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Synthesis of Polymers by a Solar Photocatalytic Microreactor System

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Abstract- The present work aimed to study the feasibility of microreaction process for polyaniline synthesis under solar light. A chemical method to prepare polyaniline is presented in which a continuous operated solar photocatalytic microreactor is utilized to promote the polymerization of aniline. The photopolymerization method yields a polymeric material that has been scanned by electron microscopy (SEM). Results showed that the initial operating temperature has a positive impact on the rate of polymerization but affects negatively the yield of polyaniline. The yielded of polyaniline is decreased as LHSV of the microreactor increased. An optimum (oxidant/aniline) molar ratio of about 1.25 is found to give the maximum yield of polyaniline. Comparison between microreactor's performance and performance of previous published works were presented. Results of the present study confirmed the feasibility of the solar microreaction process for synthesis of polymeric materials.

Keywords: microreaction; solar irradiation; continuous process; photocatalysis; polymerization.

1. INTRODUCTION

Polyaniline (PANI) has been considered a valuable electric-conductive polymer due to its superior characteristics of conductivity, stability, different structures, feasible cost and other excellent performance (Benabdellah *et al.*, 2011). PANI has been applied in many industrial fields such as LED, electrode manufacturing, isomerization of electro-materials, electrodes of storage batteries, enzyme fixation and etc. Langer *et al.* (2001). PANI has been synthesized by different methods such as chemical, co-mixing of solution, and co-blending by agitation (Malinauskas, 2004). The synthesis of PANI using ammonium persulfate (APS) as oxidizing agent was demonstrated by (Stejskal, 2002). Silver nitrate (AgNO_3) was used as oxidizing agent for aniline polymerization in the aqueous solution of HNO_3 by (Blinova *et al.*, 2009). The effect of light adsorption on the macroscopic structure of polymer was investigated theoretically and experimentally by (Daset *et al.*, 2005). They concluded that polymerization of aniline is induced by light of suitable wavelength. A minimization in the time of aniline

polymerization under UV-irradiation was reported by (Gustavo *et al.*, 2010). Most the production processes of polyaniline are using batch mode (Kulkarni *et al.*, 2015). (Kulkarni *et al.* (2015) have used a spiral microreactor for the continuous production of polyaniline nanoparticles of size of 245.3 nm from a mixture of 0.04 M concentration of aniline and 0.05 M concentration of AgNO_3 as oxidizing agent. They reported that AgNO_3 acts as a mild oxidizing agent and it was found to be more effective for obtaining nanosize of PANI particles. The effects of neutron and gamma radiations on the electrical, optical, chemical and structural properties of PANI for the same batch were studied by (Sonkawade *et al.*, 2010). They reported that PANI samples showing increase in conductivity after radiation. They observed the formation of new bands after irradiation which may be due to the cross-linking of polymer chain after irradiation.

Recently, microreaction process has been evolved as a novel technology which has been utilized to establish new concept for design, trouble shooting, and control in many fields of industry (Šalić *et al.* 2012, Rebrov *et al.*, 2003; Kusakabe, 2002). It is well-known that countries of the Arabian Gulf have received solar incident energy for almost 300 day per year. The measured average incident UV-energy is 45 W.m^{-2} – 64 W.m^{-2} for class UV-A, and for class UV-B, the average VU-solar energy is 0.19 W.m^{-2} - 0.33 W.m^{-2} (ISERC, 2012). This makes it promising to use the UV-solar energy for many environmental and industrial applications such as wastewater treatment and synthesis of polymeric materials. Solar irradiation for desulfurization of gas oil in a Y-shaped catalytic microreactor was utilized by (Abid, 2015). He investigated the effect of different operating variables (e.g., concentration of dibenzothiophene, liquid hour space velocity, initial feed temperature, and hydrogen peroxide: dibenzothiophene ratio) on the reactor performance. He reported that the percentage removal of sulfur in the Y-shaped microreactor was 65% in approximately 9 (min) comparing to 340-400 (min) in a batch reactor of macroscopic scale used for desulfurization operation of gas oil.

Aniline in 1 M HCL solution could be polymerized using (APS) as oxidant through two steps. The first is the oxidation to form PANI (emeraldine) hydrochloride. The second step is the deprotonation in

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ammonium hydroxide solution to yield PANI -emeraldine base (Faris, 2007; Sapurina and Stejskal, 2010). An overview on formation of image with PANI by photo-induced reaction was presented by (Kobayashi *et al.*, 1998). They proposed that photogenerated holes on the irradiated surface of the sensitizer could oxidize the aniline derivatives initiate polymerization while the metal complexes reduced by the photogenerated electrons and precipitated on part of the sensitizer which needed to regenerate (flushed) after periods of operating time. The fractional degradation (x) of aniline was calculated according to equation 1. The percentage yield of PANI was calculated on the basis of the unreacted aniline and estimated according to equation 2:

$$\text{Aniline conversion } (x) = \frac{C_0 - C(t)}{C_0} \quad (1)$$

Where C_0 and $C(t)$ are the initial and instantaneous concentration of aniline in solution, respectively.

$$\% \text{ PANI yield} = \frac{\text{weight of PANI produced}}{\text{Initial weight of aniline}} \times 100 \quad (2)$$

The aim of the present study was to design, fabrication and application of a photocatalytic microreactor for a continuous operation of PANI synthesis under incident solar energy. Another objective was to investigate the influence of the operating variables (e.g., APS/aniline molar ratio, inlet mixture flow rate, and initial feed temperature) on the morphology of the produced aniline and also on performance of the microreactor.

II. MATERIALS AND METHODS

a) Materials

Chemicals used in the present study are: TiO_2 (80% (w/w) anatasa, average particle size 20nm, and

specific surface area $60 \pm 10 \text{ m}^2/\text{g}$) was supplied from Xinyue Chemical Co., China and used as a sensitizer. Aniline (99% w/w) was obtained from Thomas Baker Chemicals. Ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98% w/w) was purchased from Fluke Chemical Co. Cobalt (II) chloride-6-water ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was obtained from Merk and used as an electron acceptor. Hydrochloric acid (36% w/w) and caustic soda (Flakes) were obtained from Bayer. Water used was obtained from the RO plant.

b) Methods

i. Analytical methods

UV-Visible spectrophotometer type Shimadzu (UB-1201 PC) was used to record the UV-Vis spectrum of aniline in HCl. Scanning electron microscope (SEM) (Model: Inspect 50S, supplied by FEI-USA) was used to test the deposition process of photo-catalyst nanoparticles on the microchannel and also to examine the surface morphology of the polyaniline produced. To construct a calibration curve of aniline concentration vs. light absorbance, using UV-Vis spectrophotometer, different amounts of aniline (0.0027, 0.005, 0.0107, 0.032, 0.054, 0.086 and 0.107 mmole) is dissolved in 10 ml of 1 M HCl, respectively. Figure 1 illustrates the obtained calibration curve of aniline in HCl.

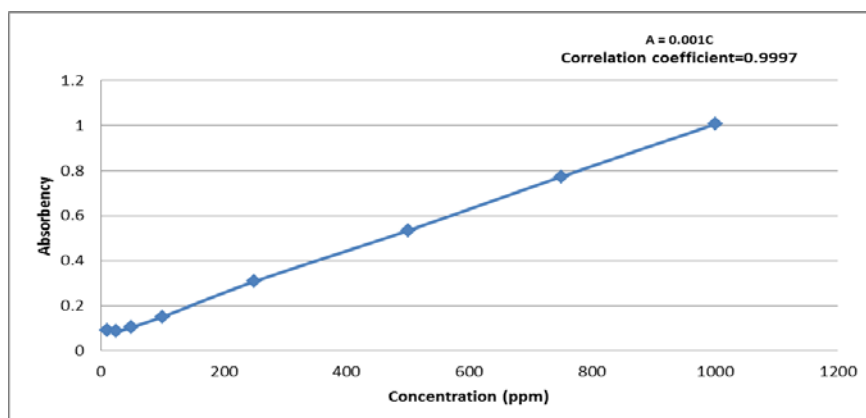


Figure 1: Calibration curve of aniline in HCl

III. MICROREACTOR DESIGN AND FABRICATION

Diffusion concepts were used to correlate the microreactor's dimensions with the time scales of mass and heat transports according to the following equations (Wegenet *et al.*, 1996; Branebjerget *et al.*, 2005):

Transport of heat: $\tau \sim \frac{L}{\gamma} \sim \frac{L}{u} \quad (3)$

Transport of mass: $\tau \sim \frac{L^2}{D_m} \sim \frac{L}{u} \quad (4)$

$$\frac{L^2}{\gamma \cdot \tau} = \frac{L^2 \cdot u}{\gamma \cdot L} \sim 1 \quad (5)$$

$$\frac{L^2}{D_m \cdot \tau} \sim \frac{L^2 \cdot u}{D_m \cdot l} \sim 1 \quad (6)$$

where

l : length of travelling, τ : time, L : diffusion distance, γ : thermal diffusivity of liquid, D_m : mass diffusivity, U : fluid speed

The design steps of the microreactor are found elsewhere in (Abid, 2015; Al-Raie, 2005; Wang et al.,

2013; Yong and Sangmo, 2003). Figure 2 shows the dimensions of the reactor pattern as designed and schemed using 2D AUTOCAD software. CNC milling machine type C-tek, at the workshops of the University of Technology (UOT), was used to fabricate the microreactor which consisted of two parts, the upper one was made of a transparent elastic polymer and the lower one was made of aluminum alloy.

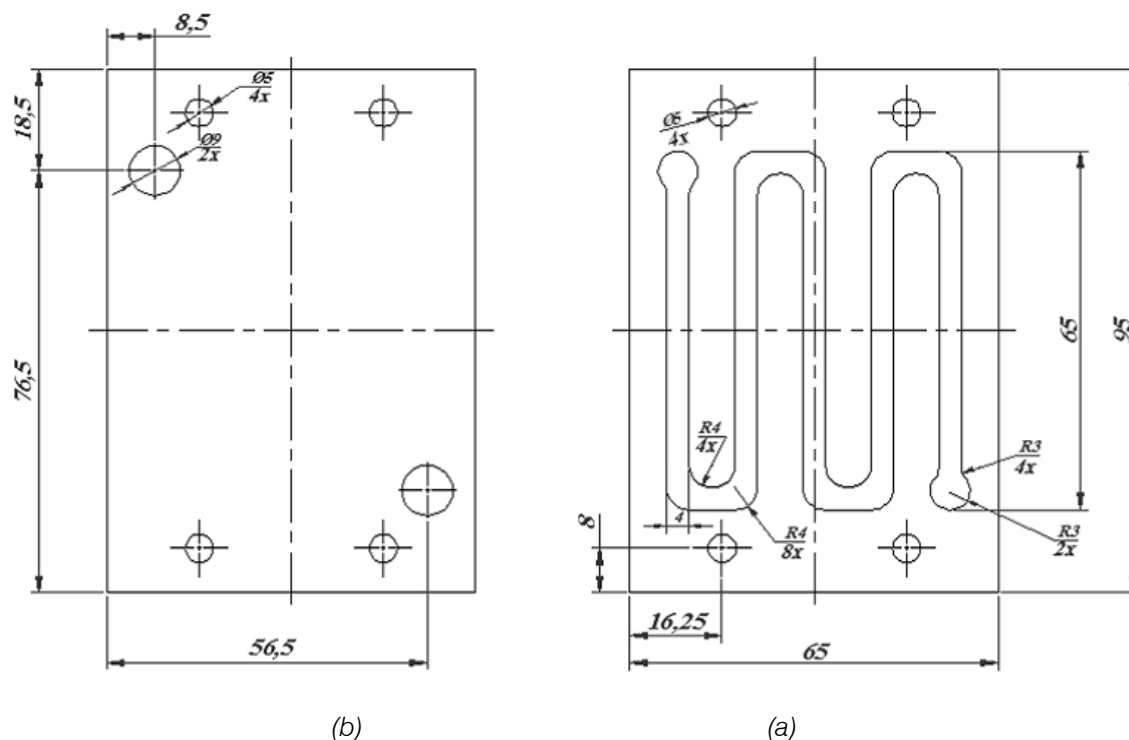


Figure 2: 2D AUTOCAD schematic of the microreactor, (a) lower part and (b) upper part (all dimensions are in mm)

a) Catalyst

To enhance the polymerization reaction, TiO_2 particles were deposited onto the microchannel of the lower part of microreactor as follows (Abid, 2015):

1. The microchannel was first washed with a 5 wt% of caustic soda solution.
2. In a 25 ml beaker, half gram of TiO_2 catalyst was added to a mixture of 5 mL (5 % w/w HNO_3) and 10 mL of 50% (w/w) methanol. The mixture was intensively homogenized with a magnetic stirrer at 400 rpm.
3. After 30 minutes of agitation, a syringe was used to draw a 5 ml of the well-dispersed mixture and injected it into the microchannel. The microchannel which was filled with suspension allowed drying at 120°C for two hours into an electric oven.
4. The deposition process could be carried several times so as to avoid naked batches. Microchannel was scanned using SEM (model Inspect S50, S/N 9922650, FEI Company, USA). Scanning procedure was carried out at the Department of Applied Sciences, UOT.

b) Experimental setup

Figure 3a and Figure 3b show a schematic and an image of the experimental setup, respectively. The experiments were carried out under solar light and being repeated under indirect solar irradiation conditions by installing the experimental setup under shadow. The operating conditions (i.e., APS: aniline molar ratio, inlet mixture flow rate, and initial feed temperature) are kept the same so as to obtain a fair comparison between the two cases. 200 mL of a mixture of aniline in HCl was contained in a 250 mL graduated glass bottle connected to a micropump (model 200.015.230.016 by Williamson Co., England) via a regulating valve. Another 250 mL glass graduated bottle contained 200 mL of APS in HCl with 0.2 g of $(\text{CoCl}_2 \cdot 6\text{H}_2\text{O})$ was connected to a second micropump. Temperature of the two bottles was kept constant by a temperature-controlling water bath. The mixtures into the two bottles were kept in good homogeneity by placing the water bath on a magnetic stirrer as shown in Figure 3a. The suction valves were calibrated against the level in each container, so different flow rates could be delivered to the

microreactor separately in each run. The feed reactants fed to the microreactor via the two micropumps. The initial feed temperature was measured by two mercury thermometers immersed into the bottles. Microreactor effluent was collected in a graduated 500 mL container. After passing through the microreactor, the solution was collected in a product vial containing 1 M NH_4OH for converting polyaniline hydrochloride to a polyaniline

base. Reaction mixture was filtered under vacuum and washed with ethanol and then dried at 60°C for 6 h to obtain PANI emeraldine salt (ES) as a green powder. All containers and tubing outside the microreactor were shielded from UV-exposure. Flowrates of 0.75, 1, 1.5, and $2\text{ L}\cdot\text{min}^{-1}$ were used which correlate to 6.9, 5.2, 3.46, and 2.6 min residence times, respectively. Each run was repeated at different molar ratios of (APS: aniline).

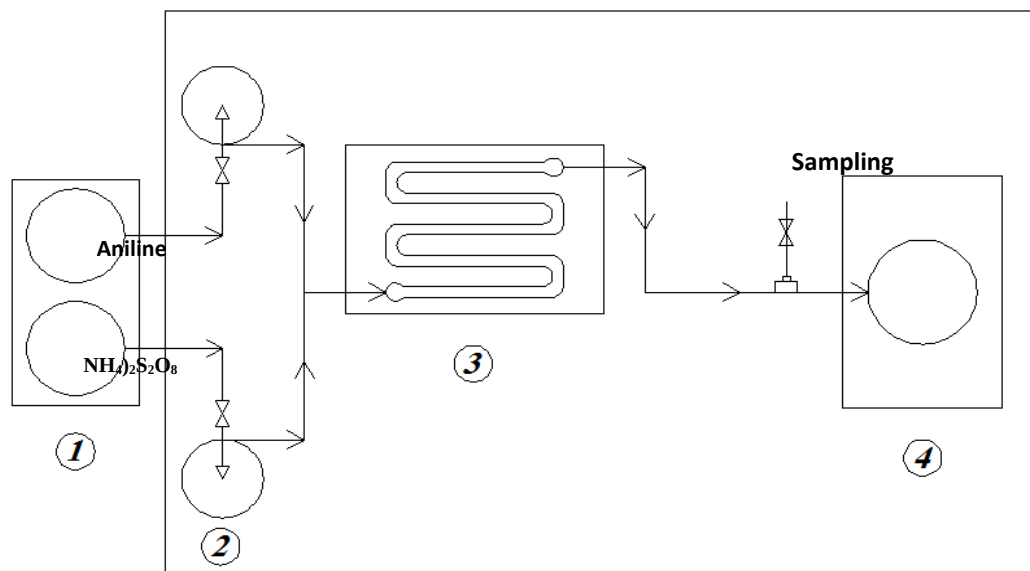


Figure 3 a: Schematic diagram of the experimental setup

1: Magnetic stirrer with temperature-controlling bath; 2: Micropumps; 3: Microreactor; 4: Product collector

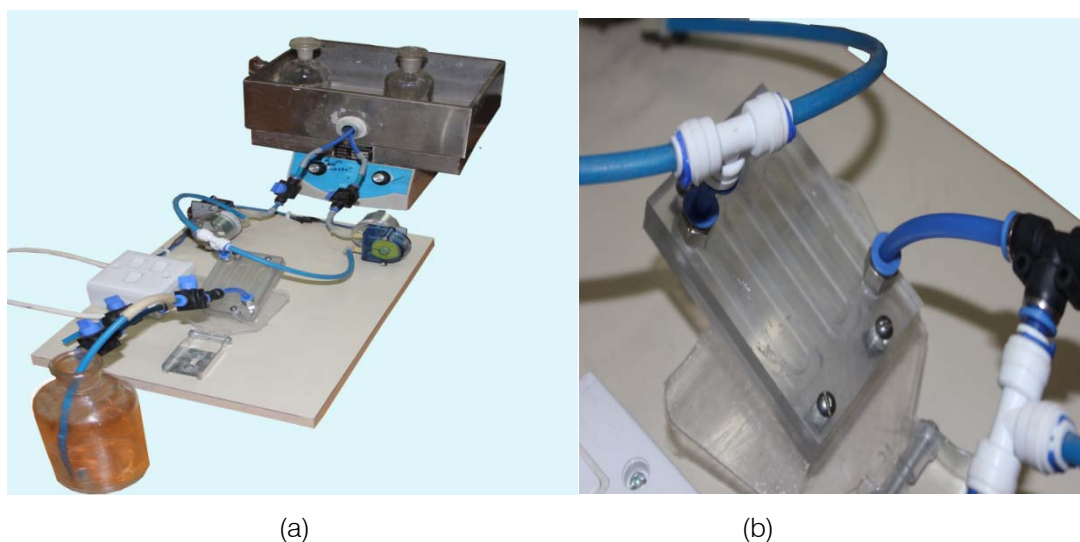


Figure 3 b: Images of the experimental setup (a) and microreactor (b)

IV. EXPERIMENTAL DESIGN

The experimental runs were designed using the factorial method which has a high reliability. Real values of the controlled variables (F) such as (initial feed temperature, mixture flow rate, and molar ratio of APS: aniline) and their corresponding levels (Le) are shown in

Table (1). Each experiment was repeated twice to get accurate results.

Table 1: Selected levels and factors

F Le	Real variables		
	Initial feed temperature [°C]	Mixture flow rate[ml. min ⁻¹]	(APS: aniline) [molar ratio]
1	25	0.75	0.8
2	5	1.00	1.0
3		1.5	1.2
4		2	1.4

V. RESULTS AND DISCUSSION

a) Catalyst deposition

As can be seen in Figure 4 (a and b), the third coating with TiO₂ nanoparticles onto the microchannel lead to complete coverage. The total thickness of

coating was approximately calculated by estimating the actual weight of TiO₂ nanoparticles used for coating, the area covered, and the known bulk density of dried nanoparticles. The total thickness was approximately estimated to be 6 µm.

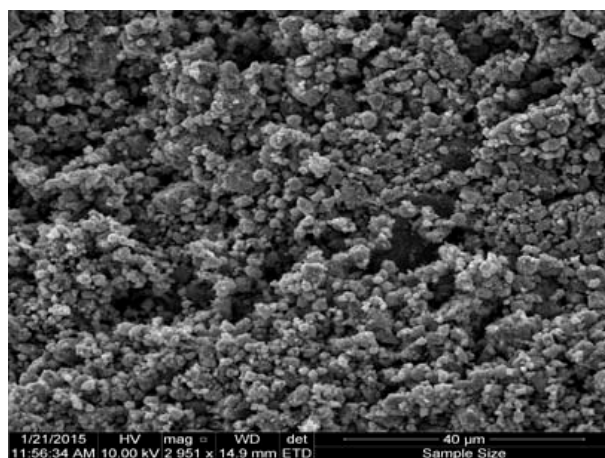
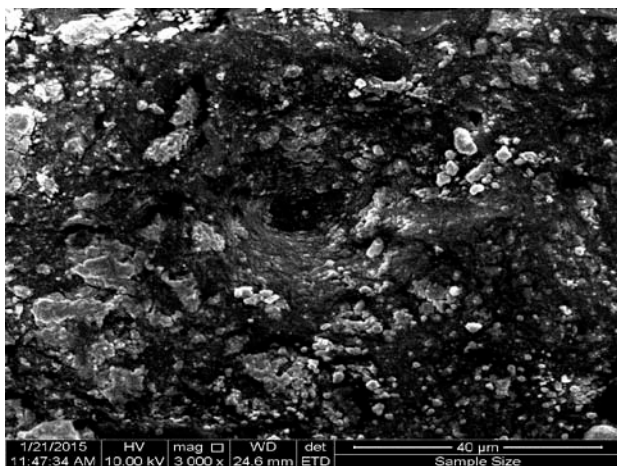


Figure 4: SEM images of different coatings of nanoTiO₂, after 1st coating (left) and after 3rd coating (right)

b) Morphological Analysis

Figure (5) shows the morphology of PANI powder synthesized under indirect solar light at 25°C and under direct solar light at 5 and 25 °C, respectively. As can be seen in Figure (5a) a surface of porous structure composed mainly of granular sharp edges in size ~ 15 µm. Figure (5b) shows a granular sharp edge surface but with less porosity. This may be attributed to the effect of solar irradiant which indicated that the morphology of the conducting polymer is strongly dependent on the irradiated excitation wavelength (Sonkawade, 2010; de Barros *et al.* 2003). Micrograph of Figure (5c) shows an agglomeration of nano-crystals in size ~ 2 to 4 µm. This agglomeration may be increased as the operating temperature is reduced further (Faris, 2007). The SEM micrographs of Figures (5b) and (5c) confirmed that the morphology of PANI depends on the solar incident energy and initial feed

temperature used for the preparation. The data reported by (Faris, 2007; Mattoso *et al.*, 1994) indicated that decreasing of synthesis temperature may give a polymer of shorter chains with higher molecular weight.

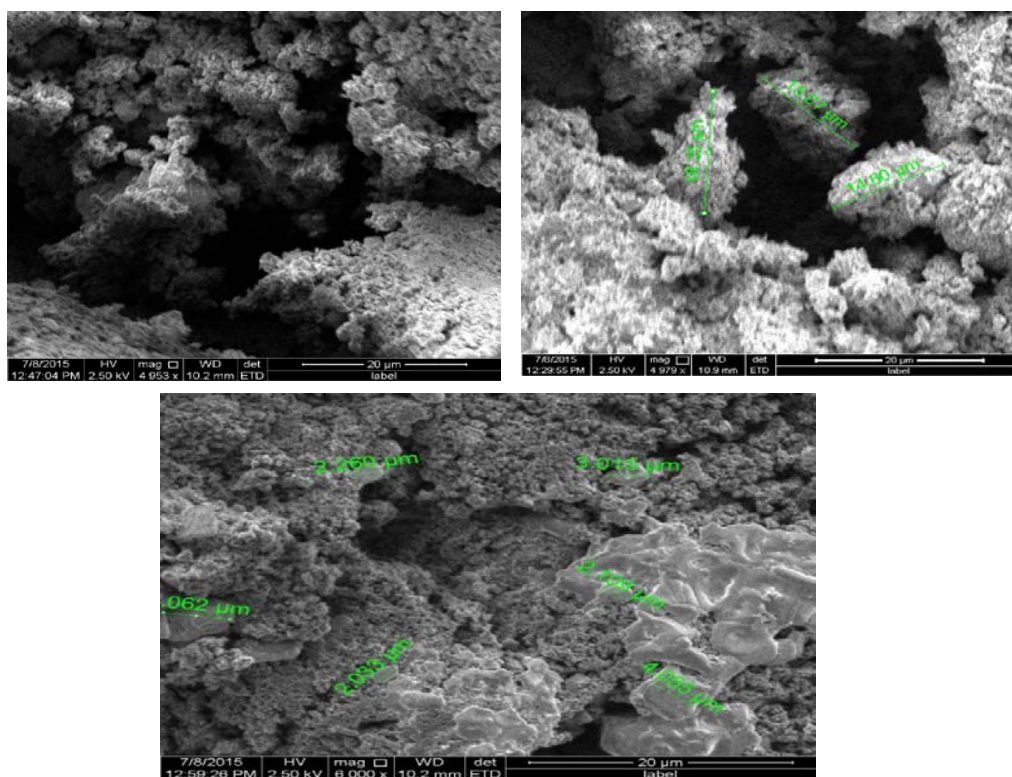


Figure 5: SEM micrographs of produced samples (a) Upper left: indirect solar light at 25 °C; (b) Upper right: direct solar light at 25 °C; (c) down middle: direct solar light at 5 °C

c) Influence of solar incident energy on polymerization process

Figure (6) plots the effect of solar irradiant intensity on normalized aniline concentration at different reaction time at (oxidant-to aniline molar ratio ~ 1.25 and $LHSV = 0.145 \text{ min}^{-1}$). As can be seen in Fig.6, the photocatalytic process affects negatively the time span of polymerization and positively impacted the yield of PANI. Table 2 list the influence of solar incident energy

and initial feed temperature on % yield of the microreactor at 11.5 min of polymerization time. It could be observed that solar incident irradiation enhanced the average yield by 5% over that of indirect solar while the average time of polymerization is reduced by 17%. The polymerization time was reduced by 20 to 27% when increasing temperature from 5 to 25 °C under indirect solar and direct solar, respectively.

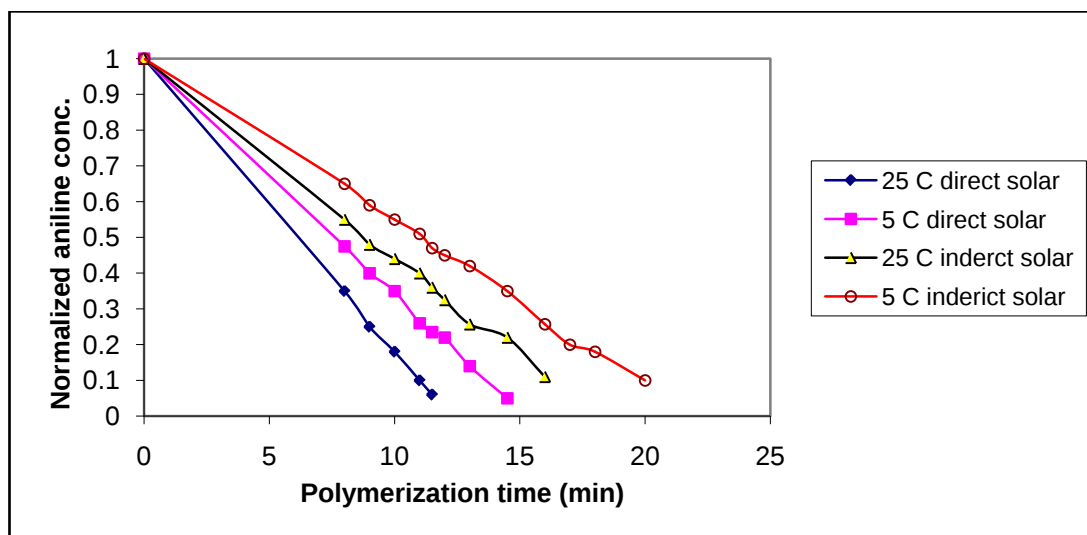


Figure 6: Effect of solar intensity on normalized aniline concentration at different reaction time at (molar ratio of APS: aniline=1.25, and $LHSV=0.145 \text{ min}^{-1}$)

Table 2: Effect of solar energy and initial feed temperature on yield at 11.5 min of polymerization time

	Direct solar		Indirect solar	
Temperature [°C]	5	25	5	25
yield [%]	76.5	94	53	64

d) Influence of LHSV and Initial feed temperature

The effect of LHSV and initial feed temperature on yield of polyaniline synthesized under solar light is illustrated in Figure 7. As can be observed, yield is reduced as LHSV is increased while initial feed temperature shows a different image. The explanation for these trends is that increasing LHSV resulted in decreasing retention time of reactant in the photocatalytic microreactor, consequently the rate of oxidation within the reactor is reduced. The yield of

polyaniline is reduced from 94.0 to 84.2% as LHSV is increased from 0.145 to 0.385 min^{-1} at temperature of 25 °C. The influence of initial feed temperature on polyaniline yield could be also seen in Figure 7. The yield increased from 94.0 to 95.1% as the temperature is reduced from 25 to 5 °C at LHSV = 0.145 min^{-1} . As can be observed, at lower temperature, the increase of polyaniline yield was predominant. This could be due to the molecular chains which have less structural defects at lower temperature.

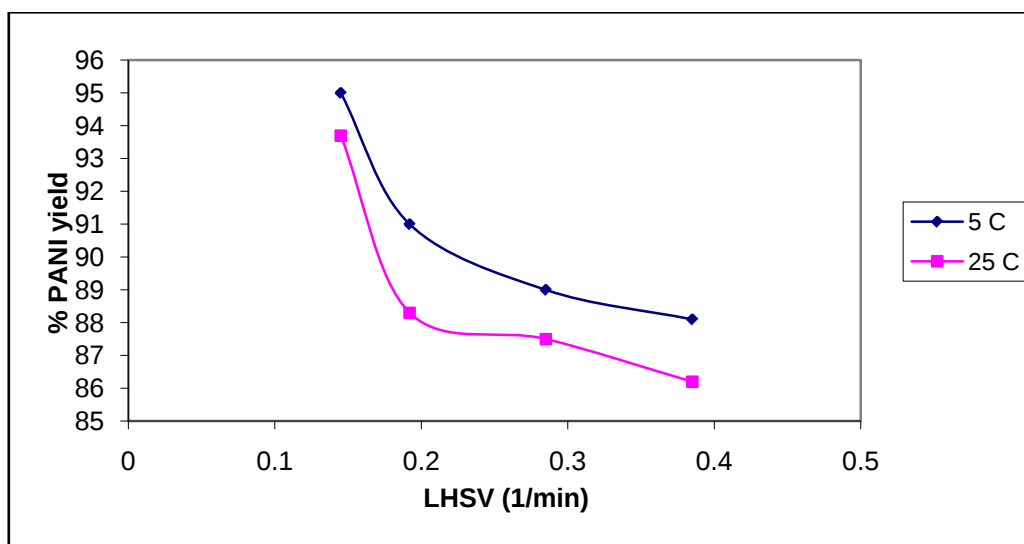
**Figure 7:** Variation of polyaniline yield against LHSV at different initial feed temperature and APS-to-aniline molar ratio = 1.25**e) Influence of (APS: aniline) molar ratio on yield**

Figure 8 shows the influence of (APS: aniline) molar ratio on polyaniline yield. As can be seen when the APS: aniline ratio gradually increased, the yield of PANI increases correspondingly keeping other operating parameters unchanged. The yield reaches maximum value (i.e., 95.1%) after then further increase in molar ratio resulted a gradual decreasing of yield. It is expected that all the aniline which consumed by thereaction at the ratio higher than 1.25 would not increasethe yield but may cause its decrease because the over- oxidationmay convert part of the PANI to quinone. Furthermore, color of the filtrate solution was changed from green-blue to purple when the APS: aniline ratio was more than 1.25: 1. This could be an indication that chain of polyaniline begin to break up. These results agree well with the findings of (Natalia *et al.*, 2007; Adams *et al.*, 1996).

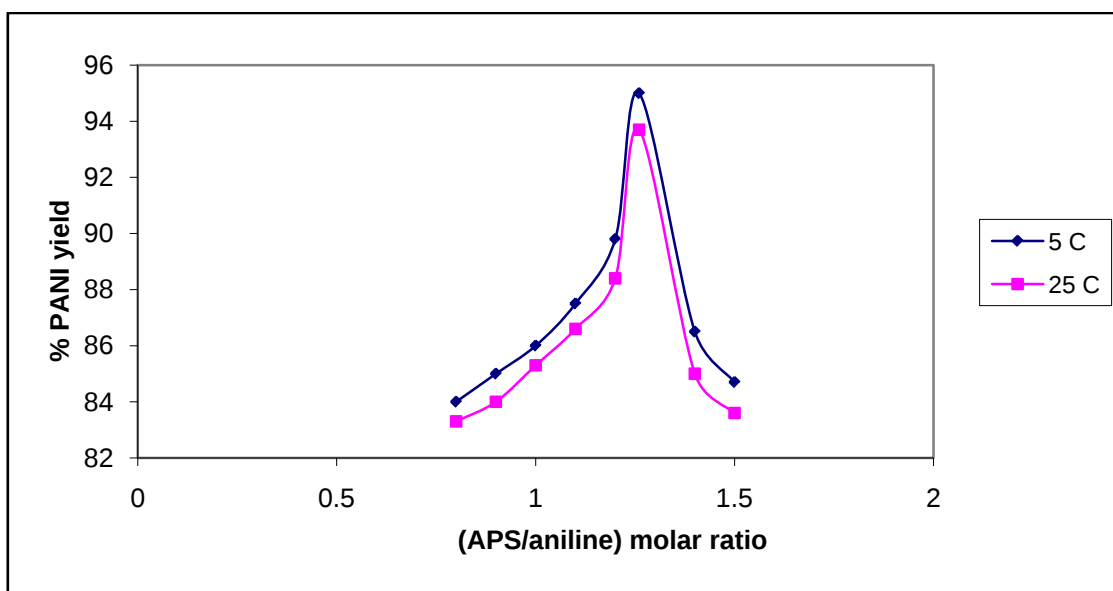


Figure 8: Influence of (APS: aniline) molar ratio on the yield of polyaniline at different initial operating temperature and LHSV = 0.145 min⁻¹

f) Comparison of performance between present study and previous published works

Comparison of performance between present study and previous published works of (Faris, 2007; Adams *et al.*, 1996; Rodolfo *et al.*, 2005; Gordana *et al.*, 2006) is presented. Different operating temperatures to synthesis chemically polyaniline with APS at equal molar ratio of (aniline: oxidant) and 1 mol/L hydrochloric acid in a stirred batch reactor was used by (Faris, 2007). He reported yields of (86.4, 89, and 90.4%) at operating temperatures of (25, 0, and -25 °C), respectively. The Synthesis of polyaniline (PANI) catalyzed by soybean peroxidase (SBP) at 1°C in either aqueous or partially organic media in a batch stirred reactor was studied by (Rodolfo *et al.*, 2005). They claimed a yield of 71% at the optimum conditions of their experimental run. Gordana *et al.* (2006) investigated the kinetics of aniline polymerization in acid solution with ferric chloride as oxidant. They performed the polymerization in a special electro-cell batch reactor at 25 °C. They reported a

maximum yield of 50%. The oxidative chemical polymerization of aniline in hydrochloric acid solution at low temperature was studied by (Rodolfo *et al.*, 2005). They reported that among the reaction parameters studied which affected the molecular weight and yield of the polymer were: (a) reaction temperature; (b) solution pH at the start of the reaction; (c) molar ratio of oxidant: aniline; (d) total reaction time. They concluded that polyaniline of high molecular weight may be obtained by carrying out the polymerization at low temperatures, typically between - 25 and - 30 °C which required the use of an inert solute (lithium chloride was the preferred choice) to keep the aqueous reaction medium mobile. They reported that molecular weight (daltons) and yield% of synthesized PANI were (133000±10000, 94.2%), (153000±9000, 97.5%), (138000±7000, 94.9%) at reaction temperature -20, -25, -30 respectively and reaction time of approximately 15 h. Table 3 summarizes the results obtained by different authors.

Table 3: Comparison of performance between present study and previous published works

Substrate	Process	Type of reactor	Retention time, [min]	Yield [%]	reference
Aniline	Chemical (APS)	batch	120 (0 °C)	89	Faris (2007)
	Enzymatic (SBP) + H ₂ O ₂	batch	480 (1 °C)	71	Rodolfo <i>et al.</i> , 2005
	Electrochemical (FeCl ₃)	Batch electro-cell	180 (25 °C)	50	Gordana <i>et al.</i> , 2006
	Chemical (APS)	batch	~900 (-20, -25, -30 °C)	94.2, 97.5, 94.9 (respectively)	Adams <i>et al.</i> , 1996
	Solar photocatalysis (APS)	S-shaped microreactor	14.5 (5 °C)	95	Present work

V. CONCLUSION

The present work aimed to study the feasibility of microreaction process for PANI synthesis under solar light. The chemical polymerization of aniline in aqueous HCl solution with APS as the oxidant was investigated in a continuous operated solar photocatalytic microreactor with TiO₂ nanoparticles as photocatalyst. The performance of the system was studied at different operating conditions (e.g. initial feed temperature, LHSV, and (APS/aniline) molar ratio). Scanning electron microscopy (SEM) was used to test the surface characteristics of the polymeric material produced. It was shown that surface morphology of PANI samples affected by solar incident energy characterized by reduced surface porosity. This could improve the conductivity of the polymer as confirmed by other published data. Results showed that initial temperature has positively affected the rate of polymerization but it affects negatively the yield of polyaniline, yield of polyaniline was decreased as LHSV of the microreactor increased, and an optimum (APS: aniline) molar ratio of 1.25 was found to give the maximum yield of polyaniline. Results indicated that solar incident irradiation enhanced the average yield by 5% over that of indirect solar while the average time of polymerization was reduced by 17%. The polymerization time was reduced by 20 to 27% when increasing temperature from 5 to 25 °C under indirect solar and direct solar, respectively. Data of batch reactors from published literature were used for performance comparison with the present work. Results showed that the solar microreaction system offered an excellent result (i.e., a yield of 95% under solar light at 5 °C within 14.5 min.) compared with other published data presented in this study. Results of the present work confirmed the feasibility of the microreaction process for aniline polymerization under solar irradiation.

VI. ACKNOWLEDEMENT

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