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Preface to Second Issue (Special Issue)

Under the ownership of Burdur Mehmet Akif Ersoy University, Scientific Journal of Mehmet Akif Ersoy University (Techno-Science) has been published as of September-2018. Devotion and effort are required for a qualified academic journal. The DergiPark scholar journal management system has provided great convenience to control the processes of this journal. Of course there is a young, dynamic, original and hard-working team to control the processes of this journal. When everyone does their mission well, the management of all processes is perfect.

Although we plan to publish 3 issues per year, sometimes there is a need to publish special issues. Although we are a young journal, the interest of scientists in our journal is very intense. This is our second issue and first special issue. We plan to publish a special issue again in December.

We would like to thank all the authors of their original papers for their efforts in the evaluation of these papers. It's about to meet the next issue.

November 20, 2018
Prof. Dr. Afşin GÜNGÖR
Executive Manager and Editor
On behalf of the Editorial Board

Techno-Science

Scientific Journal of Mehmet Akif Ersoy University

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[3]. Carbone, G., Ceccarelli, M. (2005). Legged robotic systems. Kordić, V., Lazinica, A., Merdan, M. (eds.), *Cutting Edge Robotics*. Pro literatur Verlag, Mammendorf, p. 553-576.

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[5]. BS EN 14214:2012+A1:2014. *Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods.* The British Standards Institution. London.

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[6]. Tsukahara, E., Takurou, K. (2015). *U.S. Patent No. 9010288*. Shizuoka: U.S. Patent and Trademark Office.

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[8]. Yager, J. (2000). *Practice guidelines for the treatment of patients with eating disorders* (2nd ed.). Washington, DC: American Psychiatric Association.

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Original Research Article

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PRODUCTION OF BIOGAS AS AN ENERGY SOURCE IN COLDER AREA, USING FLAT PLATE THERMAL COLLECTOR

Naqeeb Ullah Kakar[1*], **Jafar Khan Kasi**[1,2], **Ajab Khan Kasi**[1], **Samiullah Tareen**[1]

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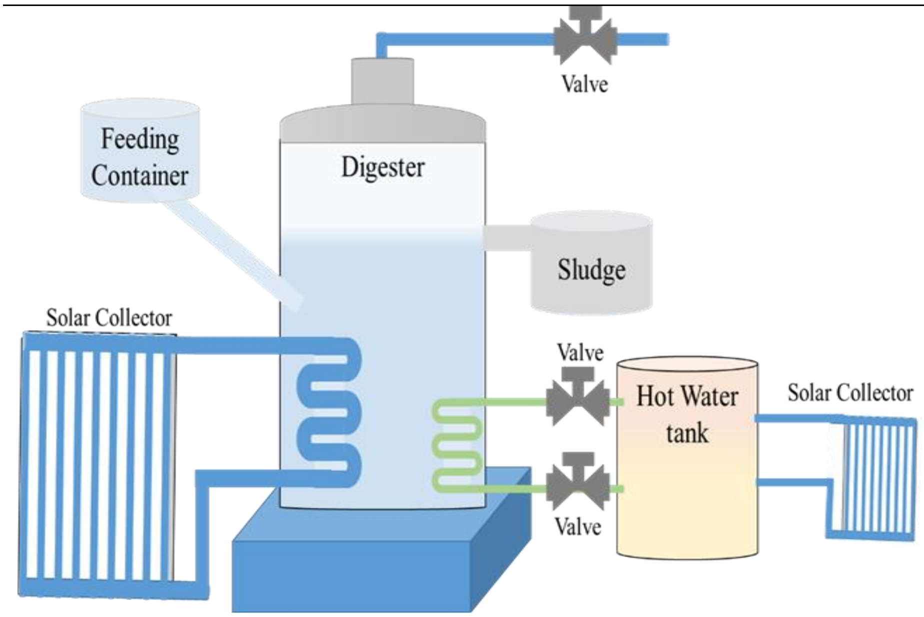
HIGHLIGHTS

- Two pilot scale anaerobic digesters each of volume 750 litters were installed for this research.
- For the heating of slurry, solar flat plate thermal collectors were used in winter in colder areas.
- Hot water was circulated inside digester via copper pipe coils.
- Cow dung was used as starting manure and food waste was filled daily into digester.
- The temperature of digested slurry was enhanced (19-23 °C) during winter in cold climate
- Production of biogas was 2954L that was 3.5 times higher than without thermal collector.
- Fraction of methane was 61% but without thermal collector it was 56%.

GRAPHICAL ABSTRACT



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ABSTRACT

Biogas is a good source of renewable energy. This research work has been done for the design, fabrication, and investigation of a digester with solar thermal flat plate collector to heat slurry inside the digester in order to maintain the temperature in appropriate range (35±2). For production of continuous biogas in winter, a minimum temperature is required for the slurry 3 kg COD/m³ organic waste. The Hydraulic Retention time for this research experiment was 10 days. Flat plat thermal collector is used in this research to heat water and circulate it inside the digester. The hot water is circulated by copper coils during the winter season. By adopting this method the temperature of the slurry enhanced to required minimum temperature and the production of biogas was continued through the whole year in the colder area. The data collected from the experiment showed that using of flat plat thermal solar collector is the appropriate method for heating slurry to produce biogas through the whole year in the colder area in winter season.

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1. INTRODUCTION

To maintain the up going prices of fuels and sources of energy we need an alternative source to replace it. The converting of biomass into energy by anaerobic digestion is convenient way of replacement. In addition to this, biomass technology is a key to control the environmental pollution by converting methane from greenhouse gas into renewable energy source. The anaerobic digestion technologies of food waste is the convenient way for food waste management because of controlling the increasing basic essentials for renewable energy generation and reducing the greenhouse gasses emitting from wasted materials [1]. The management of food waste in the modern world is a major problem faced to various nations [2]. Pakistan Environmental Agency (PEPA) 2005 reported that the average solid waste generation in Pakistan is .613 kg per capita daily and 90% solid waste is biodegradable [3]. The miss management of these wasted materials is a very big source for environmental pollution [2]. Due to high content of water, food waste is easily biodegradable and a big reason for production of bad odour [4].This also emits greenhouse gasses (Methane) in landfills [5]. Heat trapping power and warming effect of methane as compare to carbon dioxide is 25 times and 72 times respectively higher than carbon dioxide [6]. Therefore it is very important to manage these wasted materials in a proper manner. The anaerobic digestion is a best choice for the management of wasted materials [5]. This oxygen free process (Anaerobic digestion) has two types: wet (<10% total solid) and dry (>20% total solid) [7].

Due to many reasons like a renewable energy cause, bio manure, pollution control, management of environment, suitable technology and recycling of wasted materials, many developed and developing countries have a great interest in anaerobic digestion process of biogas technology [8]. This is a natural process where bacteria break or decompose the organic matter in oxygen free environment. The anaerobic digestion treatment is focused due to low power utilization, long cleaning cycle, little sewage volume etc. [9]. The decomposing of organic matter results in 60% methane, 37% Carbon dioxide, 3% Nitrogen, 1% Hydrogen, and 1% Hydrogen sulphide. There are four stages for transformation of organic compounds into biogas; they are Hydrolysis, Acid genesis, Acetogenesis, and Methanogenesis. In the hydrolysis, the organic compound transfer into smaller components. In Acid genesis bacteria use these smaller components to produce volatile fatty acid, ethanol, Carbon dioxide and hydrogen. In Acetogenesis, bacteria transfer these products in CH_3COOH (acetic acid) CO_2 and H. At last Methanogenesis bacteria use hydrogen and acetate to create methane and Carbon dioxide.

The anaerobic digester is designed to accomplish the decomposition. It is constructed in such a way that it can run under mesophilic temperature (20-45°C) or thermophilic temperature (40-60°C) ranges. In addition to these temperatures, Methanogenesis is possible under low temperature less than 20°C. This process is called psychrophilic digestion. But this method is not explored as thermophilic and mesophilic.

Biogas is a mixture of different gases. Methane (CH_4) is main component of biogas. It also contains carbon dioxide (CO_2), hydrogen sulphide (H_2S), nitrogen (N). Methane is odourless, inflammable, and a colourless gas. Biogas is also called marsh gas, sludge gas, sewerage gas, klar gas, gobar gas, bioenergy, and fuel of future. There are 50 to 70% of CH_4, 30 to 40% of CO_2, 3% of N and 1% of H_2S. A 1000 ft^3 biogas is equal to 600 ft3 of natural gas, 5.2 gallons of gasoline, or 4.6 gallons of diesel oil. A family of four members can consume 150 ft^3 (4227L) biogas per day for their lighting and cooking purposes. This amount of biogas can produce from the dung of three cows and family night soil [10]. Methane is a greenhouse gas and plays an important role in the warming of atmosphere. The emission of methane to the atmosphere can be reduced by anaerobic digestion process. The process of production of biogas from digestion method has many benefits like heating, lightning, fuel, converting of organic waste into the best quality fertilizer, reduction of work for collection of firewood and cooking purpose. In spite of above benefits, the most important and the best benefit is the protection of environment from the greenhouse gases.

The production of biogas from the digester depends upon following factors, Material kind, solids loading, ambient temperature, retention time, the temperature of the slurry in the digester. It also depends upon pH level, nitrogen inhibition, Carbon to nitrogen ratio, retention time [10]. Among them, temperature is the most important factor that influences the production of biogas [11]. Up and down in temperature can result in decreasing bacteria or death of bacteria which result in decreasing of production of biogas [12]. Dioha et al 2006 reported that decrease in biogas production in colder season is due to the changes in atmospheric temperature which influenced the soil temperature [13]. Therefore we need a heating system for the slurry of digester. Many sources are used to control and maintain the temperature of the digester like insulation of digester, heat exchanger, heating elements, water bath and steam injection. The solar collector is the most suitable source for heating the slurry inside the digester in order to maintain the temperature to enhance the production of biogas. In winter, to warm up the biogas plant, solar collector is used for this purpose to maintain suitable temperature for fermentation. In the winter season in colder area, the rate of production of biogas is decreased due to the decrease in atmospheric temperature. To obtain optimum range of biogas we should maintain the temperature of the digester up to a certain level. The suitable range of temperature for the production of biogas is 35±2°C [11].

In this research a flat plate thermal collector has been used to maintain the required temperature of the digested slurry. Heat stored in the water tank can be used as source of heating through circulation in the digester in the absence of solar radiations.

2. METHODOLOGY

2.1. Experimental Setup

A pilot scale two anaerobic digesters each of volume 750 litters was used for this research. The dimensions of the digester are width: 88 cm and length: 195 cm. The walls of the digester are 2 mm thick. Two valves one for inlet and other for outlet were connected with digester. One of the digester is shown in the following Fig. 1. The schematic diagram is given as in the Fig.2.

The inlet valve was used for feeding while outlet valve used for withdrawal of digestate. There are two valves for biogas on the upper portion of the reactor. One of the valves was linked with gas pressure meter and other was joined with gas meter with the help of gas pipes. The ISE50-02-62L gas pressure meter was used. The daily biogas was temporary collected in the upper part of the digester which was well sealed. All the valves were closed tightly with screw caps. A temperature probe with temperature range of -30^{o}C to +55^{o}C with accuracy $\pm$1 were used for measuring the temperatures of ambient air, the digester, surrounding soil and slurry mixing tank. A DC motor stirrer of 1000 rounds per minute was also fixed in the reactor for mingling the digested slurry as shown in Fig. 3. The length of the stirrer was 40cm. It was tightly connected with the digester by screw.

Fig. 1. *A 750L biogas digester*

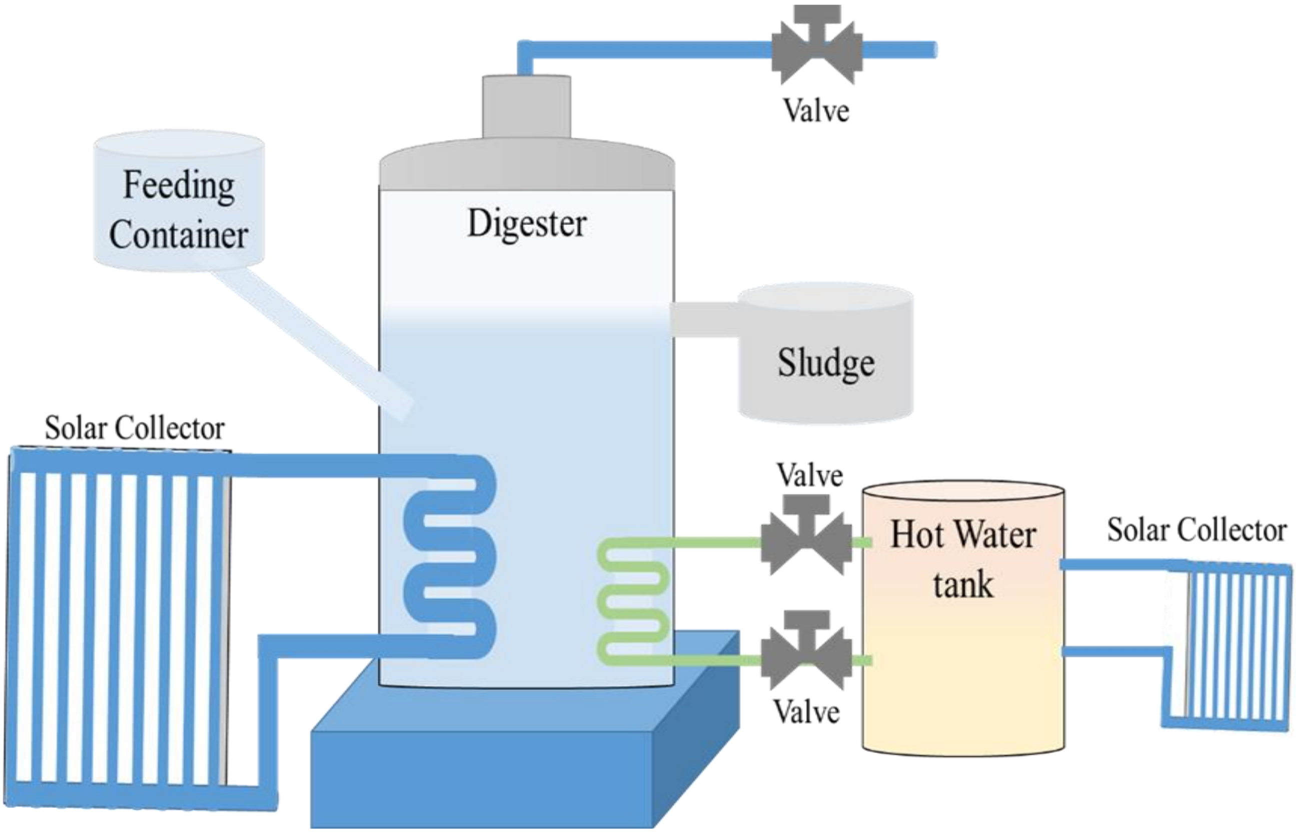

Fig. 2. *Schematic of experimental setup*

Fig. 3. *A DC motor stirrers*

The solar heating system consists of two flat plate thermal collectors each of 2m^2 area and 24^o slope is there for each collector. The spare hot water tank is insulated with 0.8mm black woolen cloth. Water is the heat transfer fluid. One of the collector is applied with the digester in such a way that the cold water comes into the below inlet and the hot water flow out through the above outlet of collector. A copper pipe of diameter 0.75 inch and length 50 feet was whirled inside the digester in a circular shape as shown in Fig. 4. Two valves were used for copper pipe in which one was used for outlet and other was for inlet of hot water.

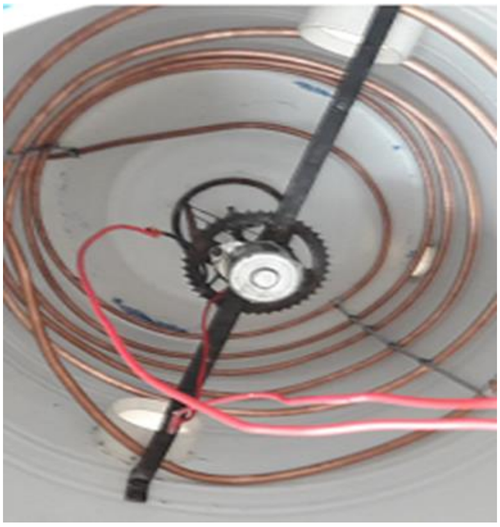

Fig.4. *Inner view of digester with copper coil and stirrer*

The purpose of the collector is to enhance the temperature of the bio digester in cold weather in colder area. This heating system of digested slurry by solar collector is activated automatically when the difference of temperature between output of collector and slurry of digester passes 6^{o}C and the temperature of digester is less than 35^{o}C. When these situations occur the hot water circulates through copper coils which are whirled inside the digester. The digester was placed vertically at a plane piece of wood above earth at 10 centimeters. Water was pumped through the digester to test for leakage before using it for experiment. The digester was insulated by black woolen cloth at night time. A flat plate thermal collector was also applied with digester.

2.2. Feedstock and operating conditions

The initial feeding stock was 400 L slurry of 50% fresh cow dung and 50% of water with 2% dry matter accounting for almost 60% of digester volume was poured into the digester for day 1 of the experiment. The system was left for 10 days to develop microbial community inside the digester. 3kg food waste with water was filled into the digester daily. The cow dung used for this experiment was collected from a farm where the cows were kept in an open cow house. A sample of cow dung was collected for dry matter (DM) finding. A separate mixing tank was also used for storing of cow dung slurry to feed into the digester. The pH of the slurry was determined by OHAUS-ST10 pH meter. The volatile solid (VS), dry matter, total nitrogen, total ammonia nitrogen, volatile fatty acids (VFA), crude fiber (CF) and crude lipid were determined. The temperature of the digester was measured at three different position of the digester that is at middle, bottom and below the surface of digested slurry. Food waste is obtained from different hotels of the city. The different indigestible materials like egg shells, plastic, bones, etc. are removed from food waste. Food waste is cooked rice, potatoes, vegetables, chicken and meat. Then these food wasted materials are chopped to the size of 12mm and filled it into the digester.

3. RESULTS AND DISCUSSION

The main aim of this research work is to utilize the ability of solar radiations via solar flat plate thermal collector to maintain the temperature of digester in winter. The optimal temperature for the production of biogas is 35±2 [11]. In winter, the average temperature of the digester decreases with ambient temperature causes low production of biogas. In this research two methods were used: Using a solar collector to circulate hot water through the digester and without solar collector. The data from these two techniques were compared with each other. The light intensity and atmospheric temperature were measured. The tendency of light and temperature for both methods were same. The intensity of light and air temperature for both methods was similar. That confirms the amount of solar radiations for both methods are identical. Therefore the variance in the yielding of biogas is improved only by method of utilizing of solar radiations to heat up digested slurry. The composition of the gas and pH of the digested slurry was studied and recorded in table 1. The pH value of digested slurry for the production of biogas was in the range of 6.9-7.2. It was also observed that pH value for both methods were at moderate level. For the activity of bacteria, this natural pH value is applicable. The composition of the biogas was analysed during the experiment and recorded in table 1. From this recorded data it was cleared that using flat plate thermal collector, the methane gas was yielded (58-61%) while without collector it was (53-56%). The % composition of other components of biogas was also recorded in table 1. As the organic matter was used as a feeding material in this research therefore the proportion of hydrogen sulphide (H_2S) was very low. The high % proportion of hydrogen sulphide (H_2S) could damage metallic parts of bio reactor [13].

A comparison of different components of biogas, total amount of produced biogas and pH value of the two methods were studied and recorded in the following table 1.

Table 1. *A comparison of biogas composition with and without solar collector*

Experimental Conditions	CH_4%	CO_2%	H_2S%	N%	pH value	Total biogas (L)
Using flat plat solar collector	58-61	30-39	0.4-1	2-9	6.9-7.4	2954
Without solar flat plate collector	53-56	36-44	0.4-1	2-10	6.9-7.4	856

Temperature of the slurry at different positions of digester with and without solar collector was recorded as shown in the Fig. 5 and Fig. 6. The temperature of the digester was measured at three different positions; just under the surface of slurry, middle and bottom of digester. Figure 5 shows the temperature at bottom of the digester. When solar collector was used, the temperature was in the appropriate range but it was lower than optimal range without solar collector. The solar collector continuously maintained the digester temperature from 7:00 am to 6:00 pm directly. From 7:00 pm to 6:00 am the slurry was heated by spare heated hot water tank. Figure 6 shows the calculations of slurry temperature recorded at the mid of the slurry of two methods. Figure 7 shows the temperatures of two different methods (connecting thermal collector and without connecting) under the surface of digested slurry. It cleared from the recorded results that using flat plate solar collector heating system via copper pipes is the suitable method to maintain the temperature of digested slurry a long time in the optimal range of temperature. Temperature of digested slurry was strongly affected by solar radiations and temperature of air. When air temperature increased consequently the digester temperature was increased. After comparing the air temperature with internal temperature of the two methods, the temperature of the digested slurry of each method was studied.

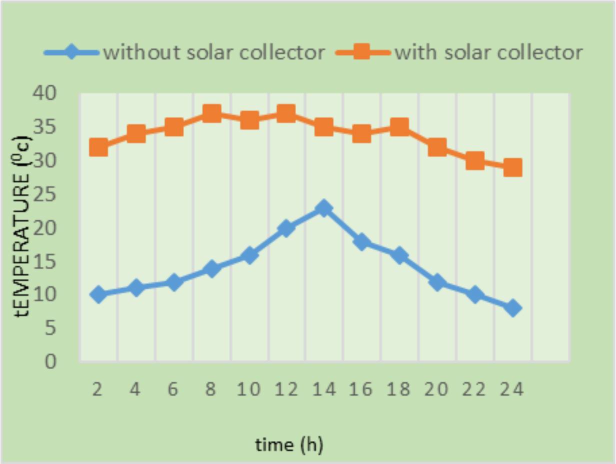

Fig. 5. *The temperature of digested slurry at bottom of digester*

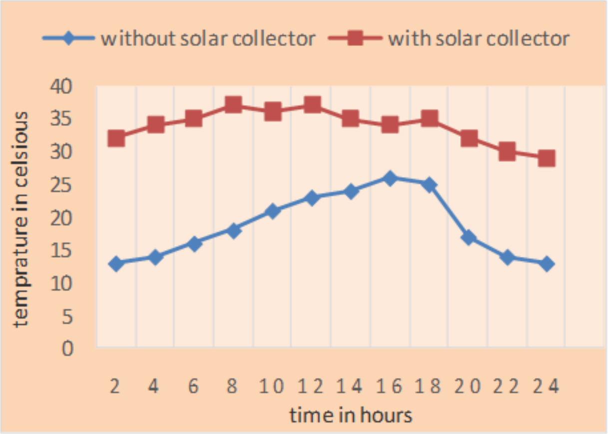

Fig. 6. *Temperature of slurry at mid of the reactor*

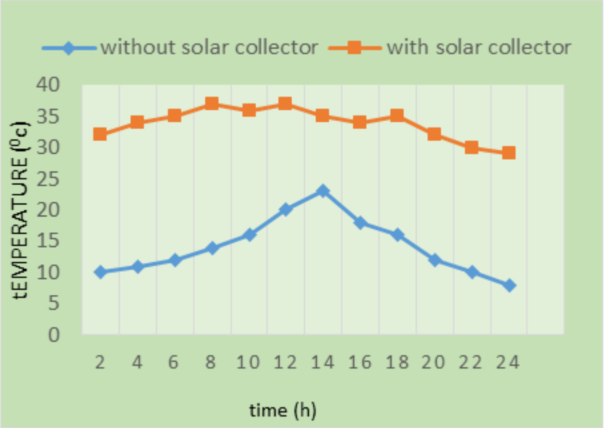

Fig. 7. *Temperature of slurry under the surface of slurry*

The technique of heating digested slurry by solar flat plate thermal collector could increase the temperature of digested slurry from 19 to23°C during the winter season. The comparison of temperatures of two techniques are recorded in the following table 2.

The fermentation process of organic waste inside the digester was increased with heating by solar collector. As in solar heating process the temperature was in proper range for a long time, therefore this technique is more effective for convert organic compound (COD) removal. The COD removal was higher in solar collector heating system than without solar heating. It was 72.4 % in solar collector but 68 % in without solar collector. The COD removal and methane fraction of two methods are illustrated in the following figures 8 and 9 respectively.

Table 2. *A comparison of change in temperature by applying thermal collector.*

Experimental conditions	December	January	February	March
Without solar collector (°C)	16	11	10	13
With solar flat plate collector (°C)	36	34	33	35

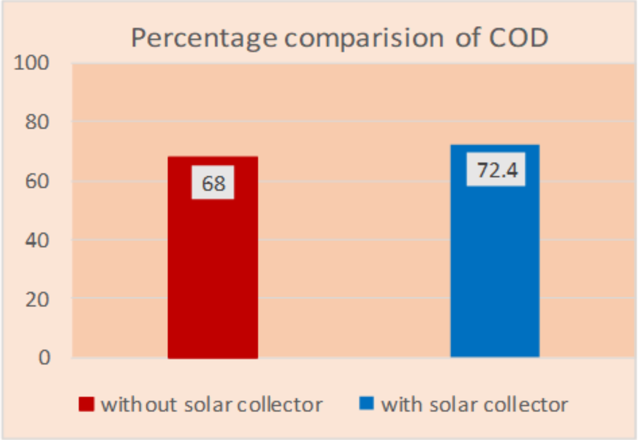

Fig. 8. *A percentage comparison of COD removal of two techniques*

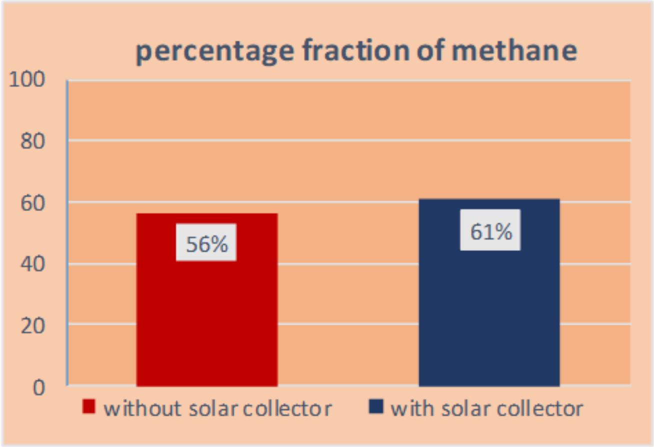

Fig. 9. *A diagram of fraction of methane for two methods*

The comparison of daily produce biogas for each method was recorded in the following table 3.

Table 3. *Production of daily biogas of two techniques.*

Days	1	2	3	4	5	6	7	8	9	10	Total Bio-gas
Non solar collector (L)	20	36	30	60	100	110	130	114	130	126	856
Solar collector (L)	200	300	300	300	300	300	354	300	300	300	2956

According to these results using of solar flat plate collector could conveniently activate the bacterial activity inside the digester. Biogas produced due to this method was greater than without using solar collector because this method maintained the optimal temperature of slurry inside the digester continuously for long time. This means that bacteria are allowed to decompose the organic matters effectively and continuously for the whole experiment [14]. In the case of production of biogas without using solar collector, the temperature of digested slurry was in the lower range of optimal temperature for bacterial activity. Therefore the production of biogas was low. For the decomposing of organic materials during this condition as compared to using solar flat plate thermal collector, the bacteria took longer time. Using of flat collector was more effective to reduce the retention time and to enhance the production of biogas. This confirms that to heat the digested slurry by solar flat plate collector increases the ability of removal of organic waste and allows the quicker immersion of organic waste for following round. A comparison between the yielded biogas with using solar heating and without solar heating methods as illustrated in fig. 11 cleared that the synthesizing of biogas was utmost by heating solar flat plate thermal collector. By using this technique, the amount of produced biogas was 2954 L that was 3.5 times higher as compared to biogas produced without heating by solar collector. The amount of biogas produced by without heating method was 856 L. The comparison of synthesized biogas of two methods is illustrated in the following Fig. 10.

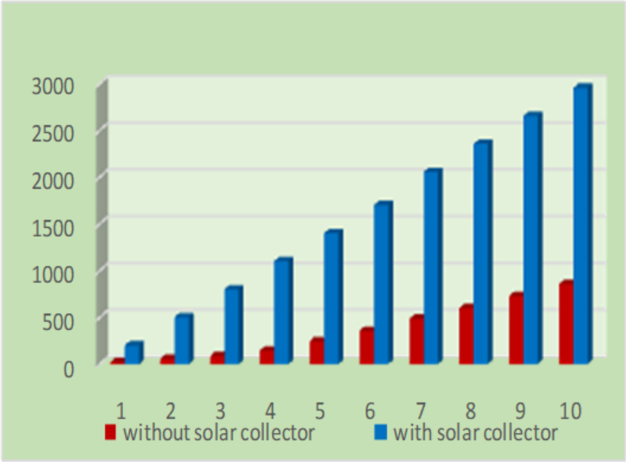

Fig. 10. *Amount of produced biogas of two experimental methods*

4. CONCLUSIONS

Time of the year strongly influenced the temperature of air which affects the temperature of slurry inside digester. Temperature of the digester was affected by the temperature of month. The main purpose of this research is to examine the ability of using radiations of sun for maintaining temperature of digested slurry of 750 L digester to get better production of biogas in winter. This approach of raising temperature consists of two solar flat plate thermal collectors each of $2m^2$ area and 200L spare hot water tank for water storage. The temperature of the slurry was enhanced by circulation of hot water via a copper pipe of diameter 0.75 inch and length of 50 feet. This approach maintained the temperature of the digester within the optimal range of 35 ± 2 °C in winter in colder area. The collected amount of biogas without solar collector was 856 L and that by using solar flat collector was 2954 L. Therefore accumulated biogas by solar heating method is 3.5 times higher than without solar method. This confirms that the use of solar flat plate collector to enhance digested slurry temperature is the most useful approach for production of biogas in colder area in winter. Moreover, from the study of composition of biogas it was confirmed that methane had highest quality by solar heating method. The produced biogas contained 58-61% CH_4, 30-44% CO_2, 2-9% N and 0.4-1% H_2S. The pH value of digested slurry for the experiment was under the range of 6.9-7.2. The COD removal was in highest percentage using solar heating method as the optimal temperature was continued for a long time. It was 72.4 % and in the case of without solar collector it was 68%. The results of this research represent only the period of winter in colder area.

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REFERENCES

[1]. Chen, X., Romano, R. T., & Zhang, R. (2010). Anaerobic digestion of food wastes for biogas production. *International Journal of Agricultural and Biological Engineering*, vol.3 *no.*4, p. 61-72.

[2]. Jabeen, M., Yousaf, S., Haider, M. R. & Malik, R. N. (2015). High-solids anaerobic co-digestion of food waste and rice husk at different organic loading rates. *International Bio deterioration & Biodegradation*, vol. 102, p.149-153

[3]. PEPA (Pakistan Environmental Protection Agency), 2005. Guideline for Solid Waste Management. Pakistan Environmental Protection Agency, Islamabad, Pakistan

[4]. Cheng, H., & Hu, (2010). Municipal solid waste (MSW) as a renewable source of energy: Current and future practices in China. *Bio resource technology*, vol.*101* p.113816-3824.

[5]. Liu, X., GAO, X., Wang, W., Zheng, L., Zhou, Y., & Sun, (2012). YPilot-scale anaerobic co-digestion of municipal biomass waste: Focusing on biogas production and GHG reduction. *Renewable energy*, vol. *44* p.463-468

[6]. Solomon, S., Qin, D., Manning, M., Averyt, K., & Marquis, M. (Eds.). (2007). *Climate change 2007-the physical science basis: Working group I contribution to the fourth assessment report of the IPCC* (Vol. 4). Cambridge university press.

[7]. Karthikeyan, O. P., & Visvanathan, C. (2012). Effect of C/N ratio and ammonia-N accumulation in a pilot-scale thermophilic dry anaerobic digester. *Bioresource Technology*, vol. P. *113*, 294-302.

[8]. Da Silva, E. J. (2010). Biogas Generation: Developments, Problems and Tasks (An Overview). *Page this volume*

[9]. Ren, Z., Chen, Z., Hou, L. A., Wang, W., Xiong, K., Xiao, X., & Zhang, W. (2012). Design investigation of a solar energy heating system for anaerobic sewage treatment. *Energy Procedia*, vol. *14*, p. 255-259.

[10]. Nirunsin, R., Setthapun, W., Dussadee, N., & Ninsonti, H. (2017). Enhancement of household biogas production by solar collector and solar greenhouse. *Journal of Renewable Energy and Smart Grid Technology*, vol.12 *no.*1, p. 103-116.

[11]. Yuan, S., Rui, T., & Hong, Y. X. (2011). Research and analysis of solar heating biogas fermentation system. *Procedia Environmental Sciences*, vol.*11*, p. 1386-1391.

[12]. Uzodinma, E. O. U., Ofoefule, A. U., Eze, J. I., & Onwuka, N. D (2007). Optimum mesophilic temperature of biogas production from blends of agro-based wastes. *Trends in Applied Sciences Research*, vol. *2 no.*1. P.39-44

[13]. Dioha, I. J., Eboatu, A. N., Sambo, A. S., & Birnin, K. A. M. (2006). Investigation of the effect of temperature on biogas production from poultry droppings and Neem tree leaves. Nig. J. *Solar Energy*, vol *16*, p. 19-24.

[14]. James, L. W., Charles, C. R., Mirhd, S. S., & Smith, S. R. (1998). Handbook on biogas utilization. *Georgia institute of Technology, Georgia*.

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Original Research Article

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FABRICATION OF MICROINJECTOR SYSTEM (SIM) USING ANODIC ALUMINUM OXIDE

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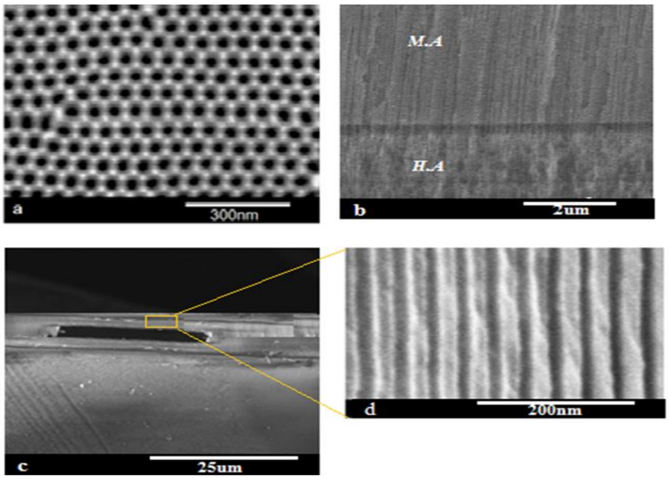
HIGHLIGHTS

- Fabrication of anodic aluminum oxide(AAO) by combing M.A and H.A
- Develope microinjector system (MIS) using anodic aluminum oxide
- First experimental study about embeded micro flow channels with injecting nozzle fabricated inside alumina membrane.

GRAPHICAL ABSTRACT



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Hard anodization(H.A)

ABSTRACT

The present study provide method to construct a novel type of micro-injector system (MIS) for microfliudic delivery inside nanoporous anodic aluminum oxide (AAO) membrane. Now a day's these micro and nano combined structure gain attention in medical and biological applications. This fabricated micro-nano structure consists of a thin film of anodic aluminum oxide having 50-100µm wider and 12µm deeper channel. A thin Anodic Aluminum Oxide (AAO) is fabricated by combing Mild anodization in oxalic and Hard anodization (H.A) in sulphuric acid. The dimension and an anisotropic etching were investigated by scanning electron microscopy (SEM). These channels are used for fluid flow on micro scale. These channels are connected with a nozzle like microchannel which can perform fluid injection function. This microinjector system is simply manufactured by embedded microchannel and there is no moving micro part inside nanoporous membrane. Fabrication process is mainly based on photolithography and wet chemical etching technique. Wet chemical etching takes place in 5 wt% of phosphoric acid solution. Dimensions and the shape of these microchannels depend solely on anodization and etching conditions. The presented system can be used into two way: in first way the fluid can be injected through nozzle like channel inside AAO and in second way the liquid can be purify and filtrate through nanoporous AAO membran. This study provides a low cost fabricated micro-nano combined structure which could be further used in different types of microfluidic devices and enable the device to perform the function of injection, filtration and purification.

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1. INTRODUCTION

Drug delivery is the process of controlling a pharmaceutical compound to acquire tonic effects in human and animals. The importance of drug delivery increases for the treatment of animals and human diseases. For this purpose several drug systems have been constructed like liposomes, microsphere, gel and many others [1]. For in vivo drug delivering applications smart particles have gaining much attention for researchers and these particles are biocapsule [2], microparticles [3] and nanoparticles [4]. Delivery of drugs at controlled rate, targeted delivery is other very significant method and pursued energetically. Microinjection is another well-established cellular technique that enables foreword of exogenous materials into cell in which needles inserted into the cell for injection [5]. Conventional LIGA process was applied to obtain high aspect ratio (HAR) solid microneedles array using biocompatible material such as PMMA. In LIGA process the plannar exposure method and layer by layer technique is used to achieve the 3D microstructure .The sharp tip microneedles was formed with deep x-rays lithography (DXRL) [6]. The device with hollow microneedles for ECG measurement provide comport home health care. The device consist two layer contain silicon die with hollow microneedles second layer is polymer die with pt electrode. The depth and diameter is around 100um which etched by using deep reactive ion etching (RIE) [7]. Current efforts to automate the microinjection technique by replacing operator with robotic but this has come at the expense of instrument and complexity [8]. Complementary efforts have to require using MEMS fabrication process to create devices which improve the reproducibility of injection and integration of numerous functions into a single chip enables simplifications relative to robotic microinjection instrumentation [9]. Since 1990 microfluidic devices has developed into versatile technology and different approaches for integrating membrane functionality in microfluidic chip is getting much attention [10]. Here in this research we purposed micro-nano structure has potential applications in the biology and medical related fields as fluidic delivery. In this paper nanoporous AAO membrane with injecting functionality is fabricated by photolithography and chemical etching technique. This simple and low cost microinjecture system could be integrated on single chip to obtain microfluidic based microinjector system.

2. EXPERIMENTAL AND METHOD

The fabrication of microinjector system was divided into five steps including membrane fabrication, deposition of adhesive layer, photolithography and chemical etching. The fabrication steps of AAO membrane with modulated pore diameter is shown schmetically in Fig 2.

2.1. Fabrication of Anodic Aluminum Oxide (AAO)membrane

Fabrication of micro injector system is based on Anodic Aluminum Oxide (AAO) nanoporous membrane formation on Aluminum (Al). In this work highly pure aluminum sheet (99.999%) of desire shape with thickness of 300um were used and work as working electrodes. Aluminum sheet were cleaned ultrasonically in acetone and DI water for 10 min and then sample were electrochemically polished in a 1:4 (volume ratio) mixture solution of ethanol and perchloric acid under vigorous stirring at 0°C. Electro polishing was done at 20V for 5 min to achieve mirror finished surface. Electro polishing eliminate the influence of oxide film on aluminum surface. After electro polishing the Al sheet were again cleaned ultrasonically in acetone and DI water for 10min.Anodization of surface finished aluminum sheet were performed under potentiostatic mode in 0.3M oxalic acid solution at 32V with vigorous magnetic stirring for 2 h and temperature were kept constant at 1°C. Porous aluminum sheet were immersed into mixture of chromic acid and (1.8 wt% and phosphoric acid 6wt% for 10 min to remove porous oxide layer completely. The resulting textured aluminum sheet was used for second anodization step. The second step of anodization comprises mild anodization (M.A) and hard anodization(H.A).M.A were carried at 32V in oxalic acid solution for 24 h at 0°C. Porous oxide layer were reanodized under potentiostatic condition in electrolyte solution of 0.3M H_2SO_4 at 38V for 15 min.

2.2. Fabrication of microinjector system

Schematically view of microinjector system is shown in Fig 1. This system was formed by selective etching of AAO which was fabricated by combining MA and H.A. A thin adhesive layer of silver was deposit on template by using plasma sputtering. Uniform thin layer of photoresist was obtain by applying positive photoresist on substrate with the help of spin coater at spin speed of 1000 to 3000rmp for10 second. Soft backing was carried at 90°C for 20 min and mask of desire texture was placed in contact with AAO sample. Now the sample was exposed to ultraviolet under 1000w ultraviolet lamp for 1min. After UV exposure hard backing at 135°C for 20 min was done and the exposed substrate were immersed in developer solution. Photoresist and thin layer of silver was removed. For selective etching of H.A layer, the sample was immersed in 5wt% phosphoric acid for 20min at 45°C.

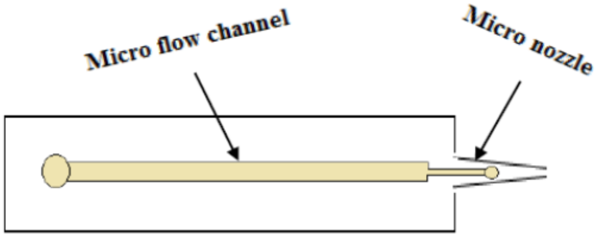

Fig. 1. *Schematic diagram of microinjector system*

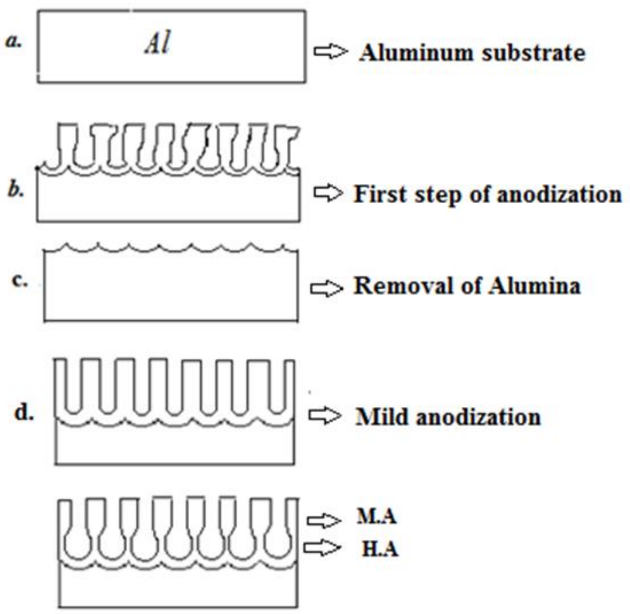

Fig.2. *Schematic representation of fabrication process of AAO membrane by combining M.A and H.A*

3. RESULT AND DISCUSSION

Scanning electron microscope was used for the analysis of AAO membrane and microchannel. Figure 3 shows the SEM analysis of microinjector system prepared in lab. AAO membrane have interpore distance of 80nm for both anodization (M.A and H.A) and thickness of membrane is about 5μm. Figure 3(a) shows upper surface morphology with uniform hexagonal nanoporous structure. The pore size and interpore distance of AAO membrane are highly depends on anodization parameters such as of electrolyte, potential difference and temperature. Fig 3(d) represents the cross sectional image of AAO membrane with well aligned regular and straight nanopores. The cross sectional view in Fig 3(b) shows chemical etching process which carried in 5wt% phosphoric solution for 5 min. The result shows that the etching process is only observed in H.A layer and no any effect of etching is detect in M.A. Microchannel with length of 50-100μm and 12μm in depth is shown in Fig 3(c).

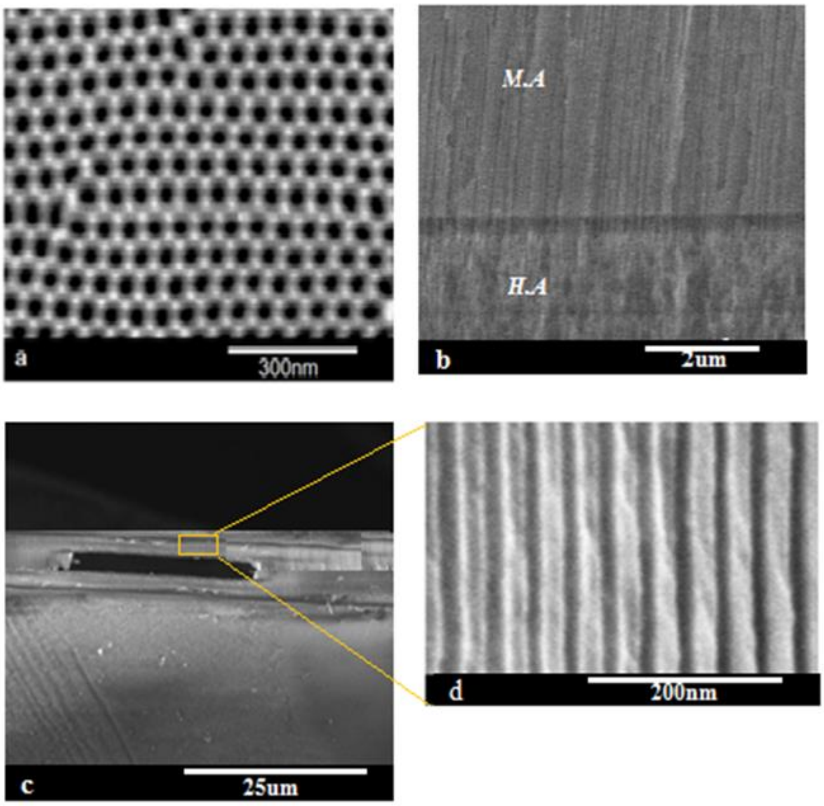

Fig. 3. *SEM images (a) top view of AAO membrane (b)cross-sectional view of Etching process in H.A (c) Cross-sectional view of Microchannel (d) cross-sectional view of upper layer*

Table 1. *The content of anions impurities in some popular electrolytes*

Electrolyte	H_2CrO_4	H_2PO_4	H_2C2O_4	H_2SO_4
Anion content (%)	0.1-0.3	6-8	2-3	10-13

The amount of anion impurities in H.A layer anodized in sulphuric is high so an anisotropic etching process was only observed in H.A layer. In our work a very attractive structure of AAO with combining M.A and H.A was used for the fabrication of microinjector system. Keeping inter pore distance similar it becomes possible to combine M.A and H.A by exchanging the electrolyte solution. The potential of 32V and 37V were applied for mild anodization in oxalic solution and hard anodization in sulphuric respectively. The porosity in oxalic based mild anodization is about 10% and in sulphuric based hard anodization it is about 30%. The interpore distance Din in H_2CO_3 and H_2SO_4 depend upon applied voltage with proportionality constant $2.5nmv^{-1}$ and $2nmv^{-1}$ for M.A and H.A. Up to our knowledge these microchannels was prepared first time inside AAO. The mechanical stability of membrane was very high and we can handle it without any damage. The microchannels with the range of 50-100μm in width and 10-15μm in deep was generated in prepared AAO sample by photolithography technique and wet etching was done in 5 wt% H_2PO_4. First the silver layer is coating on AAO membrane by plasma sputtering. The process was simplified by using positive photoresist and mask of desire microstructure. The given pattern on mask was transferred on photosensitive positive resist in UV light and by etching process the micropattern conveys in AAO membrane as show in Fig 3(c). As H.A segment was formed in H_2SO_4 in which the density of pore wall was very less and level of impurities was observed very high. This anion (SO_4^{-2}) impurity in H.A was about 88% higher as compared to the M.A segment [11]. The amount of anion impurities depends on the electrolyte and the condition of anodization. The anionic impurities content (%) for some popular electrolytes is given in table1.The density of pore walls was less and anion impurities were presented in large quantity so the chemical stability of H.A segment of AAO becomes very less in 5 wt% H_3PO_4 etchant. 50-100μm wide and 12μm deep microchannels were fabricated between uniform self-organized nanopores layer of M.A and Al substrate. Al substrate gives mechanical stabilty to microinector system. The depth of microchannel depends on thickness of H.A layer which can vary by changing anodization time. Etching time is another very important parameter so it was maintain up to20 min during etching process in phosphoric. If it increases from limited time the entire AAO membrane was etched.

4. CONCLUSIONS

In this study we reported very simple method for fabrication of micro and nano combined structure. Microchannels were formed inside anodic aluminum oxide by simple photolithography technique and wet etching technique. A thin film of anodic aluminum oxide (AAO) was fabricated by combining both the M.A anodization in oxalic acid and H.A in sulphuric acid. This novel type of microinjector system can be used to construct a microfluidic device by inegrating it on a chip. Our purposed stucture contains microchannels and can enable the devices to perform the function of injecting. This method will make fabrication easier, inexpensive, fast and simple and could be very useful in numerous applications of medical and biology.

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REFERENCES

[1]. Tiwari, G., Tiwari, R., Sriwastawa, B., Bhati, L., Pandey, S., Pandey, P., & Bannerjee, S. K. (2012). Drug delivery systems: An updated review. *International journal of pharmaceutical investigation*, 2(1), 2.

[2]. Tao, S. L., & Desai, T. A. (2003). Microfabricated drug delivery systems: from particles to pores. *Advanced drug delivery reviews*, 55(3), 315-328.

[3]. Ainslie, K. M., & Desai, T. A. (2008). Microfabricated implants for applications in therapeutic delivery, tissue engineering, and biosensing. *Lab on a Chip,* 8(11), 1864-1878.

[4]. Peer, D., Karp, J. M., Hong, S., Farokhzad, O. C., Margalit, R., & Langer, R. (2007). Nanocarriers as an emerging platform for cancer therapy. *Nature nanotechnology*, 2(12), 751.

[5]. Panchagnula R. Transdermal(1997) delivery of drugs. Indian J *Pharmacol*. ;29:140–56.

[6]. Moon, S. J., & Lee, S. S. (2005). A novel fabrication method of a microneedle array using inclined deep x-ray exposure. *Journal of Micromechanics and Microengineering*, 15(5), 903

[7]. Yu, L. M., Tay, F. E. H., Guo, D. G., Xu, L., & Yap, K. L. (2009). A microfabricated electrode with hollow microneedles for ECG measurement. *Sensors and Actuators* A: Physical, 151(1), 17-22.

[8]. Cornell, E., Fisher, W. W., Nordmeyer, R., Yegian, D., Dong, M., Biggin, M. D., ... & Jin, J. (2008). Automating fruit fly Drosophila embryo injection for high throughput transgenic studies. Review of *Scientific Instruments*, 79(1), 013705.

[9]. Zappe, S., Fish, M., Scott, M. P., & Solgaard, O. (2006). Automated MEMS-based Drosophila embryo injection system for high-throughput RNAi screens. *Lab on a Chip*, 6(8), 1012-1019.

[10]. De Jong, J., Lammertink, R. G., & Wessling, M. (2006). Membranes and microfluidics: a review. *Lab on a Chip,* 6(9), 1125-1139.

[11]. Lee, W., Schwirn, K., Steinhart, M., Pippel, E., Scholz, R., & Gösele, U. (2008). Structural engineering of nanoporous anodic aluminium oxide by pulse anodization of aluminium. *Nature nanotechnology,* 3(4), 234.

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A NOVEL N-PIVOT MACROCYCLIC LIGAND AND ITS COBALT(II) PHTHALOCYANINE DERIVATIVE: SYNTHESIS, CHARACTERIZATION AND EXTRACTANT PROPERTIES

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ABSTRACT

*In this study, the synthesis of a novel N-pivot 12-membered macrocyclic ligand with mixed donor atoms **2**, which is a phthalonitrile derivative, and a new cobalt(II) phthalocyanine complex **3** obtained by cyclotetramerization reaction of **2** were described. Newly synthesized compounds were characterized by using several spectroscopic techniques such as IR, UV-Vis, ^{1}H and ^{13}C NMR, MS and elemental analysis. These macrocyclic systems **2** and **3** were investigated as extractants in liquid-liquid extraction technique to reveal metal ion binding capability towards transition metals such as Ag(I), Hg(II), Cd(II), Zn(II), Cu(II), Ni(II), Pb(II) and Co(II). The highest extractability from aqueous phase to organic phase was found for Hg(II) cation over the other metal cations with cobalt(II) phthalocyanine **3**. The extraction percentage of Hg(II) cation from aqueous phase to chloroform in the presence of cobalt(II) phthalocyanine **3** as extractant was found as 96.0%.*

1. INTRODUCTION

First synthesis of macrocycles was reported by Pedersen in 1967 [1]. Since then, hundreds of macrocycles have been synthesized [2] and applied in most of research areas, such as removing heavy metals from aqueous solution [3], recognition of anions/cations, receptor for neutral molecules, due to their unique architecture, stabilities and functions [4]. Various types of macrocycles including a variety of type of donor atoms such as oxygen, sulfur, nitrogen and phosphorus have been studied for understanding of metal-ion binding properties of macrocycles [5]. These studies showed that designing of a macrocyclic ligand with appropriate size and donor atoms is the key step to achieve a selective complexation of metal ion. The hard-soft acid-base concept is the preliminary guide for selection of donor atom type. According to this concept, macrocycles with soft donor atoms such as sulfur prefer to bind soft transition metal ions whereas hard oxygen containing macrocyclic ligands show a binding preference toward alkali metal cation.

In 1934, the synthesis of phthalocyanines by the reaction of o-cyanobenzamide with cupper(I) cyanide at high temperature were reported by Linstead [6]. They have been mostly used as green and blue dyes since their first synthesis. Nowadays, these compounds have attracted great attention due to the potential applications in cancer therapy as photodynamic reagent [7], solar cells as dye material [8], catalysis as catalyst and computer science as optical materials. Incorporation of macrocycles into a phthalocyanine skeleton was presented as first in 1986 by Bekaroğlu and co-workers [9]. Later on, the complexation properties of this new molecule, phthalocyanine-bearing macrocycle, were reported by Musluoğlu [10]. Until now, many numbers of phthalocyanines bearing macrocycle with different ring size and type of donor atoms at peripheral or non-peripheral positions have been synthesized [11] and found potential application in removing metal ion from aqueous media [12].

In our previous work, we have reported the synthesis of metal-free and metallophthalocyanines bearing macrocycles with different ring size and mixed donor atoms, and investigation of their metal-ion binding properties towards transition metals [12]. As part of going interest toward investigation of complexation behavior of phthalocyanine bearing macrocycle, herein, we wish to report the synthesis, characterization and

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extractant properties of a novel 12-membered macrocycle with mixed donor atoms and its cobalt(II) phthalocyanine derivative.

2. METHODS

The extractant properties of newly synthesized compounds **2** and **3** towards transition metal ions such as Ag(I), Hg(II), Cd(II), Zn(II), Cu(II), Ni(II), Pb(II), and Co(II) were investigated by the method of solvent extraction based on non-mixing biphasic liquid-liquid system. The experiments were performed by following the well-established literature procedure [13-15]. For liquid-liquid solvent extraction, the metal picrate solutions were prepared by mixing of metal nitrates and picric acid in distilled water. Chloroform was chosen as an organic solvent. 10 mL of chloroform containing 1.25 x 10^{-4} M ligand and 10 mL of metal picrate solutions (picric acid, 1.25 x 10^{-5} M; metal nitrate, 1 x 10^{-2} M) was placed together in stoppered flask and then shaken for 2 h at 20 ± 0.1 °C followed by standing for at least 2 h at the same temperature in order to complete the phase separation. The aqueous phase was measured at 355 nm by UV-Vis spectrophotometer to determine the remaining picrate ion concentration. By following the same experiment procedure in the absence of macrocycles **2** and **3**, the blank experiments were also performed and no picrate extraction was determined at the measurements.

The extraction percentage (E%) of each metal cation was calculated by using the following equation [16, 17]:

$$E(\%) = \frac{[A_0 - A]}{A_0} x100 \qquad (1)$$

A_0: the absorbance of the tested transition metal picrate in the absence of ligand

A: the absorbance of the tested transition metal picrate in the aqueous phase after extraction

During the solvent extraction process, the general extraction equilibrium can be proposed as:

$$M_{aq}^{n+} + nPic_{aq}^{-} + mL_{org} \Leftrightarrow [M(Pic)_n(L)_m]_{org} \qquad (2)$$

If the Eq.(2) is reorganized by using distrubition ratio *D* and extraction equilibrium constant *K* as below, the plot of log {D/$[Pic^-]^n$} as a function of log [L] should give a straight line with a slope of *m* and log K_{ex} can be calculated from the intercept by using Eq.(3), which is valid for the extraction system [13-15]. For these studies, we used the macrocycles concentration in the range of 2.5 x 10^{-6} to 7.5 x 10^{-5} M.

$$\log\left(\frac{D}{[Pic^-]^n}\right) = \log K_{ex} + m\log[L] \qquad (3)$$

3. EXPERIMENTAL

3.1. Materials and Equipment

Starting precursor named as N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1** was prepared by following the published procedure [18]. All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [19].

FTIR spectra were measured on a Perkin Elmer Spectrum 65 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer in $CDCl_3$. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV-Vis region with a PG-T80+ spectrophotometer in 1 cm path length cuvettes at room temperature. The elemental analyses were obtained with a LECO Elemental Analyzer (CHNS 0932) spectrophotometer. The melting points were determined with an electrothermal apparatus and are reported without correction. In solvent extraction experiment Selecta type shaker with thermostat was used.

3.2. Synthesis

3.2.1. 10-(2-chloroacetyl)-12-oxo-10,11,12,13-tetrahydrotribenzo[b,e,k][1,4]dithia[7,10]diazacyclododecine-2,3-dicarbonitrile (2)

Compound **1** (1.0 g, 1.9 mmol) was added to a solution of 10 mL THF containing KOH (0.16 g, 2.85 mmol) as the base. The resulting reaction mixture was cooled to 0 °C and stirred for 10 h under nitrogen atmosphere. Reaction progress was followed by TLC using a solvent mixture of ethyl acetate-hexane (4:6). When the reaction was completed, 20 mL of water and 50 mL of dichloromethane were added to the reaction mixture and stirred for further 20 min at room temperature. Dichloromethane phase was separated and washed with 5% NaCl solution (15 mL) and water (2 x15 mL), respectively. Later, the combined organic layer was separated and anhydrous Na_2SO_4 was added to remove trace of water from the organic phase. Then, the Na_2SO_4 in dichloromethane was separated by filtration. Removing the solvent under reduced pressure afforded the crude product which was purified by silica gel chromatography. The elution was carried out with hexane-ethyl acetate (7:3). The product was obtained as pale yellow solid and then dried in vacuum. The yield was 0.5 g (52%). mp 185-187 ^{o}C. Anal. calcd for $C_{24}H_{15}ClN_4O_2S_2$: C, 58.71; H, 3.08; N, 11.41; S, 13.06%. Found: C, 58.52; H, 3.34; N, 10.93; S, 12.22%. IR (KBr disc) ν_{max}/cm^{-1}: 3322(NH), 3092, 3062 (CH_{Ar}), 2924 (CH_3), 2232 (C≡N), 1689 (C=O), 1580, 1519, 1476, 1436, 1298, 1258, 1129, 1037, 755, 663, 527. ^{1}H NMR ($CDCl_3$) δ: 8.86 (s, H, NH), 8.59 (d, H, ArH), 7.63 (s, H, ArH), 7.62 (t, H, ArH), 7.54 (t, H, ArH), 7.51 (d, H, ArH), 7.27 (t, H, ArH), 7.19-7.13 (m, 2H, ArH), 7.02 (s, H, ArH), 6.46 (m, H, ArH), 4.16 (H_a, J_{AB}=14,5 Hz), 4.13 (H_b, J_{AB}=14,5 Hz), 3.66 (H_c, J_{CD}=14,5 Hz), 3.65 (H_d, J_{CD}=14,5 Hz). ^{13}C NMR ($CDCl_3$) δ:

164.67, 164.51, 146.27, 140.05, 140.01, 138.37, 137.65, 134.81, 133.43, 131.11, 129.06, 127.77, 126.04, 125.23, 123.97, 121.92, 118.78, 116.61, 114.52, 114.39, 114.31, 113.68, 43.29, 31.81. MS (LC-MS/MS) m/z: 491.27 $[M+H]^+$, 513.17 $[M+Na]^+$,

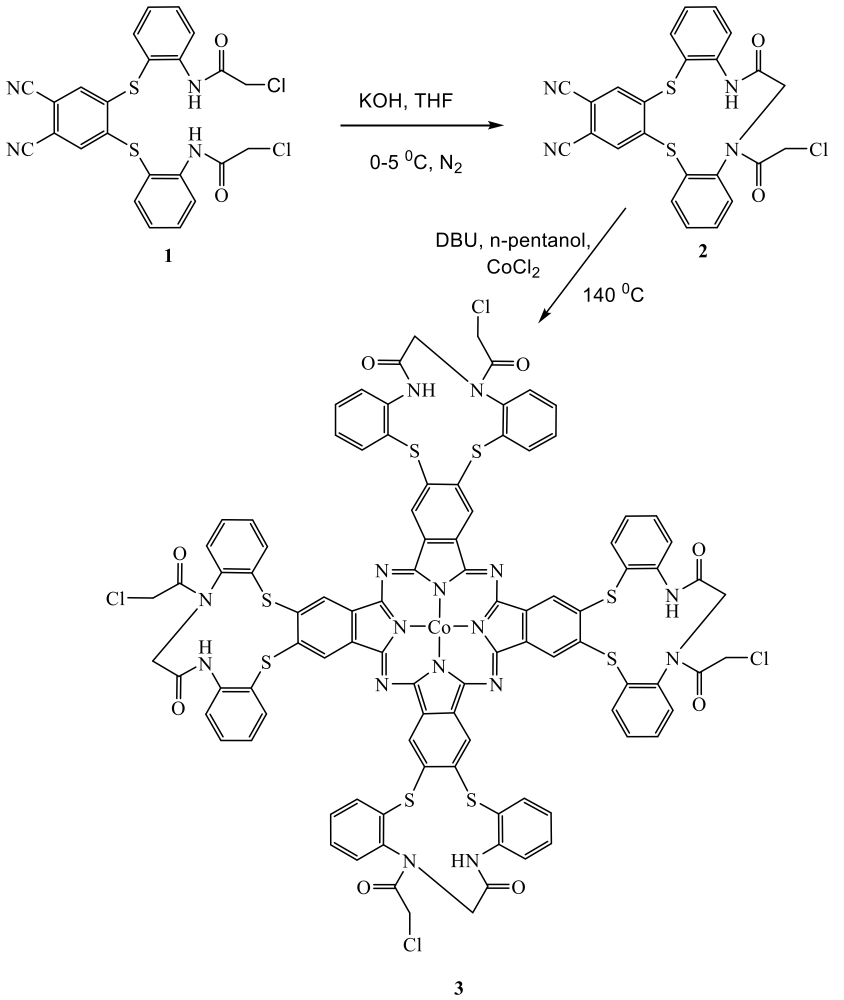
3.2.1. Cobalt(II) phthalocyanine (3)

The cyclotetramerization reaction of 10-(2-chloroacetyl)-12-oxo-10,11,12,13-tetrahydrotribenzo[b,e,k][1,4]dithia[7,10]diazacyclododecine-2,3-dicarbonitrile **2** (0.15g; 0.30 mmol) in the presence of anhydrous $Co(CH_3CO_2)_2$ (0.016g; 0.092 mmol) and 2 mL of quinolone was accomplished in a Schlenk tube under nitrogen atmosphere at 190 °C for 7 h. At the end of this period, the reaction mixture was cooled to room temperature and 10 mL of ethanol was added to this stirring reaction mixture. The precipitate was filtered off and washed several times with ethanol. The crude product was further purified by refluxing with ethanol in a Soxhlet extractor for 4h. The product was then filtered and washed with ethanol and diethyl ether and then dried under vacuum. The yield was 0.040g (21%). mp: >300 °C. Anal. calcd for $C_{96}H_{60}Cl_4CoN_{16}O_8S_8$: C, 57.00; H, 2.99; N, 11.08%. Found: C, 56.52; H, 3.18; N, 10.87%. IR (KBr disc) ν_{max}/cm^{-1}: 3359 (-NH), 3061, 2923, 1683 (C=O), 1583, 1507, 1476, 1441, 1335, 1294, 1259, 1079, 751. UV-Vis (DMF): λ_{max}, nm (log ε): 352 (4.73), 476 (4.01), 690 (4.69); MALDI-TOF (ESI^+) (*m/z*): calculated $[M+4H_2O]^+$ for $C_{96}H_{68}Cl_4CoN_{16}O_{12}S_8$: 2094.1 found: 2093.9.

4. RESULTS AND DISCUSSION

4.1. Synthesis and Characterization

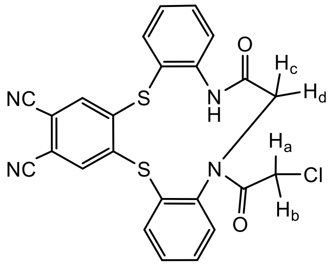
The synthetic pathway for preparation of N-pivot 12-membered macrocyclic ligand **2** and cobalt(II) phthalocyanine **3** is summarized in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^1H NMR, ^{13}C NMR, IR, UV-vis and MS spectral data.



Scheme 1. *Synthetic route of macrocyclic ligand **2** and its cobalt(II) phthalocyanine derivative **3***

Reaction of N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1** and KOH in THF at 0 ^0C under nitrogen atmosphere afforded 10-(2-chloroacetyl)-12-oxo-10,11,12,13-tetrahydrotribenzo[b,e,k][1,4]dithia[7,10]diazacyclododecine-2,3-dicarbonitrile **2** in 52% yield after purification by column chromatography using hexane-ethyl acetate

(7:3) as solvent system. The formation of 12 membered N_2S_2 mixed donor macrocyclic compound was occurred by self condensation reaction one of two N-substituted 2-chloroamides of **1**. The cyclization reaction was confirmed by the appearance of the specific stretching vibration of the –NH groups 3322 cm^{-1} in the IR spectrum of **2**. The intense vibrations at 2232 cm^{-1} and 1689 cm^{-1} was attributed to the C≡N and C=O groups in the structure of **2**, respectively. In the ^{1}H NMR spectrum of **2**, the singlet for -NH proton in the amide moiety was observed at δ = 8.86 ppm as expected. Protons of the nitrile substituted benzene ring were appeared as two singlets at δ = 7.63 and 7.02 ppm. Macrocycle **2** has four diastereotopic protons due to its asymmetric structure. These diastereotopic protons were shown in Scheme 2 and were appeared as AB spin system at δ = 4.16, 4.13 and 3.66, 3.64 ppm with a coupling constant of J = 14.5 Hz.



(2)

Scheme 2. *Diastereotopic protons (H_a, H_b, H_c, H_d) of macrocyclic ligand **2***

The ^{13}C NMR spectrum of **2** indicated the presence of carbonil and methylene carbons at δ = 164.57, 164.51 and 43.29, 31.81 ppm, respectively. The mass spectrum of macrocycle **2** was obtained by LC-MS/MS technique and the expected molecular ion peak for **2** was observed at m/z = 491.27 $[M+H]^+$ and 513.17 $[M+Na]^+$.

The cyclotetramerization of the phthalonitrile derivative **2** in the presence of cobalt(II) acetate to the cobalt(II) phthalocyanine **3** was accomplished in quinoline at 190 °C for 7 h under nitrogen in a Schlenk tube to afford **3** in 21% as green amorphous solids after purification by soxhlet extraction. After conversion of the dinitrile precursors containing macrocycle **2** to the phthalocyanines, the sharp C≡N vibration around 2232 cm^{-1} disappeared in the IR spectra of phthalocyanine derivatives. IR spectra of cobalt(II) phthalocyanine **3** is very similar to the IR spectra of **2** and indicated the aromatic groups at around 3060 cm^{-1}, the aliphatic groups at around 2900 cm^{-1} and the C=O group at around 1683 cm^{-1} by intense bands. A close investigation of the mass spectra of the cobalt(II) phthalocyanine **3** confirmed the proposed structure. Acquired MALDI-TOF spectra of phthalocyanine derivative **3** has allowed us to record molecular ion peaks at m/z = 2093.9 $[M+4H_2O]^+$, confirmed the proposed structure. In addition to the mass spectra, the electronic absorption spectrum of the studied phthalocyanine was recorded in DMF. Phthalocyanine complex showed the expected absorptions with the main peaks of the Q and B bands, appearing a band at λ_{max} = 690 nm and 352 nm, respectively. Appearance of single intense Q band is characteristic for metallophthalocyanines with D_{4h} symmetry [20].

4.2. Extractability

The metal ion-binding properties of macrocycle **2** and cobalt(II) phthalocyanine **3** was performed by using solvent extraction experiments in order to estimate the extractability of metal ions such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Co^{2+} from aqueous phase to the organic phase. Chloroform was used as an organic solvent to reveal extraction efficiency. The results related to the extractability of above metal picrates from aqueous phase to organic phase are given in Table 1.

Table 1. *The extractability of aqueous metal picrates for **2** and **3** into chloroform phase*

Compound*	**Extractability (%)**							
	Ni^{2+}	Cu^{2+}	Hg^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Pb^{2+}	Co^{2+}
(2)	<1	<1	6.8±0.4	<1	5.8±0.4	<1	<1	<1
(3)	67.0±1.2	92.2±2.1	96.0±1.1	41.7±2.3	92.7±0.8	77.0±1.2	92.1±1.9	62.6± 0.3

**Temperature: 20.0±0.1 °C; aqueous phase (10 mL); $[pic^-] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 1.25 \times 10^{-4}$ M; The values calculated from three independent extraction experiments.*

As seen from Table 1, macrocyclic ligand **2** exhibited the lowest extraction efficiency for all the metal ions in both solvents. The best extractability belongs to Hg^{2+} ion and Ag^+ ion in chloroform, but they were only 6.8% and 5.8%, respectively. The cation binding properties of the macrocycles depend upon different factors such as macrocylic effect, cavity size, and the type and number of donor atoms [4, 5]. As seen from Scheme 1, the cobalt(II) phthalocyanine **3** contains four macrocycle unit and it is expected to transport metal cations more effectively with respect to macrocycle **2** for the same conditions. In addition to that, the cobalt (II) phthalocyanine **3** has a planar structure. The E% values obtained for cobalt(II) phthalocyanine **3** was higher than those of macrocycle **2** in chloroform. The obtained extraction values in the presence of cobalt(II) phthalocyanine **3** for Ag^+, Hg^{2+}, Pb^{2+} and Cu^{2+} in chloroform were high when compared to other metal cations. The highest extractability belongs to Hg^{2+} and Ag^+ cations with cobalt(II) phthalocyanine **3** . The values of extractability belonging to Hg^{2+} and Ag^+ are 96.0% and 92.7% in chloroform, respectively. In the case of cobalt(II) phthalocyanine **3**, increasing in extraction capability may be due to the result of planarity of cobalt(II) phthalocyanine **3** or the number of donor atoms in compound **3**. From the experimental results, we can conclude that the cobalt(II) phthalocyanine **3** is much more effective than macrocyclic ligand **2** in the extractability of metal cations from aqueous phase to organic phase under these conditions.

To determine complex composition (M:L) between cobalt(II) phthalocyanine **3** and the most extracted two metal cations which are Hg^{2+} and Ag^{+}, and extraction constant log K_{ex} of those extracted complex species, the distribution ratio D of the cation between the aqueous phase and the organic phase upon concentration of cobalt(II) phthalocyanine **3** was examined. Fig. 1 and Table 2 showed the obtained results from these experiments. As shown from the results, the liquid-liquid extraction experiments with different metal cations such as Hg^{2+} and Ag^{+} in the presence of cobalt(II) phthalocyanine **3** resulted in same complex compositions. Hg^{2+} and Ag^{+} metal ions gave 3:2 complex composition with cobalt(II) phthalocyanine **3** for chloroform. The log K_{ex} values for 3:2 complex composition between Hg^{2+} and Ag^{+}, and cobalt(II) phthalocyanine **3** were 12.5 and 11.5, respectively.

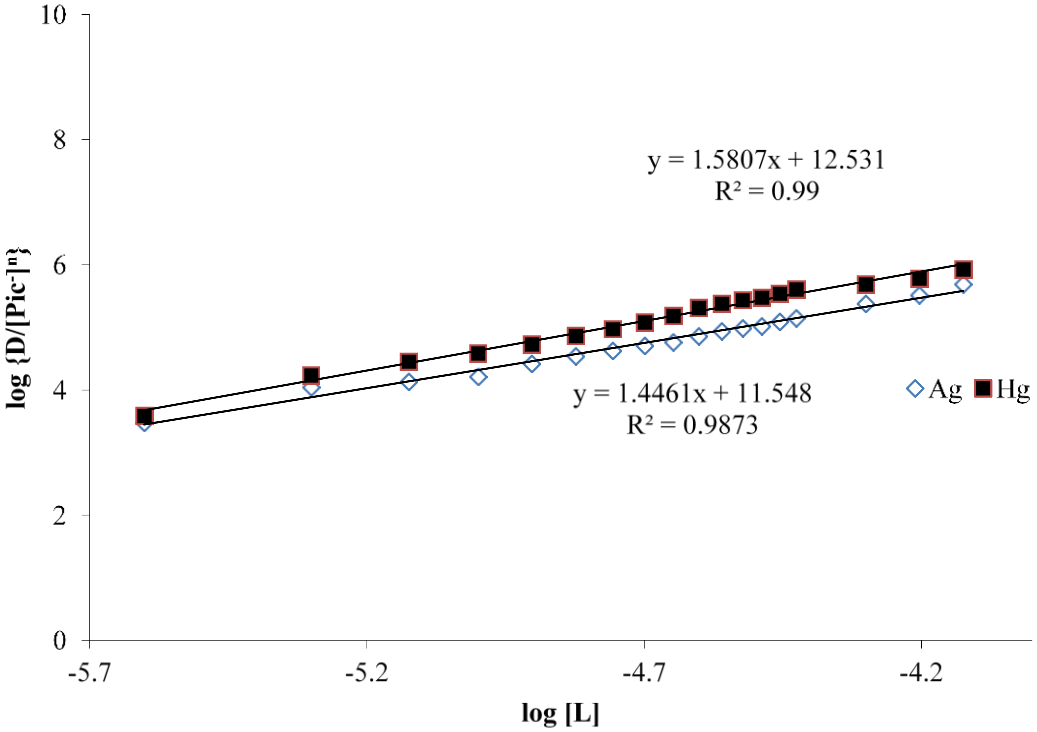


Figure 1. *log {D/[Pic⁻]ⁿ} versus log [L] for the extraction of Ag(I) and Hg(II) -picrate with cobalt(II) phthalocyanine **3**, solvent:chloroform*

Table 2. *The relationship between composition and extraction constant for cobalt(II) phthalocyanine **3**-Ag(I) and Hg(II) complexes in chloroform phase*

Cation	Extraction constant (logK$_{ex}$)	m (the slope)	Complex composition (L:M)
Ag(I)	11.5 ± 0.4	1.4 ± 0.1	3:2
Hg(II)	12.5 ± 0.3	1.6 ± 0.1	3:2

5. CONCLUSIONS

We described the synthesis of a new N-pivot 12-membered macrocyclic ligand with diazadithia donor atoms and its cobalt(II) phthalocyanine derivative. The characterization of newly synthesized compounds **2** and **3** was performed by a combination of FT-IR, UV-Vis, ^{1}H and ^{13}C NMR, MS and elemental analysis measurements. After that, solvent extraction method was carried out to reveal the metal-ion binding properties of macrocyles **2** and **3**. UV-Vis measurements to determine the remaining picrate ion concentration in the aqueous phase following the liquid-liquid extraction experiment showed that cobalt(II) phthalocyanine complex **3** has higher cation binding capacity that macrocycle **2**. The highest extraction value was obtained for Hg^{2+} among the other cations with cobalt(II) phthalocyanine **3**. The extraction percentage of Hg^{2+} with **3** from aqueous phase to chloroform was found as 96.0%. Furthermore, obtaining a very high extraction constant log K_{ex} value such as 12.5 between Hg^{2+} cation and cobalt(II) phthalocyanine **3** proved the stability of the formed complex. As a result, cobalt(II) phthalocyanine have the potential to be used in extraction of Hg^{2+} ion from industrial wastewaters successfully.

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REFERENCES

[1]. Pedersen, C. J. (1967). Cyclic polyethers and their complexes with metal salts. Journal of the American Chemical Society vol. 89 p. 7017-7065, DOI: 10.1021/ja01002a035.

[2]. An, H., Bradshaw, J. S., Izatt, R. M. (1992). Macropolycyclic polyethers and related compounds. Chemical Reviews vol. 92, no. 4, p. 543-572, DOI: 10.1021/cr00012a004.

[3]. Yordanov, A.T. Roundhill, D.M. (1998). Solution extraction of transition and post-transition heavy and precious metals by chelate and macrocyclic ligands. Coordination Chemistry Reviews vol. 170, no. 1, p. 93–124, DOI: 10.1016/S0010-8545(97)00074-X

[4]. Lindoy, L. F. (1989). The chemistry of macrocyclic ligand complexes. Cambridge: Cambridge University Press.

[5]. Hancock, R. D, Martell, A. E. (1989). Ligand design for selective complexetion of metal ions in aqueous solution. Chemical Reviews vol. 89, no. 8, p. 1875-1914. DOI: 10.1021/cr00098a011

[6]. Byrne, G. T., Linstead, R. P., Lowe. (1934). Phthalocyanines. Part II. The Preparation of Phthalocyanine and Some Metallic Derivatives from o-Cyanobenzamide and Phthalimide. Journal of Chemical Society, p. 1017-1022. DOI: 10.1039/JR9340001017

[7]. Allen, C. M., Sharman, W. M., Van Lier, J. E. (2001). Current status of phthalocyanines in the photodynamic therapy of cancer. Journals of Porphyrins and Phthalocyanines v. 5, no. 2, p.161-169, DOI:10.1002/jpp.324.

[8]. Cho, K.T., Trukhina, O., Roldán-Carmona, C., Ince, M., Gratia, P., Grancini, G., Gao, P., Marszalek, T., Pisula, W., Reddy, P.Y., Torres, T., Nazeeruddin, M.K. (2017). Molecularly Engineered Phthalocyanines as Hole-Transporting Materials in Perovskite Solar Cells Reaching Power Conversion Efficiency of 17.5%. Advenced Energy Materials vol. 7, 1601733, DOI: 10.1002/aenm.201601733.

[9]. Koray, A. R., Ahsen, V., Bekaroğlu, Ö. (1986). Preparation of a novel, soluble copper phthalocyanine with crown ether moieties. Journal of the Chemical Society, Chemical Communication p. 932-933. DOI: 10.1039/C39860000932.

[10]. Musluoğlu, E., Ahsen, V., Gül, A., Bekaroğlu, Ö. (1991). Water-soluble phthalocyanines containing aza-crown ether substituents. Chemiche Berichte vol. 124, no. 11, p. 2531-2536. DOI: 10.1002/cber.19911241123.

[11]. Gök, H. Z., Kantekin, H., Gök, Y., Herman G. (2007). The synthesis and characterization of novel metal-free and metallo-phthalocyanines bearing four 27-membered dioxadiazapentathia macrocycles. Dyes and Pigments, Vol.74, no. 3, p. 699-705. DOI: 10.1016/j.dyepig.2006.05.002.

[12]. Gök, H.Z. (2015). Synthesis of metal-free and metallophthalocyanines containing 18- and 21-membered macrocycles with mixed donor atoms and their metal-ion binding properties. Turkish Journal of Chemistry vol. 39, p. 750-763, DOI: 10.3906/kim-1501-54.

[13]. Gök, H. Z., Alp, H., Kantekin, H., Ocak, Ü. (2007). The synthesis and characterization of 22-membered diazapentathia macrocycles and investigation of their ion extraction capability from aqueous media. Transition Metal Chemistry vol. 32, no. 8, p. 1073-1078, DOI: 10.1007/s11243-007-0290-7.

[14]. Alp, H., Gök, H. Z., Kantekin, H., Ocak, Ü. (2008). Synthesis and metal ion binding properties of thiaaza crown macrocycles, Journal of Hazardous Materials vol. 159, no. 2-3, p. 519-522, DOI: 10.1016/j.jhazmat.2008.02.093.

[15]. Gök, H. Z., Gök, Y. (2017). Synthesis, characterization and metal-ion binding properties of a new macrobicyclic ligand with dioxadiazaoctathia donor atoms. Heteroatom Chemistry vol. 28, e21374; https://doi.org/10.1002/hc.21374

[16]. Alp, H., Bıyıklıoğlu, Z., Ocak, M., Ocak, Ü., Kantekin, H., Dilber, G. (2007). New heavy metal ion-selective macrocyclic ligands with nitrogen and sulfur donor atoms and their extractant properties. Separation Science and Technology vol. 42, no.4, p. 835-845 DOI: 10.1080/01496390601174000.

[17]. Kantekin, H., Kılıçaslan, M. B., Ağın, F., Alp, H., Ocak, Ü. (2010). New heavy metal ion-selective macrocyclic ligands with mixed-donor atoms and their extractant properties. Journal of Coordination Chemistry vol. 63, no. 11, p. 1921-1932, DOI: 10.1080/00958972.2010.494303.

[18]. Gök H. Z., Farsak B. (2013). Synthesis, characterisation and aggregation properties of novel metal-free and metallophthalocyanines containing four 21-membered oxatetrathiadiaza macrocycles. Journal of Organometallic Chemistry vol. 735, p. 65-71, DOI: 10.1016/j.jorganchem.2013.03.019.

[19]. Perrin, D. D., Armarego , W. L. F. (1989). Purification of laboratory chemicals. 2nd ed. Oxford: Pergamon Press.

[20]. Demirayak, N., Akkuş, F., Gök Y. (2013). Synthesis and characterization of a new zinc phthalocyanine containing macrobicyclic moieties. Inorganic Chemistry Communication vol. 37, p. 97-100, DOI: 10.1016/j.inoche.2013.09.050

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