International Journal of Agriculture Innovations and Research
Volume 6, Issue 1, ISSN (Online) 2319-1473
Manuscript Processing Details (dd/mm/yyyy) :
Received: 05/07/2017 | Accepted on : 12/07/2017 | Published : 22/07/2017

Synthesis of MnO_2 Nanoparticles Catalyst and Application to Treatment of Organic Compounds in Agricultural Processing Villages- a Case Study in Duong Lieu Village, Ha Noi Capital, Viet Nam

Nguyen Thi Hong Hanh
Department of Chemistry, Faculty of Environment, Vietnam National University of Agriculture.
Corresponding author email id: Nguyenthihonghanh.vnua@gmail.com

Abstract – **MnO_2 exhibits excellent catalysis properties. In this work, nano MnO_2 catalysts were synthesized from manganese sulfate and potassium permanganate by the co-precipitation method at room temperature. The characterization of the product was performed by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDX), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results showed that this material had a small particle size about 0.5 µm and surface area about 113.0601 m^2/g. The wastewater samples taken from Duong Lieu Agricultural Processing Village after wastewater treatment system were treated with nano MnO_2 catalysts in the laboratory. The results showed that the ozonation with nano MnO_2 catalyst occurred rapidly than ozonation reaction without catalyst. In these treatment, the catalytic ozonation with 0.02 g/l could reduce the COD demand from 3814.27 mg/l to 66.14 mg/l with 98.27% efficiency. Therefore, the ozonation with nano MnO_2 catalysts can be considered as an effective and feasible means for treating the organic compounds in wastewater.**

Keywords – **Wastewater, Manganese Dioxide, Organic Compound, Agriculture, Treatment.**

I. Introduction

Nowaday, the population has been growth, the demand for food of human are increasing. The agricultural processing villages in Viet Nam increasing in terms of quantity and production scale: Noodle processing in Phu Hung village, Binh Tan commune, Tay Son district, Binh Dinh province; Noodle processing in Thanh Luong village, Bich Hoa commune, Thanh Oai district, Ha Noi capital; Sausages in Tan Uoc village, Thanh Oai district, Ha Noi capital… Production facilities in craft villages are often small, spontaneous and on a household scale. Therefore, the problem of environmental treatment is more difficult, leading to serious environmental pollution problems. The concentration of pollutants in wastewater are quite high, exceed the allowed standard BOD_5 = 2926.5 mg/l, COD = 4378 mg/l, NH_4^+ = 59.28 mg/l, PO_4^{3-} = 16.73 mg/l [1]. Therefore, effective measures should be taken to protect the environment.

There are alots of methods for treating organic compounds in wastewater that have been applied such as adsorption, flocculation, oxidation…In which, ozonation is one of the oxidation processes used for industrial wastewater treatment in which ozone molecules break down recalcitrant and toxic organic compounds into smaller molecules. The ozonation reaction is accomplished through two pathways: direct ozone oxidation and indirect free hydroxyl radical oxidation in the surface of catalysts [2] among which the latter appears to be more effective to treat various types of organic compounds. Many catalysts including metals, metal ions and metal oxides have been used for enhancing the activation of ozonation process, such as homogenous metal ions (Fe (II), Fe (III), Cu (II), Mn (II), Co (II), carbon aerogel, nano Fe, Fe/MgO, TiO_2 and MnO_2 [2, 3, 4, 5, 6]. Among these transition metal oxides, nano MnO_2 is one of the catalysts attracting the most attention due to their unique properties such as high activity, low cost, nontoxicity, high specific capacitance, rich structures and morphologies and have been widely used in the fields of supercapacitors, catalysis, Li batteries and chemical sensing. There were also many investigations to improve nano MnO_2 catalytic activity by combination with other materials [2, 4, 5].

In this research, the nano catalyst MnO_2 was synthesized and used as the reactive support and compared with free-radical initiator for ozonation of the organic compounds in Duong Lieu agriculture processing village, Ha Noi capital, Viet Nam.

II. Materials and Methods

A. Materials

The raw materials for synthesizing nano MnO_2 samples: Potassium permanganate ($KMnO_4$), manganese sulfate monohydrate ($MnSO_4$. H_2O) with analytical grade. The double-distilled deionized water was used throughout this study.

B. Synthesis of Nano MnO_2 Catalyst

Nano MnO_2 catalyst was synthesized by co-precipitation method. First, 0.507g $MnSO_4$. H_2O was dissolved in 100 ml of deionized water. Then, 0.316g $KMnO_4$ was dissolved in 100 ml of deionized water to form two homogeneous solutions, respectively. After that, the solution of potassium permanganate slowly droped into manganese sulfate solution by magnetic stirring; the speed was three drops per minute. The solution was further stirred for 15 minutes. The reactor was kept for 24 hours and the final product was obtained. Then the brown-black products were formed and washed with deionized water for several times. Finally, the products were dried in 105^0C for 2h.

C. Characterization of Nano MnO_2 Samples

The surface area and pore distributions of the material sample were determined by a Beckman Coulter SA3100 surface area analyzer based on the nitrogen adsorption-desorption isotherm at the temperature of liquid nitrogen (-196°C). The crystalline structure of MnO_2 catalyst was chareacterized by X-ray diffraction (XRD) technique using a Bruker B8 Advance X-ray powder diffractometer. The elemental composition analysis was performed by Energy dispersive analysis of X-rays (EDX, Varian Vista Ax). The size and morphology of materials were examined using scanning electron microscopy (SEM, Hitachi S-4800FEG) and transmission electron microscopy (TEM, Philips Tecnai G220 S-TWIN).

D. Sampling and Analysis Methods

The wastewater samples were taken from a household in the rice starch processing craft at Duong Lieu agricultural processing village, continuously for 30 days from May, 16th to June 14th. The samples were analyzed to determine the components in waste water (Table 1). The samples were filled in a PET bottle that was cold stored during transport and the kept in a laboratory freezer. Analysis results were compared with QCVN 40: 2011/BTNMT - National Technical Regulation on Industrial wastwater. Column B - Industrial wastwater discharged into receiving waters not used for domestic purposes.

Table 1. Indicators and methods of analysis

Parameter	Units	Analytical Methods
pH	-	Measured by pH meter
BOD_5	mg/l	Azid methods advance
COD	mg/l	Potassium bicromatate methods
Total Suspended Solids (TSS)	mg/l	Mass methods
Total Phosphorus (TP)	mg/l	Ascobic acid methods
Total Nitrogen (TN)	mg/l	Kjeldahl methods

E. Catalytic Ozone Degradation of Organic Compounds in Wastewater

A typical procedure for selective catalytic oxidation of organic compounds in wastewater: 1000 ml wastewater were put into glass beakers at room temperature. Then nano MnO_2 was added as catalysts and ozone was supplied in the aerated condition about two liters per minute. The effect of reaction time and catalytic concentration on the efficiency of organic matter treatment in wastewater samples was recorded (Table 2). To ensure the reproducibility of data, each experiment was conducted in duplicate and the average of the three measurements was computed.

Ozone was produced by an ozonizer (A-Ozone Sachben S5, Viet Nam) supplied with oxygen (2 scfm). The ozone in the inlet gas stream was analyzed by iodometric titration and was found to be 1.83 g/h.

Table 2. Experimental steps and conditions

Experiment	Conditions		
	V_{sample} (ml)	$C_{catalyst}$ (g/l)	Time (min)
Effect of time reaction	1000	0.02	0-60
Effect of catalyst concentration	1000	0-0.1	15

The catalytic activity of the catalyst was determined by the COD content of the samples. The conversion rates of COD were calculated, where C_{in} and C_{out} are the concentrations of organic compounds in samples at the inlet and outlet of the reactor, respectively (through COD parameter, mg/l). The average values of three sets of independent experiments were reported using three different batches of the samples.

$$X(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100$$

III. Results and Discussion

A. Catalyst Characterization

Nano MnO_2 catalyst was successful synthesized from potassium permanganate and manganese sulfate, by following the reaction:

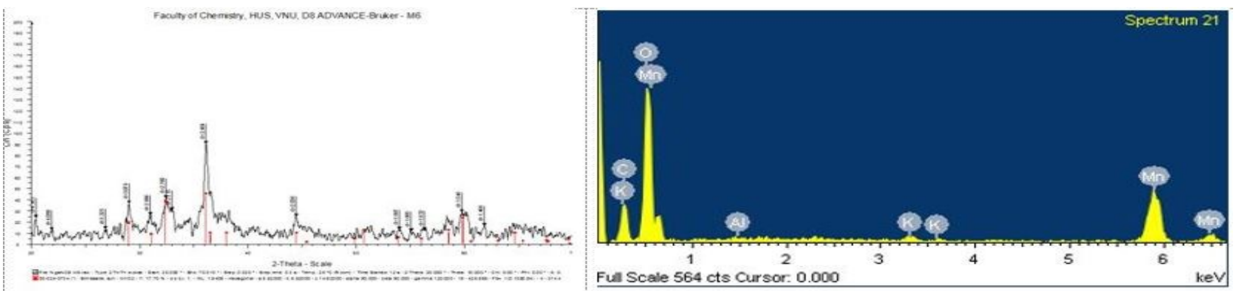
$$2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+$$

Table 3 shows the BET surface area of the samples. The nano MnO_2 sample has a BET surface area of 113.0601 m^2/g, the pore volume was 0.2070 cm^3/g, and the pore size was 7.8930 mm. It is obvious that the surface area of the synthesized material is high compared to previous reports [4].

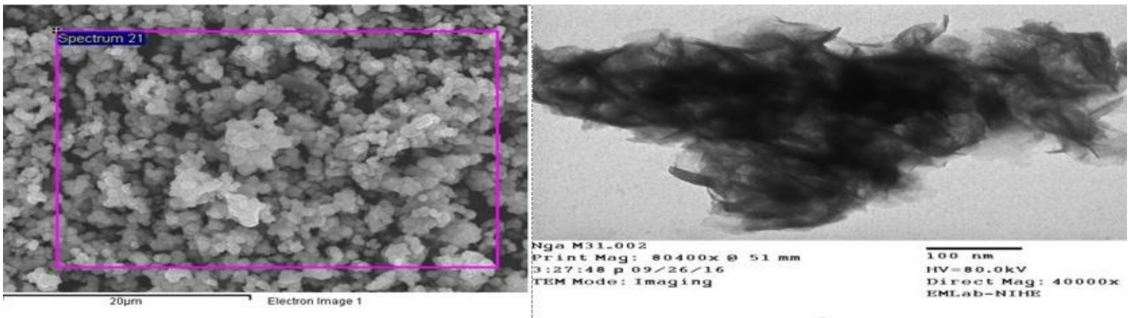
Table 3. Characteristics of the catalyst

Parameters	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Catalyst MnO_2	113.0601	0.2070	7.8936
MnO_2 [4]	81.8	0.242	-

XRD diffraction was firstly carried out to determine the crystalline structure of MnO_2 materials. The XRD pattern showed the sharp reflections characteristic of simple cubic MnO_2 at the peaks about 2θ = 28°; 37°; 43°; 55°; 57° (Fig. 1a) which can be assigned to the presence of MnO_x. Among the peaks, the peaks at 28°, 37°, and 55° were characterized for pyrolusite crystals of MnO_2 [7].



a b



c d

Fig. 1. (a) XRD diagram, (b) EDX diagram, (c) SEM and (d) TEM image of the material

The EDX analysis revealed mass fraction of the elements in the catalyst sample. Figure 1b showed that the catalysts consist of 48.25% manganese. Typical SEM and TEM images of the catalyst are shown in figure 1c and 1d. In the SEM and TEM image, the catalyst particles were observed with the average size about 0.5 µm. They were highly fractional (as seen in TEM image). This property accounts for the exceptional high surface area of the sample.

B. Catalytic Ozonation of Organic Compound in Wastewater

Composition of the Wastewater

Duong Lieu agricultural processing village was famous for its traditional products, such as: cassava starch, rice starch, candy, noodles... 85% of households in the commune participate in production activities. Annual output of about 20000 tons of cassava starch, 60000 tons of rice starch, 18000 tons of candy, 15000 tons of noodles per year.

Fig. 2. The production of noodles in the Duong Lieu agricultural processing village

But the production process is not synchronized with the waste collection and treatment system. According to recently studies and surveys, the water in Duong Lieu has been seriously polluted, including both surface and groundwater. Alots of wells in this village can not be used anymore, even smell bad. The process of producing in this village are almost handycraft. According to calculations, for every 10 tons of raw material in a household producces 7 tons solid waste and wasstewater. All poured down the sewers, canals, drainage channels around the village.

Fig. 3. The curent state of the drainage channels in the commune

The wastewater samples were taken once a day for 30 consecutive days at the outlet of the sewers of household production. They were light brown and opaque and of unpleasant odor. The organic matter in this sample was very high, 3-52 times higher than that of QCVN 40: 2011/BTNMT. The composition and characteristics of the wastewater samples are presented in table 4:

Table 4. Characteristics of the wastewater samples

Parameter	Unit	Result (n=30)			QCVN 40:2011 – Column B	Comparison with QCVN 40:2011 – Column B
		Min	Max	Med		
pH	-	3.8	4.7	4.2	5.5-9	Out of bounds
BOD_5	mg/l	2335.66	3208.91	2644.16	50	52.88 times higher
COD	mg/l	3518.72	4497.61	3993.74	150	26.62 times higher
TSS	mg/l	478.03	757.22	540.08	100	5.40 times higher
TP	mg/l	25.11	32.03	26.71	6	4.45 times higher
TN	mg/l	114.62	171.34	122.86	40	3.07 times higher

The results showed that the wastewater had a slight solution acidic with pH from 3.8 to 4.7 because of the process using acid for the material bleaching process. The content of organic substances and total suspended solids were relatively high with the average COD and BOD_5 content of 3993.74 mg/l, and 2644.16 mg/l, respectively. If the wastewater is not treated, the environment and human health will be affected.

The Effect of time on Degradation of Organic Compounds in Wastewater

In the following studies, conditions on treatment organic compounds (OC) in the wastewater were observed. We used a large amount of wastewater collected to ensure pH stability and initial components of samples. The wastewater samples had initial pH = 4.2 and COD = 3814.27 mg/l.

Proceeding oxidation of organic compounds in this wastewater without catalyst and with nano MnO_2 catalysts for 0-60 minutes the organic content was measured after the reaction through the COD content. The results are shown in Fig 4.

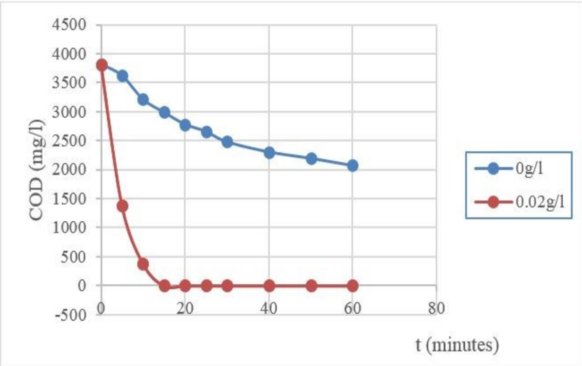


Fig. 4. The effect of time on degradation of OC

During the survey period (0-60 minutes), when the response time increased, the organic contents in the sample decreased. Without uncatalysts treatment, oxidation occured due to self-decomposing of ozone forming free radicals with slow reaction. After 60 minutes, the COD parameter is about 2074.03 mg/l. The mechamism of this reaction are:

$$O_3 + OC \rightarrow \text{Products}$$

After 60 minutes of treatment with nano MnO_2 catalyst, the COD content decreased from 3814.27 to 0 mg/l. The presence of the nano MnO_2 catalyst facilitated the formation of free radicals faster, so the reaction rate was faster. 5 minutes after treatment the efficiency reached 63.95%, and after 15 minutes the remaining COD content was 66.14 mg/l, reaching 98.27%. This value was within the allowable range of QCVN 40: 2011, column B. After 20 minutes of reaction, the treatment efficiency was 100%.

As described in literature [6-8], in acidic environment, besides the direct oxidation of ozone, ozone reacts with water to form radical $^*OH$ and then, the OC molecules are degraded by $^*OH$ (indirect oxidation):

$$O_3 + H_2O \rightarrow 2HO^* + O_2$$

$$HO^* + OC \rightarrow [OC\text{-}OH]^{+*}$$

In our catalytic process, ozonation occured indirectly by oxidation of the metal oxide catalyst. Ozone reacts with manganese dioxide to form O_2^- and then O_2^- reaction with water to form HOO^*. In the next step, hydroxyl radical is created by the reaction of ozone with HOO^*. Finally HO^* degrades OC molecules in solution

$$2O_3 + Mn^{4+} \rightarrow 2O_2^- + Mn^{6+} + O_2$$

$$O_2^- + H_2O \rightarrow HOO^* + HO^-$$

$$O_3 + HOO^* \rightarrow HO^* + O_2$$

$$OC + HO^* \rightarrow [OC\text{-}OH]^{+*}$$

In the presence of MnO_2, ozone converts to its more active component (O_2^-), this reacts with water faster than O_3 alone.

Several authors have studied the treatment of the waste water in Duong Lieu agriculture processing village by different methods. Ngo Tu Thanh was treated wastewater by anaerobic method. The results show that: the optimal quantity of additional sludge was 10%, with which the effectiveness of treatment reached 75% (biochemical oxygen demand, BOD) and the effectiveness of treatment increased by 7-11% in comparison with control without cariers. It is necessary to finish the anaerobic treatment after 6 days, when the effetiveness reached 75% (BOD) in order to begin the aerobic treatment for higher effectiveness [9].

The nano MnO_2 catalyst in the present research showed good oxidation capacity in organic slurry and this can be used in the treatment of organic matter in pollution water sources.

Effect of Catalyst Concentration on OC Ozonation

The effect of catalyst concentrations, from 0 – 0.1 g/l, on the rate of OC ozonation was tested. The rate of OC ozonation increased with the increased concentration of nano MnO_2 catalyst as shown in Fig. 5.

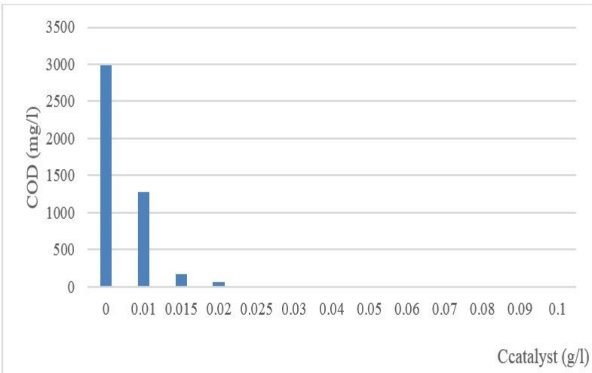


Fig. 5. The effect of catalyst concentration on degradation of OC

The OC concentration reduced quickly over reaction time. After 15 minutes, without catalyst, the degradation was influenced by the oxidation of ozone alone. The oxidation reaction OC ran slowly, making it less effective in degrading OC. The remaining COD contents was 2988.32 mg/l, degradation percentage of 21.65%. Catalytic ozonation of OC in the presence of nano MnO_2 was much more effective. With the catalyst concentration 0.02g/l, the remaing COD contents was 66.14 mg/l, the treatment efficiency was about 98.27% and the efficiency reached 100% when the catalyst concentration was about 0.025 to 0.1g/l. Higher concentrations of MnO_2 led to higher efficiencies but in a similar pattern to 0.02g/l concentration.

This fact indicates that 0.02g/l is the optimum catalyst concentration for the ozonation.

Propose Plans

In Duong Lieu village, with the current state of wastewater contains high levels of pollutants, which are not treated and discharged directly into the environment. That cause serious environmental problems so need to take measures to treatment. In this study, we propose the model of wastewater treatment in this village

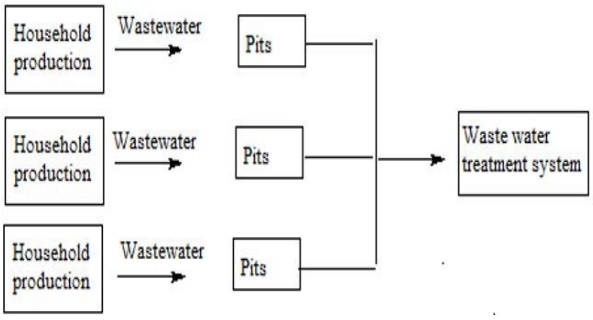


Fig. 6. Model of wastewater treatment in Duong Lieu village

Wastewater from household productions would be separated solid and suspended solids by the pits. And then, the wastewater can be collected into the convergent wastewater treatment systems. There, wastewater can be treated by adsorption, flocculation, oxidation methods.

IV. CONCLUSIONS

In the present work, nano MnO_2 catalyst were successfully prepared by the co-precipitation method at room temperature and exhibited excellent catalytic activity in ozonation of organic compound in wastewater. The nano particle catalyst had high surface area of 113.0601 m^2/g and high mesoporous showing pore size of 7.8936 mm and pore volume of 0.2070 cm^3/g. It has been proved to be a good catalyst for treatment of organic compounds in wastewater. For organic compounds in agricultural processing village, that have initial COD 3814.27 mg/l degradation. The optimum concentration of the catalyst was found to be 0.02g/l for 15 minutes.

Survey the ozonation with the nano MnO_2 catalyst at natural pH of wastewater to treat actual organic compounds in wastewater samples, the organic compound present in the samples decreased as measured by the reduced COD content from 3814.27 mg/l to 66.14 mg/l and satisfied the National technical regulation on the effluent of livestock (QCVN 40: 2011/BTNMT). This study may expand the further development of nano MnO_2 catalyst can serve as an appropriate material for treatment organic compounds in wastewater.

REFERENCES

[1] Le Thi Thuy, Nguyen Hong Son, Nguyen Truong Giang (2011), Research on posibility of water pollution from cassava starch processing by some species of aquatic plants, Science and technology Journal of Agriculture and Rural Development, Vol. 2, pp. 20-24.

[2] Snigdha Khuntia, Subrata K. Majumder, Pallab Ghosh (2016), Catalytic ozonation of dye in a microbubble system: Hydroxyl radical contribution and effect of salt, J. Environ. Chem. Eng. 4: 2250–2258.

[3] Zonggao Hu, Yafei Zhao, Jindun Liu, Jingtao Wang, Bing Zhang, Xu Xiang (2016), Ultrafine MnO_2 nanoparticles decorated on graphene oxide as a highly efficient and recyclable catalyst for aerobic oxidation of benzyl alcohol, Journal of Colloid and Interface Science, Vol.483, pp.26-33.

[4] Faheem Nawaz, Yongbing Xie, Jiadong Xiao, Hongbin Cao, Zahid Ali Ghazi, Zhuang Guo and Yue Chen (2016), The influence of the substituent on the phenol oxidation rate and reactive species in cubic MnO_2 catalytic ozonation, Catal. Sci. Technol. 6: 7875–7884.

[5] Xiuqin Tan, Yifeng Wan, Yajing Huang, Chun He, Zaili Zhang, Zhuoyan He, Lingling Hu, Jiawei Zeng and Dong Shu (2017), Three-dimensional MnO_2 porous hollow microspheres for enhanced activity as ozonation catalysts in degradation of bisphenol A, J. Hazard. Mater. 321: 162–172.

[6] Tran Manh Tri (2006) Advanced oxidation processes in water and wastewater, treatment, Science and technology publisher.

[7] Francesco Arena, Gíueppe Trunfio, Jacopo Negro, Barbara Fazio and Lorenzo Spadaro (2007), Basic Evidence of the Molecular Dispersion of MnCeOx Catalysts Synthesized via a Novel “Redox-Precipitation” Route, Chem. Mater. 19: 2269–2276.

[8] Youngze Liu, Jin Jiang, Jun. Ma, Yi Yang, Congwei Luo, Xiaoliu Huangfu and Zhongkai Guo (2015), Role of the propagation reactions on the hydroxyl radical formation in ozonation and peroxone (ozone/hydrogen peroxide) processes, Water Res. 68: 750–758.

[9] Ngo Tu Thanh, Le Van Tri, Le Thi Viet Ha (2010), Study on treatment of waste water of craft village Duong Lieu by anaerobic mean, Issues of basic research in life sciences, pp. 739-741.

AUTHOR’S PROFILE

Dr. Nguyen Thi Hong Hanh
Lecturer at Department of Chemistry, Faculty of Environmental, Vietnam National University of Agriculture. Major: Organic chemistry, Environ--mental science.
email id: nguyenthihonghanh.vnua@gmail.com