SYNTHESIS OF NANO MnO_2 CATALYST AND ITS APPLICATION TO TREATMENT OF ORGANIC COMPOUNDS IN LIVESTOCK'S WASTEWATER AFTER ANAEROBIC DIGESTION

Nguyen Thi Hong Hanh

Department of Chemistry, Vietnam National University of Agriculture

Email: nthhanh@vnua.edu.vn

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ABSTRACT

In this study, 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. Slurries taken from the pig farm after anaerobic digestion of livestock disposals 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. For livestock's slurry treatment, the catalytic ozonation with 0,02 g/l could reduce the COD demand from 1138.64 mg/l to 43.27 mg/l with 96.20% efficiency. Therefore, the ozonation with nano MnO_2 catalysts can be considered as an effective and feasible means for treating the livestock's wastewater after anaerobic digestion.

Keywords: Nano manganese dioxide, livestock's wastewater, ozonation.

Chế tạo xúc tác nano MnO_2 ứng dụng xử lý chất hữu cơ trong nước thải chăn nuôi sau biogas

TÓM TẮT

Vật liệu xúc tác nano MnO_2 được tổng hợp từ mangan sunfat và kali pemanganat bằng phương pháp đồng kết tủa ở nhiệt độ thường. Các đặc trưng cấu trúc sản phẩm được phân tích bằng các phương pháp hóa lý: Diện tích bề mặt riêng (BET), nhiễu xạ tia X (XRD), phổ tán xạ năng lượng điện tử (EDX), kính hiển vi điện tử quét (SEM), kính hiển vi điện tử truyền qua (TEM). Kết quả cho thấy sản phẩm thu được có kính thước hạt nhỏ mịn 0,5 µm, diện tích bề mặt riêng lớn 113.0601 m^2/g. Nước thải được lấy sau hệ thống biogas tại trang trại chăn nuôi lợn. Bước đầu nghiên cứu sử dụng hệ xúc tác cho phản ứng ôzôn hóa xử lý chất hữu cơ trong nước thải chăn nuôi sau biogas trong phòng thí nghiệm. Kết quả cho thấy các phản ứng có xúc tác nano MnO_2 thời gian phản ứng xảy ra nhanh hơn, hiệu quả tốt hơn so với phản ứng ôzôn hóa thông thường. Kết quả xử lý của xúc tác với nồng độ 0,02 g/l mẫu nước chăn nuôi sau biogas cho kết quả hàm lượng COD giảm từ 1138,64 mg/l xuống 43,27 mg/l, đạt hiệu quả xử lý 96,20%. Phản ứng ôzôn hóa chất hữu cơ với hệ xúc tác nano MnO_2 là một phương pháp có hiệu quả, có thể áp dụng để xử lý chất hữu cơ trong nước chăn nuôi sau biogas.

Từ khóa: Nano mangan dioxit, nước thải chăn nuôi, ôzôn hóa.

1. INTRODUCTION

In recent years, environmental issues in general and environment in animal husbandry have been paid attention. The model farm economy in our country is on the trend of strong development, contributing to increase productivity and economic efficiency. The total value of livestock products accounts for 22 - 25% of the total value of the industry. By

october 1st, 2016 our country had 2.5 million buffaloes, 5.5 million cows, 29 million pigs, and 362 million poultry, consequently, large quantities of wastes or disposals were discharged into the environment. Estimates of the amount of solids released were about 80 million tons and billions cubic meter of liquid waste. However, the treatment of wastes in most pig farm production facilities is limited to the use of biogas reactor for anaerobic digestion. By the pressure of production, the capacity of the biogas reactors was overloaded and the waste water or slurry (hereinafter referred to as slurry) following the process of anaerobic digestion did not meet the discharge standard in terms of allowable limit of BOD_5 = 3900 mg/l, TN = 532 mg/l, TSS = 973 mg/l, TP = 29,27 mg/l (Ho Thanh Tam *et al.*, 2014). Therefore, effective measures should be taken to ensure sustainable livestock development

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 (Khuntia *et al.*, 2016) 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 (Khuntia *et al.*, 2016; Nawaz *et al.*, 2016; Tan *et al.*, 2017, Tran Manh Tri, 2006). Among these, nano MnO_2 is one of the catalysts attracting the most attention. There were also many investigations to improve nano MnO_2 catalytic activity by combination with other materials (Khuntia *et al.*, 2016; Nawaz *et al.*, 2016; Tan *et al.*, 2017).

In this study, 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 livestock's wastewater after anaerobic digestion.

2. MATERIALS AND METHODS

2.1. Synthesis of nano MnO_2 catalyst

Nano MnO_2 catalyst was synthesized by co-precipitation method. First, 0.507 g $MnSO_4.H_2O$ was dissolved in 100 ml of deionized water. Then, 0.316 g $KMnO_4$ was dissolved in 100 ml of deionized water 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

2.2. 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 analyzed by X-ray diffraction (XRD) technique using a Bruker B8 Advance X-ray powder diffractometer. The elemental composition was determined 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).

2.3. Sampling and analysis methods

The slurry samples were collected at the biogas reactor outlet from a pig farm in Tien Duong Commune, Dong Anh District, Hanoi. The farm is located far from the residential area. It was built and operated since 2007. The farm area is about 15,000 m^2 with of pigsty area of 4000 m^2, gardens, and fish ponds. The number of pigs include 200 piglets, 50 sows, and 250 porkers. This farm has biogas reactor

Table 1. Indicators and methods of analysis

Parameter	Units	Analytical Methods
pH	-	Measured by pH meter (TCVN 6492:2000)
BOD_5	mg/l	Azid methods advance (TCVN 6001-2:2008)
COD	mg/l	Potassium bicromatate methods (TCVN 6491:1999)
Total Suspended Solids (TSS)	mg/l	Mass methods (TCVN 6625:2000)
Total Phosphorus (TP)	mg/l	Ascobic acid methods (TCVN 6202:1996)
Total Nitrogen (TN)	mg/l	Kjeldahl methods (TCVN 5987:1995)

Table 2. Experimental steps and conditions

Experiment	Conditions			
	V_{slurry} (ml)	$C_{catalyst}$ (g/l)	pH	Time (min)
Effect of pH	1000	0,02	2 - 12	10
Effect of time reaction	1000	0,02	8	0 - 60
Effect of catalyst concentration	1000	0 - 0,1	8	10

built with brick with a capacity of 20 $m^{3.}$ The slurry samples were taken at the outlet of the biogas reactor at the time of washing the barn (8:00 - 8:30 am) continuously for 30 days from March 9th to April 8th. The samples were analyzed to determine the components in waste water (Table 1). Wastewater samples were taken according to TCVN 5999: 1995. 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 62: 2016/BTNMT - National Technical Regulation on the effluent of livestock. Column B - Livestock effluents discharged into receiving waters not used for domestic purposes.

2.4. Catalytic ozone degradation of organic compounds in livestock' wastewater after bigogas

1000 ml slurry 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 pH, 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, VietNam) 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.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

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

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

The structure of materials analyzed by modern physico-chemical methods showed that

the surface area and the total pore volume of the catalyst were 113.0601 m^2/g and 0.2070 cm^3/g, respctively, and the pore size was 7.8930nm (Table 3). It is obvious that the surface area of the synthesized material is high compared to previous reports (Nawaz *et al.*, 2016; Tan *et al.*, 2017; Jalali *et al.* 2016).

The phase composition investigated by XRD revealedthe diffraction peaks at 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 (Arene *et al.*, 2007).

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 0,5µm. They were highly fractional (as seen in TEM image). This property accounts for the exceptional high surface area of the sample.

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 (Nawaz *et al.*, 2016)	81.8	0.242	-

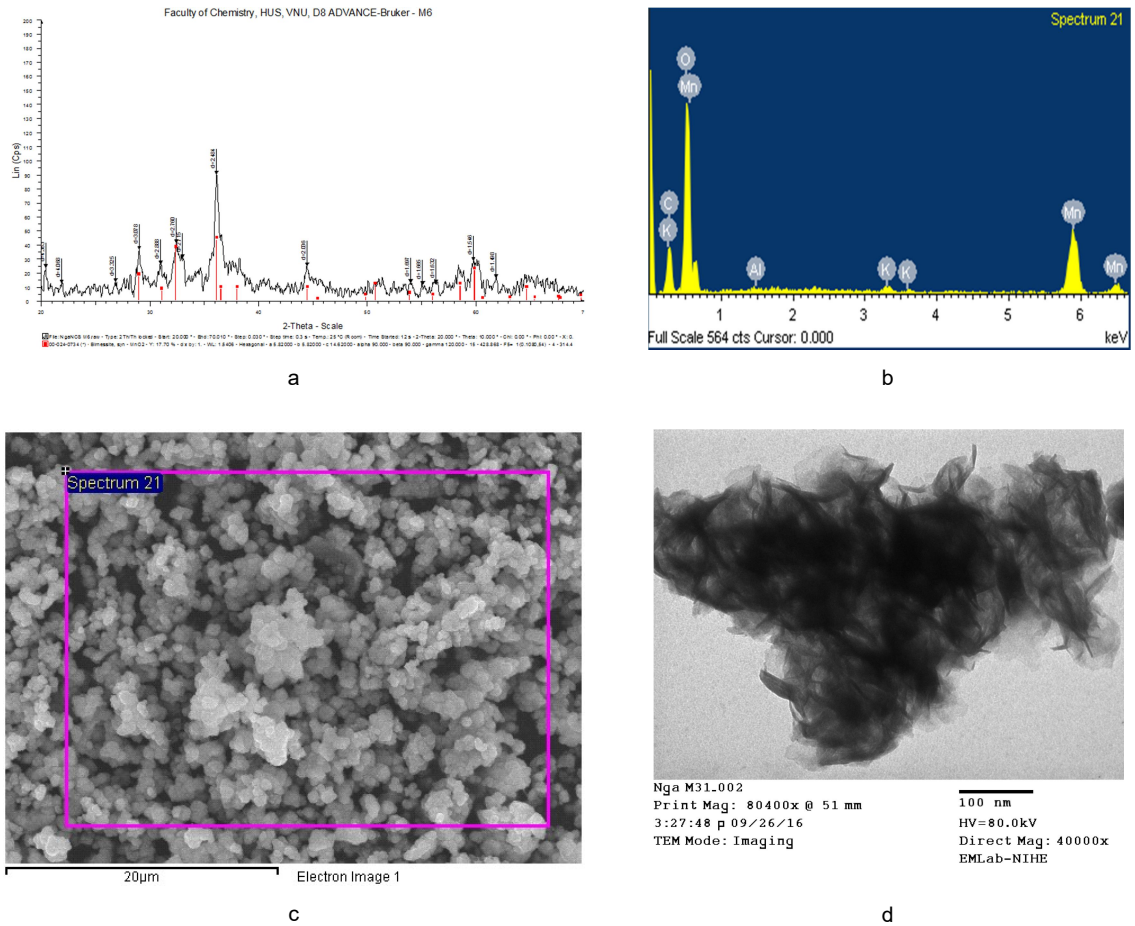

Fig 1. (a) XRD diagram, (b) EDX diagram, (c) SEM and (d) TEM image of the material

3.2. Ozonation of livestock' wastewater after biogas with MnO_2 catalysts

3.2.1. Composition of the slurry

The slurry samples taken once a day for 30 consecutive days at the outlet of the biogas reactor. They were light green and opaque and of unpleasant odor. The organic matter in the slurry was very high, 2-6 times higher than that of QCVN 62:2016/BTNMT. The composition and characteristics of the slurrysamples are presented in table 4.

The results showed that the slurry had a slight solution alkalinity with pH from 7.1 to 8.5. The content of organic substances and total suspended solids were relatively high with the average COD and BOD content of 1169.25mg/l, and 612.07mg/l, respectively. If the slurry is not treated, the environment and human health will be affected.

Wastewater from anaerobic digestion contains mainly cellulose, hemixenlulose, protein, insoluble starch (Luong Duc Pham, 2003). The sample of wastewater after anaerobic digestion in the study by Nguyen Hoai Chau *et al.* (2010) contained TSS of 1228mg/l, COD = 1195mg/l, BOD_5 = 534mg/l, TN = 518mg/l, and TP = 67mg/l. Ho Thanh Tam and Tran Hoai Phong (2014) analyzed the composition of slurry from Le Hoang Minh pig farm at Dong Hung 2 hamlet, Dong Thanh commune, Binh Minh district, Vinh Long province reported with pH = 8.2, BOD_5 = 3900mg/l, TN = 532mg/l, TSS = 973mg/l, and TP = 29.27mg/l.

3.2.2. Effect of pH solution on oxidation organic compounds (OC)

In the following studies, conditions on treatment organic compounds in the slurry were observed. We used a large amount of slurry collected to ensure pH stability and initial components of samples. Slurry samples had initial pH = 7.8 and COD = 1138.64 mg/l.

The pH of the solution plays an important role in the contaminant degradation mechanism during an oxidation process. Therefore, the effect of initial pH of the wastewater solutions on degradation was studied at pH values ranging from 2 to 12. Slurry samples were adjusted pH with HCl 1N and NaOH 1N to achieve a suitable pH value. Determine the initial organic content and the amount remaining after the reaction via the COD content. The Figure 2 shows the removal percentages of organic compounds under different pH conditions.

At the pH range form 2 to 6.5 the percentage of OC removal decreased to 30.18% but it increased with pH thereafter (Fig.2). At pH = 8, the treatment efficiency has reached 96.20% and continued to increase as the pH increases. In the subsequent studies, the treatment condition was chosen at the pH of slurry (pH ~ 8). This was the pH range in which the treatment efficiency of the MnO_2 catalyst was relatively high, suitable and simple for application in processing technology, minimizing the use of extra chemical compounds to adjust pH.

Table 4. Characteristics of the slurry samples

Parameter	Unit	Result (n=30)			QCVN 62:2016 - Column B	Comparison with QCVN 62:2016 - Column B
		Min	Max	Med		
pH	-	7.1	8.5	7.8	5.5-9	Within the allowable range
BOD_5	mg/l	416.92	867.88	612.7	100	6.12 times higher
COD	mg/l	872.33	1336.81	1169.25	300	3.89 times higher
TSS	mg/l	503.77	961.27	765.39	150	5.10 times higher
TP	mg/l	52.04	90.65	62.81	-	-
TN	mg/l	363.19	472.02	418.03	150	2.79 times higher

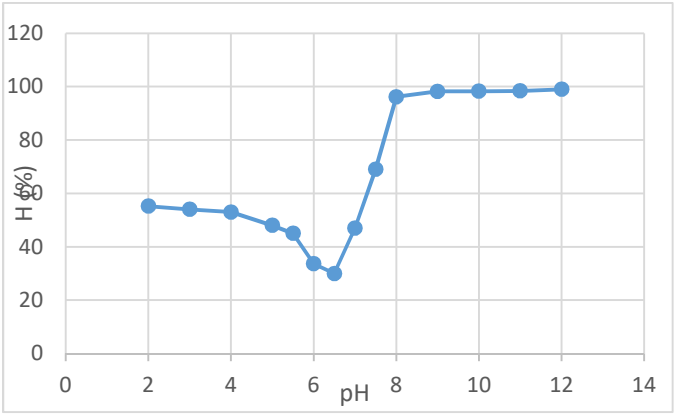

Fig 2. Effect of initial pH on degradation of organic compounds

The ability to react with organic degradation of ozone is realized in two processes: direct oxidation and indirect oxidation by hydroxyl radical (HO*) formed by ozone decomposed. At acidic pH, the high percentage of OC removal can be explained by the direct oxidation of OC molecules by ozone, which is best performed at acidic pH.

O_3 + OC → Products

As described in literature (Liu *et al.*, 2015; Tran Manh Tri, 2006), 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 alkaline condition, besides these oxidation reactions of ozone, there is also the formation of radical HOO^* that can produce O_3 molecules and make the oxidation more effective:

$$O_3 + OH^- \rightarrow HOO^* + O_2^-$$

$$O_2 + HOO^* \rightarrow O_3 + {}^*OH$$

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 MB 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.

3.2.3. The effect of time on degradation of organic compounds in wastewater

Proceeding oxidation of organic compounds in slurry without catalyst and with nano MnO_2 catalysts for 0-60 minutesthe organic content was measured after the reaction through the COD content. The results are shown in Figure 3.

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 of treatment, the COD content decreased from 1138.64mg/l to 427.81mg/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 67.76%, and after 10 minutes the remaining COD content was 43.27 mg/l, reaching 96.20%. This value was within the allowable range of QCVN 62:2016, column B. After 15 minutes of reaction, the treatment efficiency was 100%.

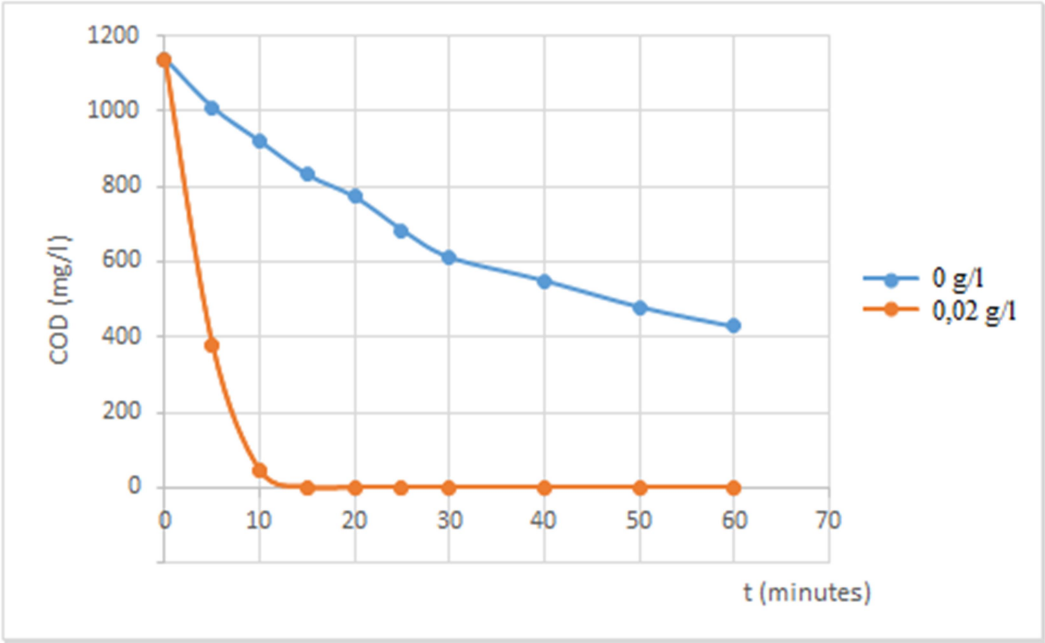

Fig 3. The effect of time on degradation of OC

Several authors have studied the treatment of the slurry by different methods. Dang Xuyen Nhu (2005), treated piggery wastewater in UASB reactor load water-hyacinth pond and reported that the system reached the steady state after three months and the organic, bacterial kinetic constants were determined for the effluent. The results indicated that the effluent from the system reached Vietnamese standards for the surface water quality standard, pH = 6.8 - 7.1, TSS < 80 mg/l, N-NO_3^- < 15 mg/l, coliform < 10.000 TB/100 ml. The parameters COD decreased 80%, N-NH_4^+ decreased 70%. Nguyen Hoai Chau, Tran Manh Hai (2010) treated waste water after anaerobic digestion with a trickle filter for good efficiency with COD reduction 80 - 92%. Ho Thanh Tam and Tran Hoai Phong (2014) used 4 strains aggregation bacteria *{Bacillus cereus* KG05, *Bacdius megaterium* VLOl, *Bacillus* sp. VLOS, *Bacillus aiyabhattai STOZ)* for treatment of piggery slury at 8 liter scale in the laboratory. The results showed that aggregation efficiency was 84 - 86%, and TSS and BOD_5 reduced 40.5 times and 144.4 times compared with controls, respectively. The parameters regarding of phosphorus and ammonium concentrations and octhophospahe level met the requirements of the standard A or B of QCVN40:2011/BTNMT after 2 treatment cycles (31 hours). A pair of *Bacillus cereus* KG05 and *Bacillus megaterium* ATJOI was selected to apply in piggery slurry treatment in the containers; 80 and 800-liter at the pig farm. The results showed that the highest aggregation efficiency was in the second cycle with 90.4% (80 liter container) and 82.6% (800 liter container), and pH, TSS, and TP reached to standard A or B of QCVN40:2011/BTNMT; while concentration of BOD_5, TN, N-NH_4^+ P-PO_4^{3-} decreased over 50% compared to the control

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.

3.2.4. Effect of catalyst concentration on OC ozonation

The effect of catalyst concentrations, from 0 -0.1g/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.4.

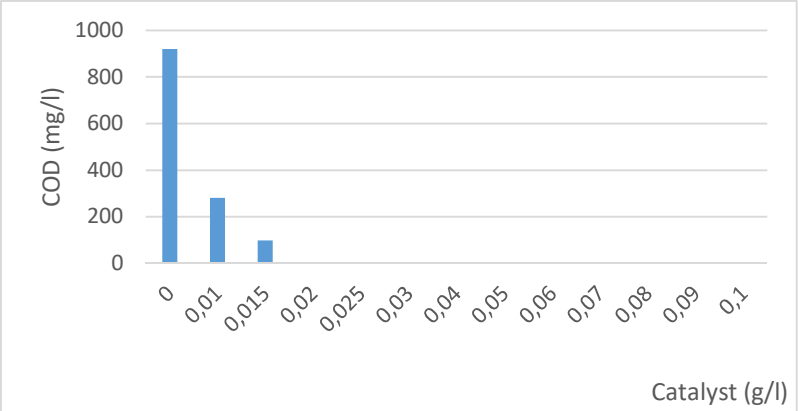

Fig 4. The effect of catalyst concentration on degradation of OC

The OC concentration reduced quickly over reaction time. After 10 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 920.14 mg/l, degradation percentage of 19.19%. Catalytic ozonation of OC in the presence of nano MnO_2 was much more effective. With the catalyst concentration 0.02 g/l, the remaing COD contents was 43.27 mg/l, the treatment efficiency was about 96.20% and the efficiency reached 100% when the catalyst concentration was about 0,025 to 0,1 g/l. Higher concentrations of MnO_2 led to higher efficiencies but in a similar pattern to 0.02 g/l concentration. This fact indicates that 0.02 g/l is the optimum catalyst concentration for the ozonation.

4. CONCLUSIONS

We have successfully synthesized nano MnO_2 catalyst by the co-precipitation method at room temperature. The nano particle catalyst had high surface area of 113.0601 m^2/g and high mesoporous showing pore size of 7.8936 nm 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 livestock' wastewater after anaerobic digestion, that have initial COD 1138.64 mg/l degradation, the catalyst showed lowest activity at neutral environment, pH = 6 (about 90%) and higher activity in alkaline environment with the degradation of 96.20% achieved at pH = 8 similar to the pH of the slurry. The optimum concentration of the catalyst was found to be 1g/L.

Applying 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 1138.64 mg/l to 43.27 mg/l and satisfied the National technical regulation on the effluent of livestock (QCVN 62:2016/BTNMT). This study confirms that nano MnO_2 catalys can serve as an appropriate material for water treatment.

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