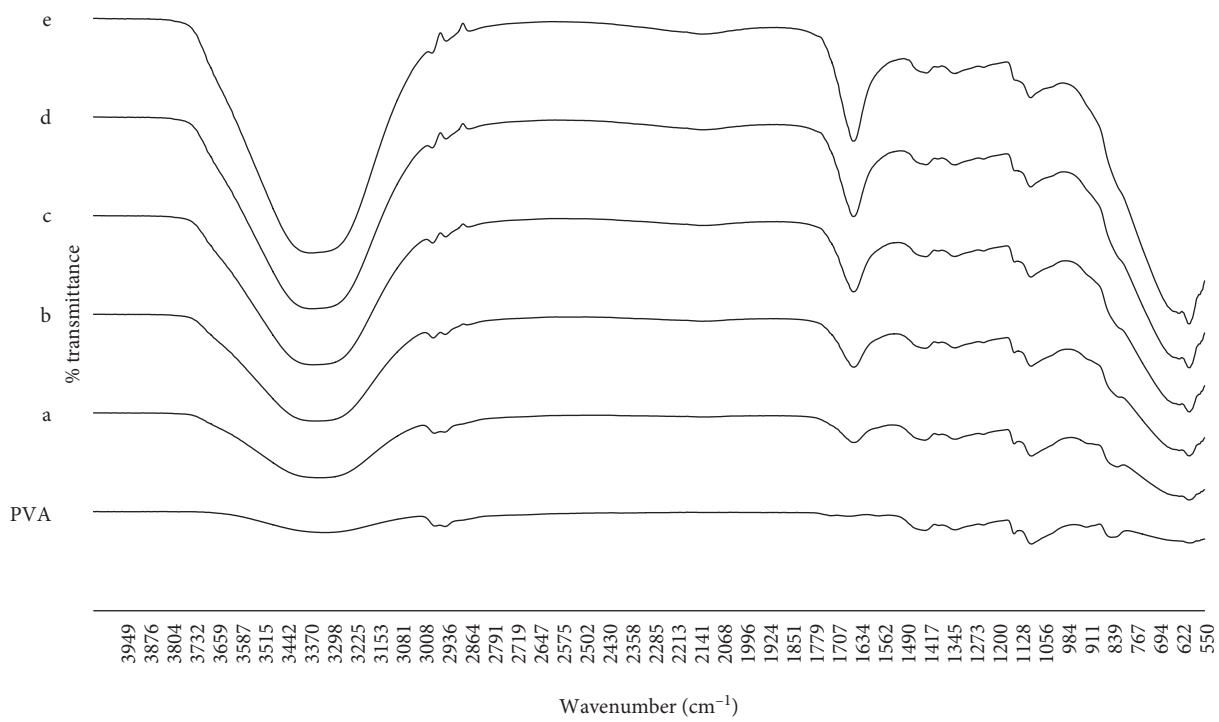


Figure 1: FTIR spectra of PVA and composite: a (PVA/Zeo/AC 1 : 1 : 1); b (PVA/Zeo/AC 1 : 1 : 0.75); c (PVA/Zeo/AC 1 : 1 : 0.5); d (PVA/Zeo/AC 1 : 1 : 0.25); e (PVA/Zeo/AC 1 : 1 : 0).

Table 2: Thermal characteristics of PVA and several PVA/Zeo/AC composites.

Samples	Temperature (°C)	
	T_g	T_m
PVA	84.2 ± 0.06	232.75 ± 2.79
PVA/Zeo/AC 1 : 1 : 1	84.15 ± 0.06	265.37 ± 3.19

T_g, glass transition; T_m, melt peak.

Zeo/AC 1 : 1 : 1 composite gives a maximum value of q_e as much as 0.79 g of water/g adsorbent. Therefore, in the process of ethanol dehydration using composite adsorbents, an increase of adsorption capacity by four times has been achieved.

Figure 5 shows the water dehydration kinetics for various adsorbents at the same temperature and initial water concentration. The composition of PVA/Zeo/AC 1 : 1 : 1 produces faster adsorption rates than other compositions at each initial concentration and the same temperature. Ethanol concentration of 99% can be reached in less than 10 minutes for this composite while the other composites with less AC need more than 10 minutes to reach the same ethanol concentration. According to the morphological analysis shown in Table 1 and Figure 2, increasing the AC ratio in the composition produces higher surface area and more pore cavities in the composite, which could provide more space to contact the water and the adsorbent. Therefore, in this composition, the adsorption performance and the rate will increase.

Figure 6 shows the effect of the temperature on the adsorption kinetic. As shown in the figure, the temperature of 22°C shows the slowest rate of adsorption. However, the fastest rate is achieved at 30°C. The higher temperature will affect better transport properties, such as diffusivity; however, higher temperature will also decrease the adsorbate surface density, which will decrease the rate of adsorption [42].

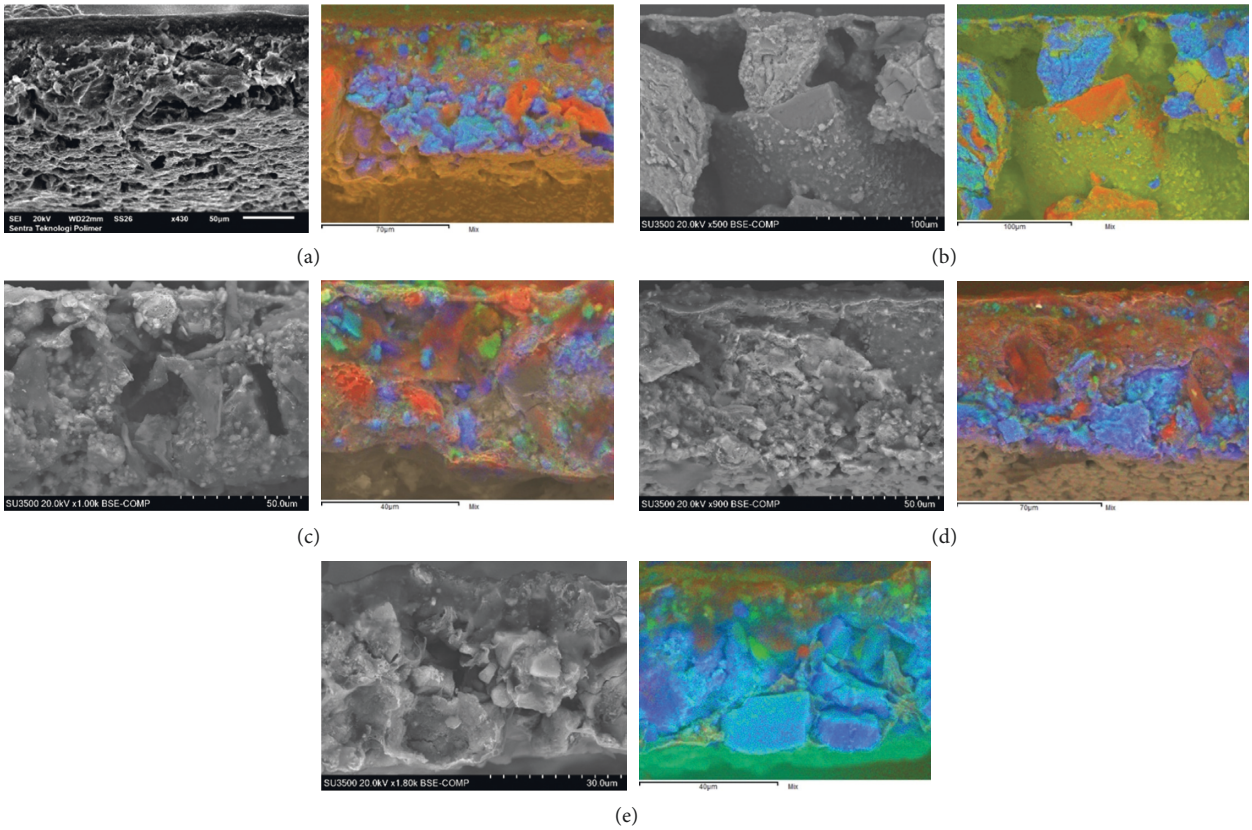


Figure 2: SEM-mapping micrograph of representative sample PVA/Zeo/AC. (a) 1 : 1 : 1; (b) 1 : 1 : 0.75; (c) 1 : 1 : 0.5; (d) 1 : 1 : 0.25; (e) 1 :1 : 0. C; O; Si.

Table 3: Determining of q_e for each experiment.

Temperature (°C)	C_0 of water (%v/v)	q_e experiment in various PVA/Zeo/AC and temperature (g of water/g adsorbent)				
		PVA/Zeo/AC 1 : 1 : 1	PVA/Zeo/AC 1 : 1 : 0.75	PVA/Zeo/AC 1 : 1 : 0.5	PVA/Zeo/AC 1 : 1 : 0.25	PVA/Zeo/AC 1 : 1 : 0
22	12	0.79	0.75	0.74	0.75	0.75
	10	0.65	0.62	0.61	0.61	0.61
	8	0.46	0.49	0.42	0.51	0.50
	6	0.36	0.33	0.33	0.35	0.37
	4	0.21	0.14	0.19	0.17	0.22
30	12	0.77	0.76	0.75	0.75	0.74
	10	0.62	0.62	0.61	0.61	0.61
	8	0.47	0.47	0.47	0.45	0.49
	6	0.29	0.31	0.32	0.32	0.35
	4	0.16	0.15	0.15	0.22	0.19
40	12	0.66	0.65	0.49	0.74	0.76
	10	0.53	0.52	0.39	0.61	0.62
	8	0.44	0.36	0.29	0.48	0.47
	6	0.37	0.22	0.22	0.32	0.35
	4	0.23	0.13	0.13	0.17	0.15
% AAD*		3.01	1.14	0.96	1.16	3.58

*Absolute average percentage deviation [42].

As shown in Figures 5 and 6, eventually, ethanol concentration greater than 99%, as fuel grade in accordance with ASTM 4806, was achieved at each process temperature using various composite adsorbent compositions in this study. In comparison, individual adsorbents for the same variation of initial ethanol concentration, as shown in Figure 7, cannot achieve the designated concentration of ethanol.

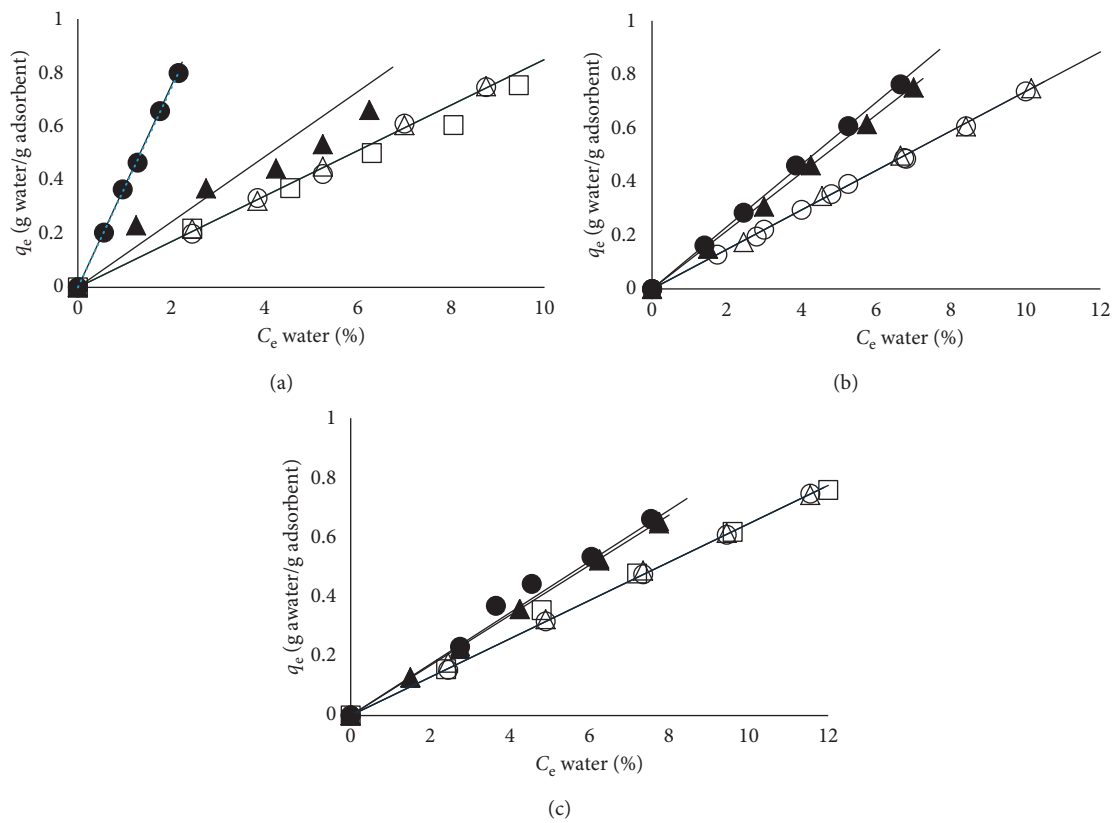


Figure 3: Adsorption isotherms of water at same temperature in various adsorbents. (a) 22°C; (b) 30°C; (c) 40°C. ●, q_{eks} PVA/Zeo/AC 1 : 1 : 1; ▲, q_{eks}PVA/Zeo/AC 1 : 1 : 0.75; ○, q_{eks} PVA/Zeo/AC 1 : 1 : 0.5; △, q_{eks} PVA/Zeo/AC 1 : 1 : 0.25; □, q_{eks} PVA/Zeo/AC 1 : 1 : 0; —, q_{mod} Langmuir.

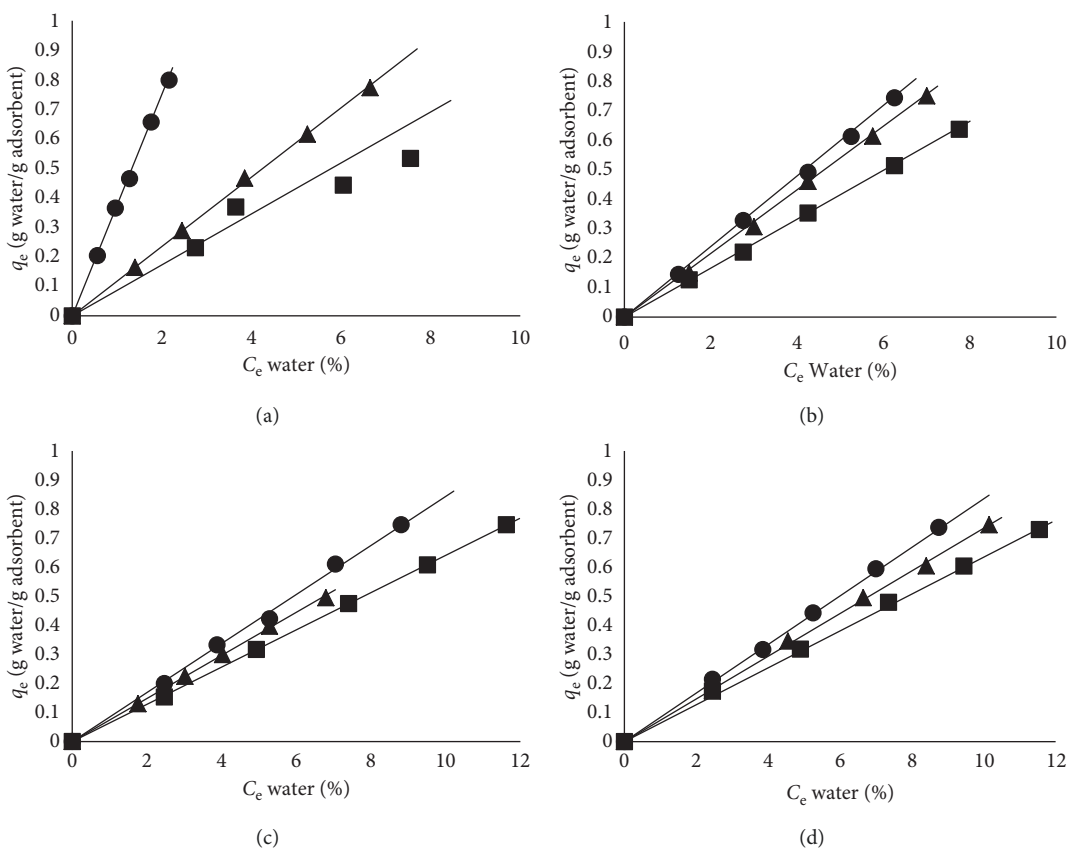
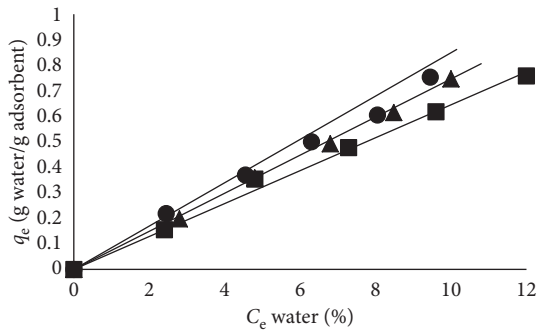
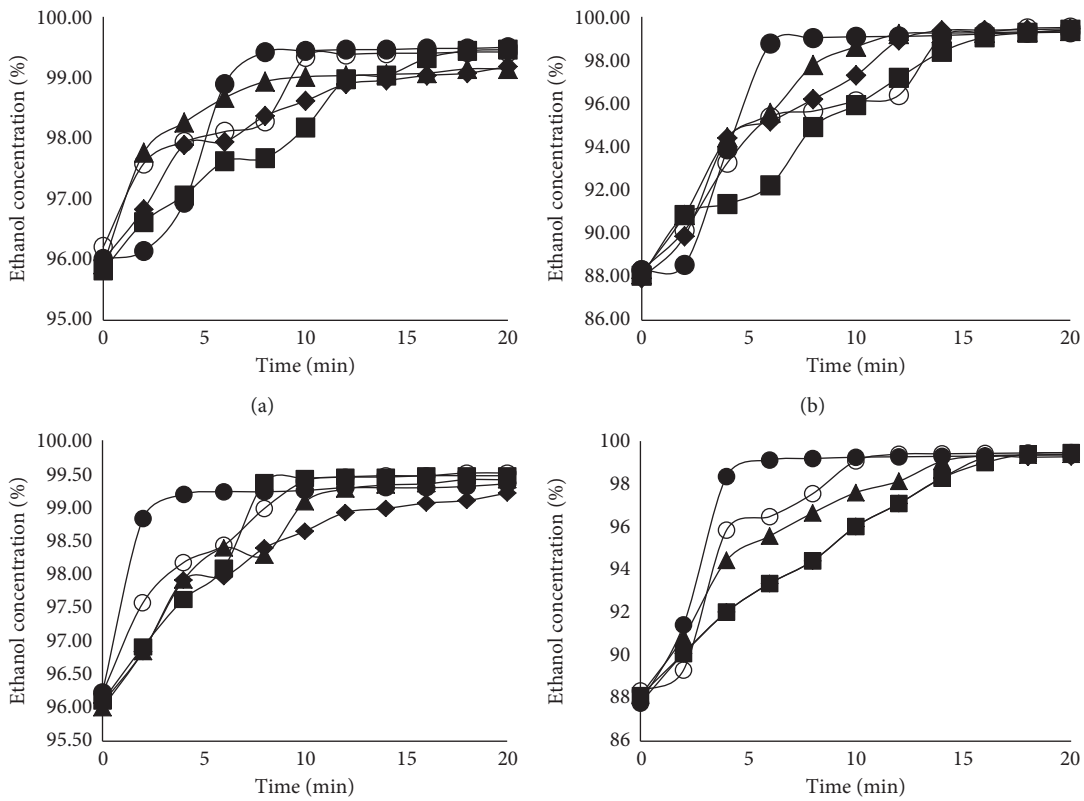


Figure 4: Continued.



(e)

Figure 4: Adsorption isotherms of water at same adsorbents in various temperatures. (a) PVA/Zeo/AC 1 : 1 : 1; (b) PVA/Zeo/AC 1 : 1 : 0.75; (c) PVA/Zeo/AC 1 : 1 : 0.5; (d) PVA/Zeo/AC 1 : 1 : 0.25; (e) PVA/Zeo/AC 1 : 1 : 0. ●, q_{eks} at 22°C; ▲, q_{eks} at 30°C; ■, q_{eks} at 40°C; —, q_{mod} Langmuir.



(a) (b) (c) (d)

Figure 5: Continued.

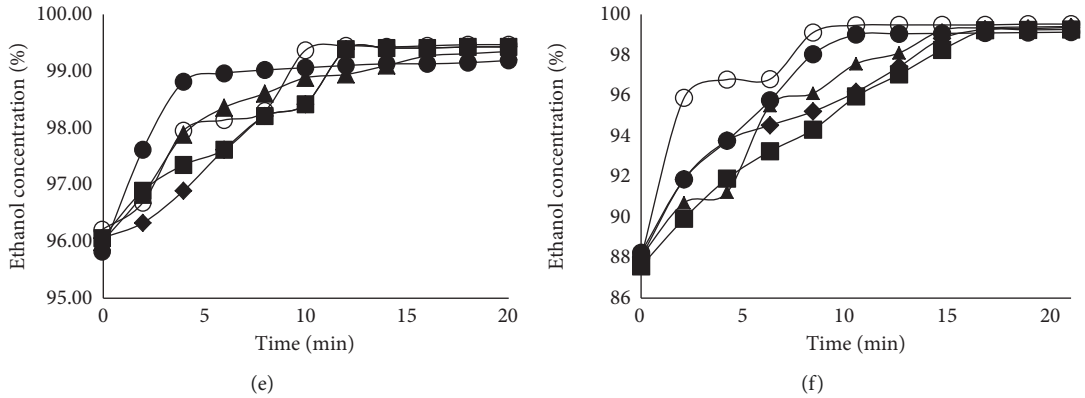


Figure 5: Ethanol concentration vs. time for various adsorbents at the same temperature and initial water concentration. (a) Ethanol concentration 96% and temperature 22°C; (b) Ethanol concentration 88% and temperature 22°C. (c) Ethanol concentration 96% and temperature 30°C. (d) Ethanol concentration 88% and temperature 30°C. (e) Ethanol concentration 96% and temperature 40°C. (f) Ethanol concentration 88% and temperature 40°C. ●, PVA/Zeo/AC 1 : 1 : 1; ■, PVA/Zeo/AC 1 : 1 : 0.75; ◆, PVA/Zeo/AC 1 : 1 : 0.5; ▲, PVA/Zeo/AC 1 : 1 : 0.25; ○, PVA/Zeo/AC 1 : 1 : 0.

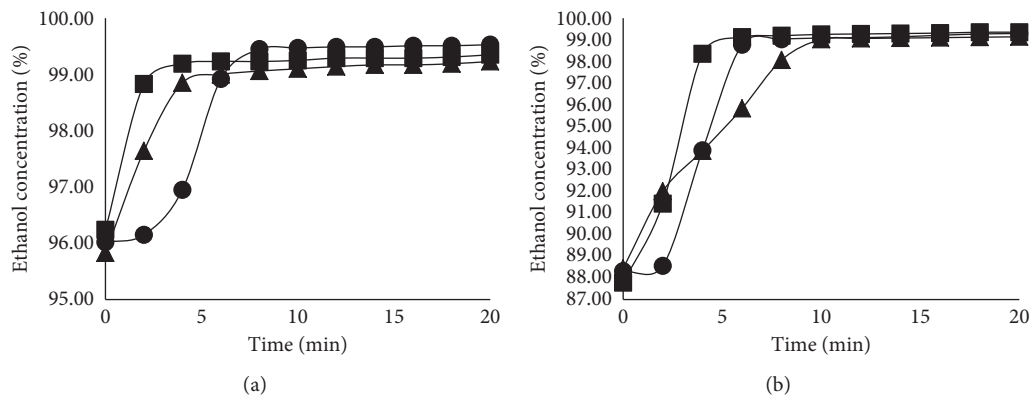


Figure 6: Ethanol concentration vs. time for various adsorbents at the different temperatures and initial water concentration. (a) 96% ethanol initial concentration for PVA/Zeo/AC 1 : 1 : 1; (b) 88% ethanol initial concentration for PVA/Zeo/AC 1 : 1 : 1. ●, 22°C; ■, 30°C; ▲, 40°C.

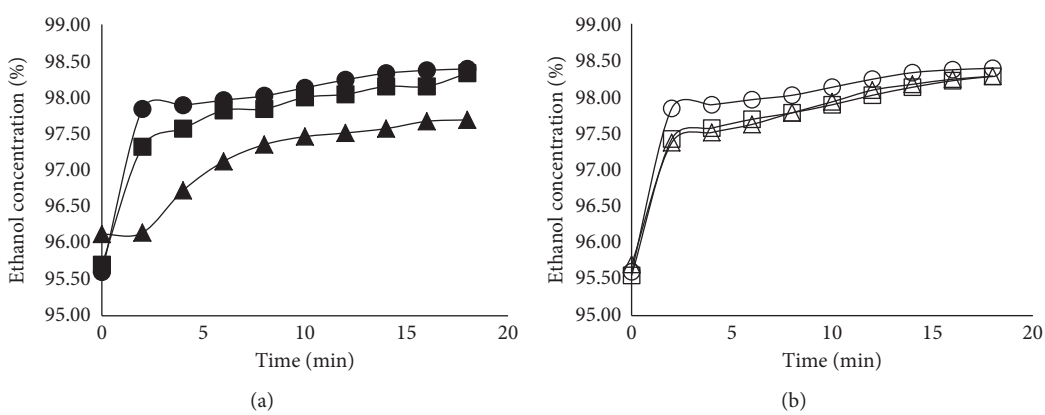


Figure 7: Ethanol concentration vs. time for individual adsorbent (a) at same temperature and different individual adsorbent (■, Zeo at 22°C; ●, AC at 22°C; ▲ PVA at 22°C) and (b) at zeolite individual adsorbent and different temperatures (○, 22°C; □, 30°C; △, 40°C).

4. Conclusion

The composite preparation with the supercritical CO_2 extraction fluid technique has provided excellent physical and chemical properties. The existence of the composite has been confirmed from FTIR analysis, as well as the SEM morphology and DSC analysis. The experimental adsorption shows that increasing the amount of AC in the composites increases approximately the capacity of water adsorption by four times (i.e., 0.80 gram of water/gram of adsorbent for PVA/Zeo/AC = 1 : 1 : 1 at 22°C). By using approximately 4.5 gram adsorbents composite in 30 ml of water-ethanol mixtures, the standard fuel grade of bioethanol (>99%) can be achieved at various temperatures from 22°C to 40°C and bioethanol initial concentration from 88% to 96%.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

Mahmud Sudibandriyo (MS) and Joddy Arya Laksmono (JAL) were responsible for the original conception, design, and overall investigation. Asep Handaya Saputra (AHS) and Agus Haryono (AH) were responsible for analysis and interpretation of data. MS and JAL were responsible for the experiment and drafting the manuscript. Each author has sufficiently participated in the work to take public responsibility for appropriate portions of the content. All authors gave critical revisions and approved the final manuscript.

Acknowledgments

The authors would like to thank Universitas Indonesia via Grant of UI's Doctoral Students Dissertation 2018 (Grant No. 1353/UN2.R3.1/HKP.05.00/2018) for financial research support.

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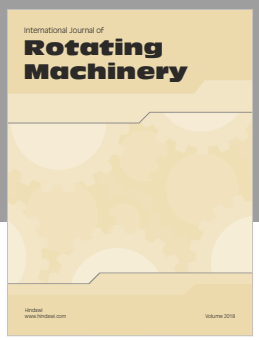

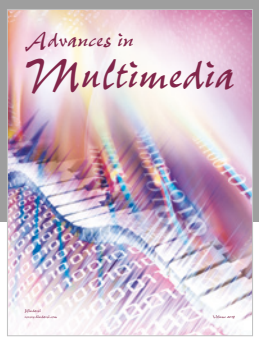

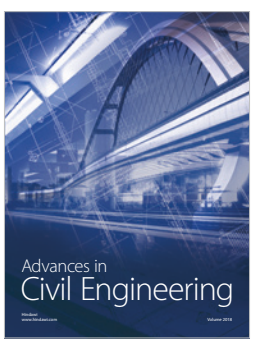

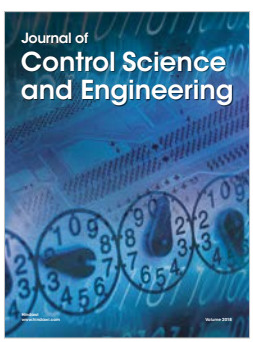

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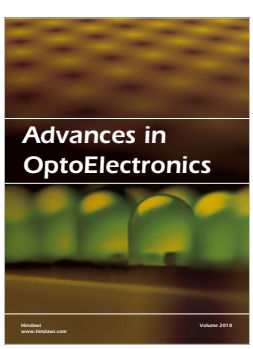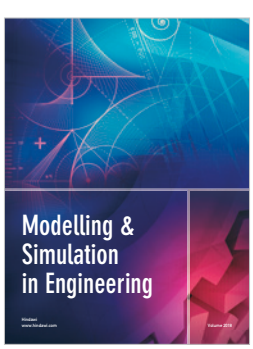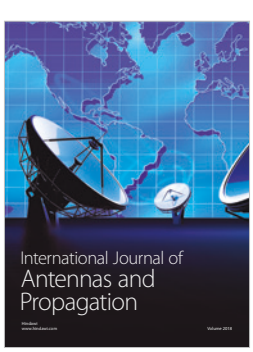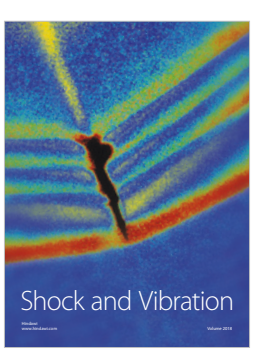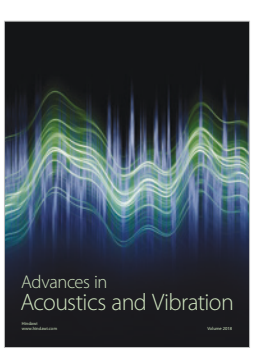
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