

Effect of Physical and Chemical Preparation on Characteristics of Activated Carbon from Agriculture Solid Waste and their Potential Application

Khadija Ahmida, Mabroka Darmoon, Fatma Al-Tohami, Mohamed Erhayem, and Mohamed Zidan

Abstract—This work focus on the effect of physical and chemical carbonization and activation processes on physicochemical properties of activated carbon from date stone (ACDS) and their applications. Twelve ACDS samples were obtained from two date stone samples at three different temperatures (300, 500, 700°C) using physical carbonization and activation, and using chemicals (NaCl, H₃PO₄, NaOH) at 500°C. The characterization of these ACDS samples were evaluated using moisture content (MC), pH, bulk density (BD), ash content (AC), conductivity (CD), total dissolved solids (TDS), salinity (SA) and carbon yield (CY), and its potential application on adsorption process as low-cost adsorbent. The CY, BD, MC, CD, TDS and SA of ACDS prepared by physical activating process decreased with increasing temperature, while the pH values increased from 4.70 to 6.74 with increasing activation process temperature from 300 to 700°C, respectively. The highest Ni(II) ions adsorbed onto ACDS was obtained from ACDS activated with chemical activating process using NaOH at 500°C. Therefore, ACDS prepared chemically by NaOH is the best to be used in waste water treatment.

Keywords—physical, chemical, preparation, characterization, date stone, Ni(II) ions, removal.

I. INTRODUCTION

CARBON materials are widely used in many applications including activated carbon, catalysis, etc. Activated carbon (AC) is a well-known material to be used in industrial applications that includes separation, purification and catalytic processes, among others. Over the last few decades, agriculture waste AC has extended its application to air and water treatment processes as green adsorbents due to its relatively low-cost materials compared to other adsorbents [1]. The properties of these materials depend on the source and preparation conditions [2].

Khadija Ahmida is with the Department of Chemistry, Sebha University, Sebha, Libya (e-mail: khadijanoor77@gmail.com).

Mabroka Darmoon is with the Department of Chemistry, Sebha University, Sebha, Libya (e-mail: m.drmoon@yahoo.com).

Fatma Al-Tohami is with the Department of Chemistry, Sebha University, Sebha, Libya (e-mail: somaia4488@yahoo.com).

Mohamed Erhayem is with the Department of Chemistry, Sebha University, Sebha, Libya (corresponding author's phone: 00218911599159; e-mail: irhim2002@yahoo.co.uk).

Mohamed Zidan is with the Department of Chemistry, Sebha University, Sebha, Libya (e-mail: zidanupm@gmail.com).

Generally, carbonization and activation of AC are the two main processes of AC production. In the carbonization process, the type of reaction can be divided into endothermic (<300°C) and exothermic (>300°C) processes. Activated carbon materials can be prepared mainly by two main ways: physical activation or chemical activation of raw natural or industrial carbon materials such as coal, lignite, wood, rice and olive stone [3]. The physical methods are typically thermal processes conducted at temperatures below 700°C using oxidizing gases like air, CO₂ and steam of H₂O as second step after pyrolysis [4]. This process is used to create a porous structure that increases the adsorption capacity of AC materials. The porous AC is produced when the oxidant converts carbon materials to form CO and CO₂ opening pores in AC materials. Chemical activation process is commonly used and involves two major steps, which are heating process and chemical treatment process. The heating process usually requires less heat than the physical activation process. During chemical treatment, chemical agents such as alkaline chemicals (KOH, NaOH, Na₂CO₃ and NaHCO₃), acid chemicals (HCl, H₂SO₄ and C₂H₄O₂) and other chemicals (ZnCl₂; etc) are added with purpose of improving the surface area or size of porous structure in AC materials. Chemical activation processes are more preferred compared to physical activation due to the higher global yield (based on weight of starting material), simplicity, lower temperature and shorter activation time [5, 6]. Physical and chemical characteristics of activated carbon affect its suitability for specific applications [5]. Therefore, these processes need to be well studied in order to understand the relationship between them and their properties.

Date stone is an abundant solid waste from date industries in Mediterranean countries especially in Libya, and is present in large amount from food industries [7]. The huge amount of date stone waste materials especially in south of Libya are being noticed as environmental waste problems. This waste material can be reused as source of AC materials and renewable energy, and also to remove odor, taste, color and heavy metals [2]. The major component of date stone is carbohydrates as 42% cellulose, 25% sugar, 18% hemicellulose, 11% lignin, 4% ash and other compounds [5]. Recently, numerous studies had been done to investigate the effect of agriculture waste materials on removal of ions from aqueous solutions by activation process. These studies include

investigation on the effect of carbonization and activation process on ACs using low cost agriculture waste and natural materials. Research on the preparation and activation of date stone samples from different regions using different physical and chemical conditions have also been conducted [5]. All of these studies considered only one part of the activation process, either by physical or chemical activation, and did not include the comparison between the two processes in terms of date stone characteristics. To the best of our knowledge, influence of activating process on the physico-chemical properties of AC from DS and its potential application have not been well investigated. The aim of this research is to study the influences of carbonization and activation conditions on the physico-chemical properties of AC produced from DS and the removal of Ni(II) ions from aqueous solutions onto ACDS.

II. MATERIALS AND METHODS

A. Materials

In order to respect the effect of DS source on the physicochemical properties and its applications, two raw date stone (DS) samples were collected locally from Howan City and Obarie City, middle south and south of Libya, shown in Fig. 1 [7-9]. The samples were washed several times with tap water to remove dirt and impurities present in raw materials, and the rinsed with distilled water. The samples were dried at room temperature overnight and then grounded and sieved into particle sizes in diameter of 0.5 mm. In order to remove the water soluble impurities such as metal ions and surface adhered particles, the ground samples were soaked in 1% HCl and then kept in 0.1M NaOH for overnight to remove lignin. The suspensions were soaked in 0.1 M CH₃COOH to remove the alkalinity. DS samples were washed with distilled water until the pH remained constant and then dried at 110°C in an oven for 3 hrs. The pretreated samples were stored in a dry container in a desiccator for subsequent experiments [3].



Fig.1 sampling sites of Date stone (*)

B. Instruments

pH meter (Thermo, Orion4 star); conductivity meter (Philips, PW-9527); atomic absorption spectrophotometer

(Thermo AA spectrometer S-series); FT-IR spectrometer.

C. Carbonization and activation processes

Carbonization and physical activation. ACDS samples were prepared by putting about 50 g of crushed raw DSs in crucible and carbonized at selected temperatures of 300, 500 and 700°C for 2 hrs under air as oxidizing agent during pyrolysis, as listed in TABLE I [10]. The ACDS samples were then left overnight to cooled at room temperature for before being and sieved with 0.5 mm sieves [3].

Carbonization and Chemical activation with H₃PO₄, NaOH and NaCl, the washed, dried and crushed DSs (50 g) were impregnated with 100ml of H₃PO₄ (30%), NaOH (0.2N) and NaCl for 24 hrs at room temperature as listed in Table 1. The DS samples were heated at constant rate 10°C/min and held at the same carbonization temperature (500°C) for 2 hrs. At the end of activation process, the ACDS was allowed to cool at room temperature, for overnight. All the ACDS samples were neutralized by either acid or base depending on the chemical used for activation before being washed for several times with distilled water until the pH of filtrate remained constant as listed in Table 1. Finally, the ACDS was dried at 110°C for 2 hrs and stored in tightly closed bottles. The physical and chemical conditions used were similar to those reported by Verla *et al* 2012 [3].

TABLE I
LIST OF DS SAMPLES

Sample code for Howan	Sample code for Obarie	Activation process	Neutralized Chemicals
HC ₁	OC ₁	Raw material	None
HC ₂	OC ₂	Pretreated raw material	None
HC ₃	OC ₃	Physical methods	At 300°C under air
HC ₄	OC ₄		At 500°C under air
HC ₅	OC ₅		At 700°C under air
HC ₆	OC ₆	Chemical methods	using NaOH at 500°C
HC ₇	OC ₇		using NaCl at 500°C
HC ₈	OC ₈		using H ₃ PO ₄ at 500°C

The characteristics of DS and ACDS were evaluated by bulk density using ASTM D6683-14 method, ash content using ASTM method D2866-94, moisture content using ASTM 2867-99 method, pH (model supplied by pH meter) and conductivity using ASTM D3838-80 method, salinity, TDS (model supplied by conductivity meter) and carbon yield. Fourier Transform Infra-Red (FT-IR) spectrophotometer was used to study the effect of activation process on the surface functional groups of DS. A few milligrams of each DS samples were placed on lenses and scanned over the wavenumber range of 400-4000 cm⁻¹.

D. Application Case

In order to evaluate the effect of DS activation process on its potential application, 10 mg of DS was added to 20 ml of 20 mg/L Ni (II). The mixture was stirred for 2 hrs at room temperature and then filtered through Whatman No. 1 filter paper [11]. The residual concentration of Ni(II) ions in the

filtered solution was determined by AAS. The percentage removal was calculated using the following equation (1):

$$\text{Removal \%} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

C_o and C_e are the concentrations of Ni(II) before and after addition of ACDS, respectively.

III. RESULTS AND DISCUSSION

Fig. 2 shows FTIR spectra for all ACDS prepared with different activation process. The results revealed the peaks at 3300; 2980; 2300; 1740; 1680; 1540; 1425; 1360; 1220 and 1030 cm^{-1} corresponding to the presence of -OH, NH or NH_2 ; -CH (SP^3 stretching); C=C or CO_2 ; -C=O; -C=O; amide; -C-O and C-O-C functional groups, respectively. The presence of a broad peak at 3350 to 3450 cm^{-1} for -OH functional groups suggested that ACDS samples traps moisture either on its surface or inside the pores during sample handling. Generally, ACDS samples showed clearer peaks reduction than raw materials. The intensity of -OH functional groups decreased with increasing carbonization temperature with one exception at 700°C and in the presence of different chemicals. Therefore, these activating agents can be used as drying agents at low temperature. It was also noted that the decrease in the intensity of C=O functional groups present at 1740 cm^{-1} with increasing activation temperature between 200 and 300°C was probably due to the elimination of hydrogen and oxygen in forms of CO, CO_2 and H_2O leaving pores inside ACDS [4]. The peak appearing in the region of about 1540 cm^{-1} is assigned to C=C stretching vibrations in the aromatic ring which generally appears in carbonaceous materials [12]. The peak at 1425 cm^{-1} represents bending vibrations of C-H groups in alkyl group such as - CH_3 , indicative of lignin [12]. Two important peaks for adsorption appeared at 1220 and 1030 cm^{-1} corresponding to stretching C-O functional group. The increase in intensities of these peaks may be due to the increase in the adsorption capacities as shown in Fig. 2. Furthermore, the decrease in all functional group intensities were probably due to the degradation of cellulose between 240 and 360°C [4].

The FTIR spectra indicate the presence of oxygen groups such as hydroxyl, carbonyl and carboxyl, at the surface of the ACDS. The intensities of these functional groups increased with increasing carbonization temperature (CT) from 300 to 500°C due to the presence of more oxygen functional groups on the surface of ACDS. The surface modifications of ACDS with NaCl, NaOH and H_3PO_4 were expected to extend the surface functional groups of -OH, -COOH and C=O. At 900°C, the carbon residue is the remaining product.

TABLE II shows the properties of raw carbon material and ACDS using different activation process. One of the most important characteristics for AC is the bulk density (BD), which gives a measure of the adsorbent amount per volume unit [2]. C_6 has the lowest bulk density and the highest adsorption capacity. It has been reported that the low density will enhance adsorption in gas and liquid phase systems [13]. Another parameter used is moisture content (MC). In general, based on the results listed in TABLE II, the activation agents used in this work seems to act as dehydrating agent for ACDS.

As expected, the MC for ACDS was decreased with an increasing in CT with one exception at higher CT. This could be because ACDS adsorb the moisture from air in the transporting stage between the oven and desiccator. H_3PO_4 activating agent was noted as the best drying agent to be used. Carbon yield was decreased with an increasing in the CT. This is probably due to more volatile component being lost at higher temperature [2]. Generally, the carbon yield of ACDS in physical activation process was poor probably due to the presence of air as oxidizing agent, which causes a burnout inside the pores and external surface of carbon. On the other hand, the carbon yield of AC from chemical processes was higher than those from physical processes. This may be due to the highly porous structure created during the chemical processes, which enabling a high adsorption capacity. Chemical activation is therefore more favorable with one exception; further washing stage is required for removing all chemicals used. The pH of ACDS was found to be between 4-7 which is acceptable for most application such as water treatment process and sugar decolorization etc [12]. The pH values of physically prepared ACDS (C_3 , C_4 and C_5) for both sources were generally acidic and increased with increasing activation temperature, with the exception of OC_5 (nearly neutral). These values are desirable for most AC applications. For chemically prepared ACDS, the pH values for both sources depended on the chemical used for activation. High ash content in AC is undesirable as it will cause a reduction in the overall activity and mechanical strength of AC [13]. In this research, ash content for Howon and Obari samples were 5% and 6.67%, and could be related to the insignificant differences between the adsorption capacities of the two samples, as listed in TABLE I.

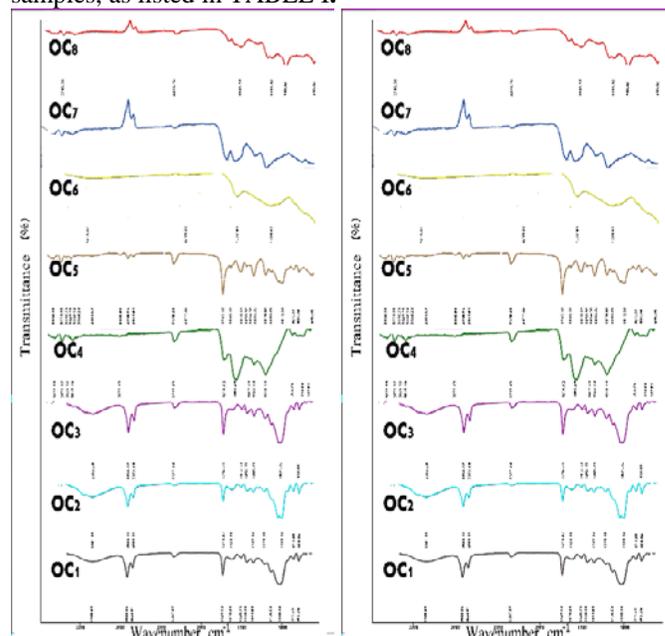


Fig. 2 FTIR spectra for DS samples before and after activation process

TABLE II
Physical characteristics of DS samples

Sample Codes	pH	Moisture content (%)	Conductivity (mS/cm)	Salinity ($\mu\text{g/L}$)	TDS (mg/L)	Bulk density g/ml	Ni(II) Removal (%)	Carbon Yield (%)
HC ₁	9.92	2.29	0.0998	42.8	31	0.267	6.99	--
HC ₂	5.73	0.538	0.0655	0.00	1608	0.38	6.46	--
HC ₃	4.92	0.101	1.567	0.90	829	0.382	5.83	56.1
HC ₄	6.89	2.96	0.592	0.30	311	0.25	8.43	87.3
HC ₅	6.75	0.074	1.376	0.10	106	0.243	8.28	98.5
HC ₆	10.2	0.361	5.410	4.10	3669	0.199	23.1	66.4
HC ₇	3.88	0.742	0.284	0.10	97	0.22	1.76	47.2
HC ₈	2.50	0.062	3.400	1.60	1493	0.666	4.72	52.4
OC ₁	6.92	2.03	0.257	0.10	74	0.257	7.93	98.7
OC ₂	5.91	1.59	0.135	0.10	159	0.328	8.30	58.9
OC ₃	4.70	1.24	1.070	0.30	327	0.249	6.32	60.2
OC ₄	5.02	0.818	0.268	0.10	148	0.142	7.11	14.8
OC ₅	6.74	2.35	0.235	0.10	126	0.416	9.00	35.9
OC ₆	7.02	2.35	0.103	0.00	45	0.263	27.3	8.51
OC ₇	4.95	1.12	0.0961	5.20	4608	0.374	4.56	30.9

Fig. 3 shows the effect of activation parameters on the adsorption capacity of ACDS. The adsorption capacities increased in the order of C3, C4 and C5 due to the increase in the activation temperature, which leads to an increase in the degree of pyrolysis, surface area and removal of non-carbonaceous volatile materials [[14]]. The higher temperature processes leads to an increase in the adsorption capacity due to the increment in micropore size of AC [6]. At low CT, a significant increase in adsorption capacities was noted in the presence of chemicals. The change in adsorption capacities, however, was insignificant at high CT. It can be also seen from Fig. 3 that a considerable high amount of Ni(II) ions was removed onto the surface of ACDS using NaOH (8-fold) as activating agent at carbonization temperature 500°C. Chemical activation process is favorable to be used due to the low activation temperature, good development of the porous structure and change in the surface functional groups [15]. It was also noted that adsorption capacities increased in the presence of chemicals at the same temperature (500°C) with physical activating processes, the activation agents used in this work seems to act as dehydrating agent for ACDS [16]. Activation with NaOH, NaCl and H₃PO₄ could have either created more reactive sites onto the surface of ACSD for adsorption of Ni(II) ions or increased the porosity of ACDS, as shown in Fig. 3 [13].

In the presence of NaOH, the adsorption capacity of Ni(II) onto ACDS surface was increased. As reported by Ademiuyi and David West, the presence of NaOH may have increase the concentration of oxygen groups which reacts with Ni(II) [13]. The adsorption capacity of Ni(II) onto ACDS surface was decreased in the presence of H₃PO₄. Erhayem and Sohn reported a similar observation, in which the ACDS surface area available for Ni(II) adsorption was decreased due to the

poly anion effect H₃PO₄ adsorption onto the surface of ACDS [9]. This trend was also observed on ACDS activated with NaCl. Removal of Ni(II) ions onto ACDS surface is dependent on the preparation conditions and NaOH acts as the best activating agent based on adsorption capacity.

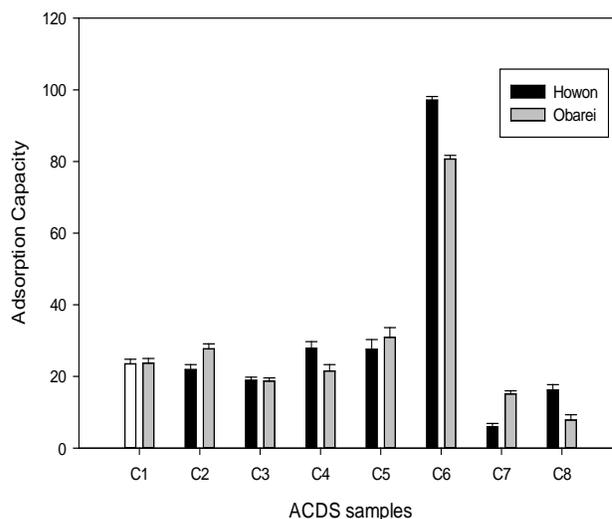


Fig.3. Relationship between adsorption ACDS parameters and adsorption capacity

IV. CONCLUSION

In this research, the effect of physical and chemical activation process using different activation temperature and chemicals, on the physic-chemical properties of date stone as source of activated carbon and its potential application for adsorption of Ni(II) ions from aqueous solutions were

investigated. The physical and chemical properties of AC were dependent on the carbonization and activation method for preparation of AC and had a significant effect on Ni(II) adsorption capacity. The adsorption capacity is dependent on activation process regardless to the source of the raw materials. Higher activation temperature favors for removal of heavy metals from aqueous solution. The findings in this research suggest that the physical and chemical condition plays a crucial role in determining the characteristics of ACDS and their applications. The process to produce the activated carbon needs to be well studied before it is used and applied. ACDS activated with NaOH can effectively be used to remove Ni(II) ions from aqueous solutions compared to using ACDS activated with NaCl and H₃PO₄ and physical activation ACDS. The finding in this work suggests that the ACDS prepared by chemical activation using NaOH can be used as effective adsorbent to remove Ni (II) ions from aqueous solutions.

ACKNOWLEDGMENT

The authors thank the technicians in Research laboratory at University of Sabha for providing assistance in sample testing and to the Department of chemistry at Sebha University for foundation.

REFERENCES

- [1] G. Z. Kyzas and M. Kostoglou, 'Green Adsorbents for Wastewaters: A Critical Review', *Materials*, vol. 7, pp. 333-364, 2014.
<http://dx.doi.org/10.3390/ma7010333>
- [2] S.E. Abechi , E. C. Gimba, A. Uzairu, Y.A. Dallatu, 'Preparation and Characterization of Activated Carbon from Palm Kernel', *Research Journal of Chemical Sciences*, vol. 3, pp. 54-61, 2013.
- [3] A. W Verla, M. Horsfall (Jnr), E.N Verla, A.I. Spiff, O.A. Ekpete, 'Preparation and Characterization of Activated Carbon from Fluted Pumpkin (*Telfairia Occidentalis* Hook.F) Seed Shell', *ASIAN JOURNAL OF NATURAL & APPLIED SCIENCES*, vol. 1, pp. 39-50, 2012.
- [4] M. L. Sekirifa, M. Hadj-Mahammed, S. Pallier, L. Baameur, D. Richard, A. H. Al-Dujaili, 'Preparation and Characterization of an Activated Carbon from a Date Stones Variety by Physical Activation with Carbon Dioxide', *Journal of Analytical and Applied Pyrolysis*, vol. 99, pp. 155-60, 2013.
<http://dx.doi.org/10.1016/j.jaap.2012.10.007>
- [5] M. J. Ahmed, S. K. Theydan, 'Physical and Chemical Characteristics of Activated Carbon Prepared by Pyrolysis of Chemically Treated Date Stones and Its Ability to Adsorb Organics', *Powder Technology*, vol. 229, pp. 237-245, 2012.
<http://dx.doi.org/10.1016/j.powtec.2012.06.043>
- [6] P. Pragma, S. Sripal and Y. Maheshkumar, 'Preparation and Study of Properties of Activated Carbon Produced from Agricultural and Industrial Waste Shells', *Research Journal of Chemical Sciences*, vol. 3, pp. 12-15, 2013.
- [7] M. Erhayem , R. Mohamed, O. Ghmeidc, A. Eljelaned, M. Elhmmalia, 'Effect of Activated Carbon Source from Date Stone on Its Physico-Chemical Properties ', in 2014 6th International Conference on Chemical, Biological and Environmental Engineering (ICBEE 2014), ed. by APCBEE Procedia (Paris, France: APCBEE procedia, 2014).
- [8] M. Erhayem, M. Sohn., Effect of humic acid source on humic acid adsorption onto titanium dioxide nanoparticles. *Science of the Total Environment*, 2014. vol. 470, pp. 92-98, 2014.
- [9] M. Erhayem, M. Sohn., Stability studies for titanium dioxide nanoparticles upon adsorption of Suwannee River humic and fulvic acids and natural organic matter. *Science of the Total Environment*, vol. 468, pp. 249-257, 2014.
<http://dx.doi.org/10.1016/j.scitotenv.2013.08.038>
- [10] A. W. Verla, M. Horsfall (Jnr), E.N Verla, A.I. Spiff, 'Some Aspects of Surface Chemistry of Activated Carbon Prepared from Fluted Pumpkin (*Telfairia Occidentalis* Hook.F) Mesocarp by Physical Activation ', *International Journal of Chemical Science and Technology*, 2, pp. 224-230, 2012.
- [11] R. Mohamed, A. Mustafa, M. Erhayem, 'Biosorption of Cr(Vi) and Cu(II) by Palm Kernel Powder and Its Potential Application', 2014 6th International Conference on Chemical, Biological and Environmental Engineering (ICBEE 2014) (2014).
- [12] S. Joshi and B. P. Pokharel, 'Preparation and Characterization of Activated Carbon from Lapsi (*Choerospondias Axillaris*) Seed Stone by Chemical Activation with Potassium Hydroxide', *Journal of the Institute of Engineering*, vol. 9, pp. 79-88, 2013.
- [13] F. T. Ademiluyi and E. O. David-West, 'Effect of Chemical Activation on the Adsorption of Heavy metals Using Activated Carbons Fromwastematerials', *International Scholarly Research Network*, pp. 1-5, 2012.
- [14] JEG Mdoe and L. L. Mkayula, 'Preparation and Characterization of Activated Carbons from Rice Husks and Shells of Palm Fruits', *Tanzania Journal of Science*, vol. 28, pp. 131-42, 2002.
- [15] N. Kumar and R. Chinnaiya, 'Development and Characterstics of Activated Carbons from *Jatropha* Husk, an Agro Industrial Solid Waste, by Chemical Activation Methods', *J. Environ. Eng. Manage*, vol. 19, pp. 173-78, 2009.
- [16] A. Y. Alhamed, 'Activated Carbon from Dates' Stone by Zncl2 Activation', *JKAU: Eng. Sci.*, vol. 17, pp. 75-100, 2006.