JREE: Vol. 4, No. 1, (Winter 2017) 36-40

Journal of Renewable Energy and Environment

Research Article

Journal Homepage: www.jree.ir

Thermal Pretreatment for Improvement of Biogas Production and Salinity Reduction by Zeolite

Rozita Asgari[a], Farida Iraji Asiabadi[b*], Hadi Radnezhad [a]

[a]Faculty of Agriculture and Natural Resources, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran.
[b]Water Research Center, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran.

P A P E R I N F O

Paper history:
Received 09 April 2017
Accepted in revised form 07 Januray 2018

Keywords:
Anaerobic digestion
Renewable energy
Pretreatment
Wastewater
Modified zeolite

A B S T R A C T

The anaerobic digestion of organic waste for biogas production can be affected by some variables such as temperature; concentration of the biogas feed solution, bacteria populations, and pressure. This study investigated the effects of thermal pretreatment at 50, 75, and 100 ºC on the biogas produced by simultaneous anaerobic digestion of cow manure, mushroom waste, and wheat straw at thermophilic temperature. Moreover, the effects of a zeolite on reducing the salinity of the wastewater were evaluated. Cow manure, mushroom waste, and wheat straw were mixed to yield a mixture with an optimum carbon to nitrogen ratio of 20-30 and TS of 25-35%. Each thermal pretreatment was prepared in four replicates and placed in a steam bath with a temperature of 55 ºC. The amount of gas produced by each thermal pretreatment was measured every day for 15 days. On day 15, the electrical conductivity of the produced wastewater was measured and the wastewater was exposed to a modified zeolite. The results showed that the greatest level of biogas was produced by thermal pretreatment at 75 ºC, which gave the biogas yield of 0.197 L/gVS after 15 days observation while, the other thermal pretreatments at 50, and 100 ºC gave the biogas yield 0.147, and 0.169 L/gVS, respectively. The highest amount of biogas was achieved on the third day for every three thermal pretreatments. Moreover, the modified zeolite reduced the wastewater salinity by 25%. These results confirmed that thermal pretreatment at 75 ºC is an effective pretreatment for biogas production improvement from the mixture of cow manure, mushroom waste, and wheat straw, and the modified zeolite could be used for salinity reduction of wastewater discharged from the process.

1. INTRODUCTION

Serious concerns raised by the continued decline of fossil fuels have necessitated searches for new energy sources including renewable energies such as solar energy, biogas, biodiesel, wind energy, and tidal energy [1]. Among various sources of energy, biogas is an efficient, renewable, and environment-friendly alternative for fossil fuels and can facilitate the preservation of invaluable oil and natural gas reserves throughout the world. In addition, its use will significantly reduce the greenhouse gas emissions [2]. This fuel is mostly produced from organic waste such as cow manure, food waste, agricultural waste, and human waste [3- 9]. Adding manure can effectively enhance the biogas production from agricultural waste as it directly introduces biogas-producing bacteria to the digestion environment at the beginning of the process and thus helps the decomposition process to be initiated at an earlier stage [10]. Furthermore, some pretreatments such as thermal, thermo-chemical, mechanical, biological pretreatment are important for enhancing the biogas production and/or anaerobic digestion. All pretreatments have strengths and weaknesses, the most appropriate technique will depend on the characteristics of each feedstock. However, pretreatment techniques must be economically feasible and environmental friendly, so they should have low energy, chemicals and water requirements. The main advantage of applying thermal pretreatment, especially temperatures below the 100ºC, is the low energy demand for biomass heating. In fact, energy requirements may be fulfilled using waste heat from cogeneration engines fueled by biogas [11]. Thermal pre-treatment appears as a very interesting option and a potential solution for a large quantity of lignocellulosic biomass [12]. The use of a thermal pre-treatment to enhance the anaerobic digestion of sewage sludge has also been reported in several references and has been developed in full scale. It is suitable for the improvement of stabilization, enhancement of

*Corresponding Author's Email: f.irajy@khuisf.ac.ir (F. Asiabadi)

dewatering of the sludge, and reduction of the numbers of pathogens [13]. However, the thermal pretreatment application to other organic wastes such as agricultural wastes [14, 15] or manure is very recent, and still open to research. Some references can be found concerning thermal pretreatment to chicken manure [16, 17], swine manure [18, 19], and pig manure [20, 12]. In this study, thermal pretreatment is used for improvement of biogas produced by simultaneous anaerobic digestion of mushroom waste, cow manure and wheat straw.

On the other side, biogas production is the high demand water process which has negative effects on the quality of the discharged wastewater in which the salinity is one of the main issues. Considering the fact that Iran is located in arid and semiarid region suffered from long-term drought and water shortage, water management has an important role on using the convenient and inconvenient sources of water such as waste water discharged from biogas production process. Absorbents such as zeolites are suggested for improving the wastewater quality. Zeolites are hydrated aluminosilicate crystals containing alkaline and alkaline earth metal cations.

Cation exchange and reversible water adsorption and loss (without any major molecular change) are among the main characteristics of these compounds [21]. Several studies have been carried out on the use of zeolite for wastewater treatment, such as the salinity reduction of groundwater with natural and modified zeolites [22], adsorption of heavy metals in mine wastewater by Mongolian natural zeolite [23], arsenate adsorption on iron modified artificial zeolite made from coal fly ash [24], and removal of MTBE in the columns filled with modified natural zeolites [25]. A zeolite was hence used in this study to reduce the wastewater salinity.

This study sought to investigate the effects of thermal pretreatment on the amount of biogas produced from cow manure, mushroom waste, and wheat straw. It was also tried to clarify the effects of zeolites on reducing the salinity of the wastewater produced during the anaerobic digestion of these materials. The results of this study can provide solutions for organic waste management. In addition, wastewater salinity reduction through zeolites facilitates the use of wastewater in the irrigation of urban green spaces.

2. METHODS

2.1. Thermal pretreatment preparation and biogas production measurement

Cow manure and wheat straw were sampled from the agricultural farm of the Isfahan (Khorasgan) Branch, Islamic Azad University. Mushroom waste was collected from Jarghoie Yecta mushroom factory. Then, Mushroom waste was dried at temperature of 150 ºC for 4 hours in an oven. The dried mushroom waste and wheat straw were milled to obtain particle sizes of less than 3 mm. Samples were analyzed for total solids (TS), carbon to nitrogen ratio (C/N) according to the standard methods for the examination of water and wastewater [26], EC, and pH. The materials' characteristics are presented in Table 1.

TABLE 1. Characterization of the raw materials investigated in this work

	Cow manure	**Mushroom waste**	**Wheat straw**
EC(mS/Cm)	5.26	10.35	1.1
pH	7.45	6.5	7.2
C%	33.7	32.13	50.5
N%	2.28	2.08	0.6
C/N	14.79	15.4	84.15
TS%	66.35	70.05	9.15

Carbon to nitrogen ratios (C/N) between 20 and 30 are believed to optimize biogas production from organic waste [27]. Therefore, based on the C/N of cow manure, mushroom waste, and wheat straw (Table 1), 8 g of grinded wheat straw, 52 g of grinded mushroom waste, and 40 g of cow manure were required to obtain a C/N of 20-30 and a TS of 25-35% for 100 g of the final mixture. This mixture of was prepared in four replicates for each thermal pretreatment (50, 75, and 100 ºC). In the next stage, the pH and EC of each pretreatment were measured (Table 2) and the prepared thermal pretreatments were transferred to specifically designed glass bottles. These one-liter bottles had a vent and a venting valve to allow the addition of materials. Each bottle was filled with 140 cc of the mentioned mixture and 560 cc of distilled water. The remaining 300 cc were left empty to provide adequate space for the produced gas.

TABLE 2. Electrical conductivity (EC) and pH of the thermal pretreatments

Pretreatment	**pH**	**EC (mS /Cm)**
Pretreatment 50	7.7	7.56
Pretreatment 75	7.73	8.14
Pretreatment 100	7.75	7.91

The internal temperature of the steam bath was set at 55 ºC. Afterwards, serum hoses were connected to bottle valves. To enhance the biogas production, each bottle was shaken for 10 minutes every day. The water level in every bucket was measured at a specified time every day and the difference between water levels on two consecutive days was recorded as the amount of gas produced by each thermal pretreatment.

2.2. Zeolite preparation and wastewater EC measurement

The zeolite was modified using hydrochloric acid and calcium chloride. For this purpose, 10 g of zeolite was added to a solution containing 1 g calcium chloride in hydrochloride acid to obtain a solid/solution ratio of 1:10. The final solution was placed in a shaker for 24 hours. In order to extract the remaining acids, the solution was washed with distilled water and passed through a filter paper. Its pH was continuously measured until it reached a constant value. The solution was then moved to polyethylene containers and dried in fresh air [28].

The wastewater produced in the bottles in the steam bath was sampled on the 3^{th}, 9^{th}, 13^{th}, and 15^{th} days of the process. The EC of each sample was then measured and changes in wastewater EC were evaluated (Table 3). On day 15, all remaining wastewater was removed from the bottles and exposed to the modified zeolite for six hours. In order to determine the effects of the zeolite on EC reduction, wastewater EC measurements were performed before and after exposure to the modified zeolite.

TABLE 3.The wastewater EC for three evaluated thermal pretreatment on the 3^{th}, 9^{th}, 13^{th}, and 15^{th} days of the process

EC (mS /Cm)				
	3	9	13	15
TPW-50	9.67	10.78	11.07	11.23
TPW-75	9.47	10.35	10.87	10.61
TPW-100	9.37	10.15	10.81	10.56

TPW: Thermal Pretreatment Waste water

3. RESULTS AND DISCUSSION

3.1. Effects of thermal pretreatment on biogas production

The cumulative biogas produced per g organic solids for different thermal pretreatment over a 15 day digestion time at thermophilic temperature (55°C) is shown in Fig. 1. The rates of biogas production differed appreciably according to the different thermal pretreatment. Furthermore, as shown in Fig. 1, the greatest level of biogas was produced by thermal pretreatment at 75 ºC, which gave the biogas yield of 0.197 L/gVS after 15 days observation while, the other thermal pretreatments of 50, and 100 ºC gave the biogas yield 0.147 and 0.169 L/gVS, respectively. In fact, pretreatment at 75 ºC seems to be the optimum temperature for the structural decomposition of the constituents of the experimental mixture, which can facilitate the degrading bacteria's access to organic materials, and thus promote the biogas production. In addition, according to the results, the highest amount of biogas was achieved on the third day of the process for every three thermal pretreatments. Materials on the first few days of the process and microorganisms' easier access to their required food can justify this finding [29]. This is similar with the information from Taherdanak and Zilouei [29] that obtained the best improvement in the biogas production from wheat plant by pretreatment at 75 ºC for 60 min. They also reported the improvement of the biogas production using alkaline Pretreatment. Rafique et al. [30] observed that the maximum biogas production in thermo- pretreated samples was obtained at 70 ºC and then decreased with the increase in temperature.

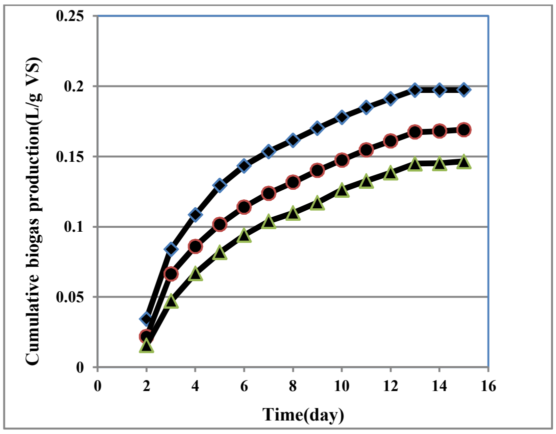

Figure 1. Cumulative biogas production at different thermal pretreatment under thermophilic conditions (55°C). (TP: Thermal Pretreatment)

TP-75 TP-100 TP-50

This indicates that the higher temperatures do not necessarily yield higher biogas production and this is attributed to the decrease in the biodegradability of substrate due to possible formation of complex organic and toxic compounds. In this study, it was also observed that the biogas production by pretreatment at 100 ºC is lower than at 75 ºC. However, these results are not in agreement with the ones- reported by Carrère et al. [31] who investigated the improvement of the thermal (70–190 ºC) treatments in order to maximize the production of methane from pig manure. They showed that the methane potential of manure soluble fraction increased with the temperature of thermal treatments whereas temperatures higher than the 135 ºC were necessary to improve the methane potential of the total fraction. The best results were obtained for the highest temperature (190 ºC). Gonza´lez-Ferna´ndez et al. [32] also investigated the effect of thermal pretreatment at two temperatures (70 and 90 ºC) applied to Scenedesmus biomass. No differences were detected in terms of organic matter upon the two tested temperatures.

Nevertheless, a different fact was observed for their anaerobic biodegradability. While raw and pretreated at 70 ºC microalgae attained 22-24% anaerobic biodegradability, microalgae pretreated at 90 ºC achieved anaerobic biodegradability of 48%. Even though similar profiles were obtained for both temperatures along the pretreatment period, the damage caused in the cell wall at 90 ºC seemed to be greater and rendered this readily degradable substrate for anaerobic digestion. After all, the results of this study highlighted the potential of thermal pretreatment for enhancing the biogas production of simultaneous anaerobic digestion of cow manure, mushroom waste, and wheat straw. However, to improve this value, further research is needed to determine the effect of biological pretreatment, the composition of biogas, as well as performance in a continuously fed reactor.

3.2. Effects of zeolite on the EC of the wastewater

The EC of the wastewater was reduced by 25% using the zeolite. The reduction in the EC of the wastewater was caused by the zeolite structure which allowed the free exchange of ions, especially water soluble ions. The complex crystalline silicate structure of the zeolites creates large continuous chains whose internal connections and component arrangement form a network of empty spaces and rack-shaped pores. These countless small empty racks, together with loosely-coupled alkaline and alkaline earth metal cations, are responsible for such unique characteristics such as absorption, cation exchange, molecule filtering, and catalyst features. Another characteristic of this mineral is its high mechanical and chemical resistance which makes it suitable for use in water and wastewater treatment. This is also related to loosely coupled ions in the zeolites that are easily exchanged with other ions. Washing zeolites with acids seems to remove their water soluble minerals. Therefore, the remaining zeolite will contain elements that are insoluble in water. These zeolites are expected to absorb higher levels of sodium and water hardness salts. They should hence be suitable for water treatment industry [33]. In this study, the replacement of sodium atoms with hydrogen ions in the zeolite modified with hydrochloric acid, increased the zeolite's capacity and thus reduced the EC of the wastewater [34-36]. This is similar with the information from Borghei et al. [22] which showed that the modified zeolite reduces EC and increases the zeolite capacity, while the use of unmodified zeolite increases the EC and salts. Shekarian et al. [37] also investigated the salt absorption by zeolite and perlit. They showed that the smaller particles of zeolite act faster than the larger particles for absorption, because factors such as the penetration path or the resistance to mass transmissions and the blockage of some penetration paths lead to reduction of the absorption efficiency.

4. CONCLUSIONS

In this study, the influence of thermal pretreatment (50, 75, and 100 ºC) on the biogas production from the mixture of cow manure, mushroom waste, and wheat straw was evaluated. The results showed that the highest amount of biogas (0.197 L/gVS) was produced for the pretreatment at 75ºC after 15 days. The highest amount of biogas was achieved on the third day for every three thermal pretreatments. Modified zeolite was investigated for the reduction of wastewaters salinity which were produced during the biogas production. The modified zeolite reduced the salinity of the wastewater by 25%. Future studies are warranted to examine the effects of microbial pretreatment on the biogas production and determination of the biogas composition.

5. ACKNOWLEDGEMENT

The authors would like to acknowledge the Water Research Center, Isfahan (Khorasgan) Branch, Islamic Azad University for sponsoring this study.

REFERENCES

1. Hung, C. and Solli, C., "Biogas from municiapal organic waste–trondheim's environmental holy grail?", ***Energy Procedia,*** Vol. 20, (2012), 11-19.
2. Hendroko, S.R., Wahono, S.K., Praptiningsih, G.A., Yudhanto, A.S., Wahyudi, I. and Dohong, S., "The study of optimization hydrolysis substrate retention time and augmentation as an effort to increasing biogas productivity from Jatropha curcas Linn. Capsule husk at two stage digestion", ***Energy Procedia,*** Vol. 47, (2014), 255-262.
3. Sitorus, B. and Panjaitan, S.D., "Biogas recovery from anaerobic digestion process of mixed fruit-vegetable wastes", ***Energy Procedia,*** Vol. 32, (2013),176-182.
4. Sharifi, M.A., Haghighi, M., Rahmani, F. and Rahemi, N., "Reforming of biogas over Co-and Cu-promoted Ni/Al_2O_3-ZrO_2 nanocatalysts synthesized via sequential impregnation method", ***Journal of Renewable Energy and Environment,*** Vol. 1, No. 1, (2014), 53-63.
5. Nosratinia, M., Tofigh, A.A. and Adl. M., "Making decision support system for utilization of biogas in Iran", ***Journal of Renewable Energy and Environment,*** Vol. 2, No. 1, (2014), 1-5.
6. Mel, M., Ihsan, S.I. and Setyobudi, R.H., "Process improvement of biogas production from anaerobic co-digestion of cow dung and corn husk", ***Procedia Chemistry,*** Vol. 14, (2015), 91-100.
7. Samani, S., Abdoli, M.A., Karbassi, A. and Amin, M.M., "Stimulation of the hydrolytic stage for biogas production from cattle manure in an electrochemical bioreactor", ***Water Science and Technology,*** Vol. 74, No. 3, (2016), 606-615.
8. Samani Majd, S., Abdoli, M.A., Karbassi, A., Pourzamani, H.R. and Rezaee, M., "Effect of Physical and Chemical Operating Parameters on Anaerobic Digestion of Manure and Biogas Production: A Review", ***Journal of Environmental Health and Sustainable Development,*** Vol. 2, No. 1, (2017), 235-247.
9. Karlsson, N.P., Halila, F., Mattsson, M. and Hoveskog, M., "Success factors for agricultural biogas production in Sweden: A case study of business model innovation", ***Journal of Cleaner Production,*** Vol. 142, (2017), 2925-2934.

10. Al-Masri, M.R., "Changes in biogas production due to different ratios of some animal and agricultural wastes", ***Bioresource Technology,*** Vol. 77, No. 1, (2001), 97-100.
11. Carrere, H., Antonopoulou, G., Affes, R., Passos, F., Battimelli, A., Lyberatos, G. and Ferrer, I., "Review of feedstock pretreatment strategies for improved anaerobic digestion: from lab-scale research to full-scale application", ***Bioresource Technology,*** Vol. 199, (2016), 386-397
12. Ferreira, L.C., Souza, T.S.O., Fdz-Polanco, F. and Pérez-Elvira, S.I., "Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure", ***Bioresource Technology,*** Vol.152, (2014), 393-398.
13. Neumann, P., Pesante, S., Venegas, M. and Vidal, G., "Developments in pre-treatment methods to improve anaerobic digestion of sewage sludge", ***Reviews in Environmental Science and Bio/Technology,*** Vol. 15, No. 1, (2016), 173-211.
14. Ferreira, L.C., Donoso-Bravo, A., Nilsen, P.J., Fdz-Polanco, F. and Pérez-Elvira, S.I., "Influence of thermal pretreatment on the biochemical methane potential of wheat straw", ***Bioresource Technology,*** Vol. 143, (2013), 251–257.
15. Qiao, W., Yan, X., Ye, J., Sun, Y., Wang, W. and Zhang, Z., "Evaluation of biogas production from different biomass wastes with/without hydrothermal pretreatment", ***Renewable Energy,*** Vol. 36, (2011), 3313–3318.
16. Ardic, I. and Taner, F., "Effects of thermal, chemical and thermochemical pretreatments to increase biogas production yield of chicken manure", ***Fresenius Environment Bulletin,*** Vol. 14, (2005), 1–8.
17. Bujoczek, G., Oleszkiewicz, J., Sparling, R. and Cenkowskic, S., "High Solid Anaerobic Digestion of Chicken Manur", ***Journal of Agricultural Engineering Research,*** Vol. 76, (2000), 51–60.
18. Chae, K.J., Jang, A., Yim, S.K. and Kim, S., "The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure", ***Bioresource Technology,*** Vol. 99, (2008), 1–6.
19. Mladenovska, Z., Hartman, H., Kvist, T., Sales-Cruz, M., Gani, R. and Ahring, B.K., "Thermal pretreatment of the solid fraction of manure: impact on the biogas reactor performance and microbial community", ***Water Science Technology,*** Vol. 53, No. 8, (2006), 59–67.
20. Menardo, S., Balsari, P., Dinuccio, E. and Gioelli, F., "Thermal pre-treatment of solid fraction from mechanically-separated raw and digested slurry to increase methane yield", ***Bioresource Technology,*** Vol. 102, (2011), 2026–2032.
21. Rau, I., Gonzalo, A. and Valiente, M., "Arsenic (V) adsorption by immobilized iron mediation. Modeling of the adsorption process and influence of interfering anions", ***Reactive and Functional Polymers,*** Vol. 54, No. 1, (2003), 85-94.
22. Borghei, M., Lahijani M., Hosni A., Salari M. and Sayyadi M., "Evaluation of the function of natural zeolites in reducing the salinity of Groundwater", ***Sharif Civil Engineering Journal,*** Vol. 3, (2014), 97-105.
23. Egashira, R., Tanabe, S. and Habaki, H., "Adsorption of heavy metals in mine wastewater by Mongolian natural zeolite", ***20th International Congress of Chemical and Process Engineering CHISA 2012,*** (2012), 25– 29, 49-57.
24. Shukla, E., johan, E., Henmi, T. and Matsue, N., "Arsenate adsorption on iron modified artificial zeolite made from coal fly ash", ***Procedia Environmental Sciences,*** Vol. 17, (2013), 279 – 284.
25. Russo, A. and Jacobo, E., "Removal of MTBE in Columns filled with Modified Natural Zeolites", ***Procedia Materials Science,*** Vol. 8, (2015), 375 – 382.
26. 2Andrew, D.E., "Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA)", 21 st ed, Washington, D.C.: APHA-AWWA-WEF, (2005).
27. Dioha, I.J., Ikeme, C.H., Nafi'u, T., Soba, N.I. and Yusuf, M.B.S., "Effect of carbon to nitrogen ratio on biogas production", ***International Research Journal of Natural Sciences,*** Vol. 1, No. 3, (2013), 1-10..
28. Chao, C.C. and Rastelli H., "Process for modifying clinoptilolite adsorbent", U.S. Patent No, 5,116,793, Washington, DC: U.S, Patent and Trademark Office, (1992).
29. Taherdanak, M. and Zilouei, H., "Improving biogas production from wheat plant using alkaline pretreatment", ***Fuel,*** Vol. 115, (2014), 714-719.
30. Rafique, R., Poulsen, T.G., Nizami, A.S., Murphy, J.D. and Kiely, G., "Effect of thermal, chemical and thermo-chemical pre-treatments to enhance methane production", ***Energy,*** Vol. 35, No. 12, (2010), 4556-4561.
31. Carrère, H., Sialve, B. and Bernet, N., "Improving pig manure conversion into biogas by thermal and thermo-chemical pretreatments", ***Bioresource Technology,*** Vol. 100, No. 15, (2009), 3690-3694.
32. González-Fernández, C., Sialve, B., Bernet, N. and Steyer, J.P., "Thermal pretreatment to improve methane production of Scenedesmus biomass", ***Biomass and bioenergy,*** Vol. 40, (2012), 105-111.
33. Sand, L.B. and Mumpton, F.A., "Natural zeolites: occurrence, properties, and use (No. CONF-760626-(Exc.))", Pergamon Press, Inc, Elmsford, NY, (1978).
34. 34. Wang, S. and Peng, Y., "Natural zeolites as effective adsorbents in water and wastewater treatment ", ***Chemical Engineering Journal,*** Vol. 156, No. 1, (2010), 11-24.
35. Wajima, T., "Ion exchange properties of Japanese natural zeolites in seawater", ***Analytical Sciences***, Vol. 29, No. 1, (2013), 139-141.
36. Liu, F., Ma, B.R., Zhou, D., Xiang, Y.H. and Xue, L.X., "Breaking through tradeoff of Polysulfone ultrafiltration membranes by zeolite 4A", ***Microporous and Mesoporous Materials,*** Vol. 186, (2014), 113-120.
37. Shekarian, F., Soleimani, K., Nematzadeh, G.H. and Biparva, P., "Evaluation of equilibrium isotherms of zeolite and perlite in adsorption Sodium chloride salt from aqueous solution", ***Journal of Ecohydrology,*** Vol. 3, (2014), 223-232.