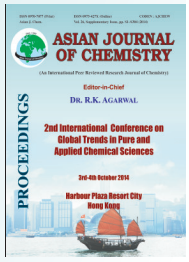
Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S110-S114

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19026



Removal of Hazardous Malachite Green from Aqueous Solution by Basic-Modified Rice Husk

MANOP SRIUTTHA[1,*], KITIYAPORN WITTAYANARAKUL[1], BUNG-ORN HEMUNG[1] and WIMONRAT TONGPOOTHORN[2]

[1]Faculty of Applied Science and Engineering, Khon Kaen University, Nong Khai Campus, Nongkhai 43000, Thailand
[2]Department of Chemistry, Faculty of Engineering Rajamangala University of Technology Isan, Khon Kaen Campus, Khon Kaen 40000, Thailand

*Corresponding author: E-mail: manosr@kku.ac.th, manulism99@gmail.com

Published online: 24 December 2014; AJC-16450

Rice husk is a waste material that potentially be used as a low cost adsorbent in wastewater treatment. Hence, the removal of malachite green dye from aqueous solution by basic modified rice husk was studied in the batch adsorption experiment. The Langmuir and Freundlich isotherms were applied to identify the adsorption type. At equilibrium time, the Langmuir isotherm model was fit rather than the Freundlich isotherm. The maximum monolayer adsorption capacity was found to be 151.51 mg g^{-1}. Kinetic analysis showed that the sorption kinetic of malachite green by basic modified rice husk obeyed the pseudo-second order sorption. According to the whole study, the basic modified rice husk had a potential to be an alternative adsorbent to remove the hazardous malachite green.

Keywords: Basic modified rice husk, Malachite green, Adsorption, Adsorbent.

INTRODUCTION

Global environmental problems have been caused by the industrialization for the developing countries. Moreover, industrial activities utilized the huge volume of water and subsequently discarded as pollutants including heavy metals, organic and inorganic compounds and dyes for textile. Malachite green, a synthetic dye, composes of the *N*-methyl diaminotriphenylmethane. It is applied in the aquaculture as the biocide and it was highly accumulated in fish flesh. Malachite green is also widely used as colorant for textile industries[1]. This process generated the waste water containing malachite green at approximately 10-200 mg/mL[2]. However, malachite green is considered to be a risk for human health. It may cause the adverse effects on the immune and reproductive systems. The carcinogenic properties and tumor promotion of malachite green have been reported[3]. Generally, malachite green strongly absorbs the sunlight resulted in a reduction of photosynthesis of phytoplankton due to insufficient of light intensity. Therefore, contamination of malachite green in natural reservoir may affect the ecosystem[4]. Therefore, removal of malachite green is necessary and also be a big challenge.

Several methods have been developed to remove dyes from waste water, based on the physical, chemical and biological methods[5,6]. Adsorption technique by activated charcoal showed the high potential for removing pollutants from waste water due to high efficiency[7]. However, high cost is somewhat limitation. There are many by-products from agricultural activity showed the potential to be alternative absorbents *e.g.*, neem leaf powder, hazel nut shells, rice hull, wood shavings, cedar sawdust[8], banana peel[9] and pineapple stem[10].

Rice husk (RH) is an agricultural by-product from the rice milling factories and available abundantly in the Southeast Asia. The rice mill production was estimated annually at about 600 million tons and 22 % this amount is produced to be rice husk. This rice husk is normally dumped as a waste. The rice husk consists of cellulose, hemicelluloses and lignin about 32.24, 21.44 and 21.34 %, respectively[11]. Thus, rice husk could be used as the absorbent due to the presentation of cellulose. However, the inner surface of rice husk is coated by wax and natural fats, inhibiting the adsorption properties by chemical or physical mechanisms[12]. Therefore, modification of rice husk is necessary to improve the adsorption ability.

Modification of rice husk can be made by acid solutions. Those methods could remove lignin and reduce the crystalline of cellulose, resulting in porous surface[13]. The physical modification of rice husk by high temperature was performed[14]. Modification of husk from rice by alkaline has been reported. However, the information regarding different varieties of rice should be thoroughly investigated. The aim of this work was to improve malachite green adsorption by husk from jasmine

rice using an alkaline treatment was investigated based on the equilibrium isotherm and adsorption kinetic.

EXPERIMENTAL

Malachite green (molar mass: 365 g mol^{-1}) was purchased from Sigma-Aldrich. The stock solution was prepared at 1,000 mg L^{-1} in double-distilled water (DI-water). The husk from Thai jasmine rice (*Oryza sativa* L.) was obtained from a rice milling factory at Nong Song Hong, Nongkhai province, Thailand.

Preparation of basically modified rice husk: Rice husk was washed repeatedly with deionized-water until the clear effluent was observed and it was dried overnight at 60 °C. The dried rice husk was mixed with NaOH solution (1 % w/v) at the ratio of rice husk:NaOH of 1:15 before autoclaving at 10 psi for 15 min. Then, the obtained sample was washed thoroughly with deionized-water until the neutral pH was observed. Finally, the rice husk was dried overnight in an oven at 60 °C before grinding to powder. The powder was sieved through the 300 μm and particle smaller than 300 μm was collected for being the basically modified rice husk.

Characterization of basic modified rice husk

Microstructure: The surface structure of basic modified rice husk was analyzed by the scanning electron microscopy (Hitachi, Model S-3000N, Japan). The samples were gold coated using a sputter coater prior to analyze at an electron acceleration voltage of 5 kV.

Fourier transform infrared spectroscopy: The sample was mixed with KBr and pressed as a pellet in order to determine functional groups within the basic modified rice husk using a FT-IR spectrometer (Spectrum One, Perkin-Elmer, England). The FT-IR spectra were scanned in the range of 4000-450 cm^{-1}.

Batch adsorption of basic modified rice husk: The adsorption of malachite green on basic modified rice husk was studied in batch equilibrium experiment. The basic modified rice husk (0.2 g) was mixed with 20 mL of malachite green solution at various concentrations (100, 200, 300, 400 and 500 mg L^{-1}). The mixture was shaken at a constant speed of 200 rpm for different times of 15, 30, 60, 180 and 360 min in the shaking bath (Model VS-8480SFN, Vision Scientific, Korea) at 40 °C. The solution was filtered through the filter paper number 41 (Wattman®) and malachite green concentration was determined by measuring the absorbance at 618 nm using the visible spectrophotometer (Model CE1021, Cecil Instruments, England). The adsorption capacity at equilibrium, q_e (mg g^{-1}) was calculated according to the method described by Hameed *et al.*[10] as shown in eqn. 1:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), V is the volume of the solution (L), W is the weight of the basic modified rice husk (g). All the experiments were performed triplicate and the average value were reported.

RESULTS AND DISCUSSION

Microstructure: SEM determination of rice husk after NaOH treatment provides insight on morphology of rice husk upon treatment. The SEM micrograph of basic modified rice husk is presented in Fig. 1. The surface of rice husk showed the cracking of conical protrusions. This suggested that the surface integrity of rice husk was modified by alkaline treatment. Moreover, the rough surface would like increase surface area. This would allow the basic modified rice husk to be the effective adsorbent. Chakraborty *et al.*[14] reported that the conical protrusions of rice husk surface were also cracked by thermo-chemical treatment, resulting in an increase in surface roughness.

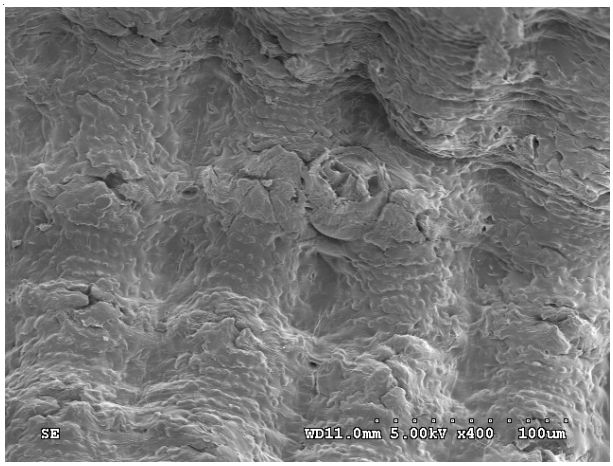


Fig. 1. SEM micrograph of basic modified rice husk

Fourier transform infrared spectroscopy: The FTIR technique is powerful tool to characterize the functional groups within biomaterial. The information would be beneficial to identify the binding mechanism of basic modified rice husk to the malachite green. The FTIR spectra of the rice husk after NaOH treatment is presented in Fig. 2. The stretching vibration was observed in the region of 3600-3200 cm^{-1}. The band stretching from OH vibrations showed the adsorption peak at around 3433 cm^{-1}. This indicated the existence of free hydroxyl groups. The C-H stretching vibration was observed at 2927 cm^{-1}, indicating the alkane groups[15]. The C=C stretching vibration between 1652-1546 cm^{-1} were found and indicated the signal from alkenes and aromatic groups. In addition, the aromatic groups were also showed in the peak around 1508 cm^{-1}. The presence of CH_2 was evidenced by the peaks at around 1459 cm^{-1}, while that for CH_3 was at 1366 cm^{-1}. The carboxyl-carbonate structures was reported at 1399 cm^{-1} and also found in basic modified rice husk. The peaks around 1237, 1102, 1020 and 862-476 cm^{-1} were from the CHOH stretching, Si-O-Si stretching, Si-O stretching and Si-H groups, respectively. According to the FTIR results, the basic modified rice husk presented more functional groups, which could be potentially adsorbed the organic dye such as malachite green.

Bath adsorption isotherm: The adsorption isotherm of basic modified rice husk toward malachite green indicated the distribution of malachite green in aqueous phase and solid phase at equilibrium (Fig. 3).

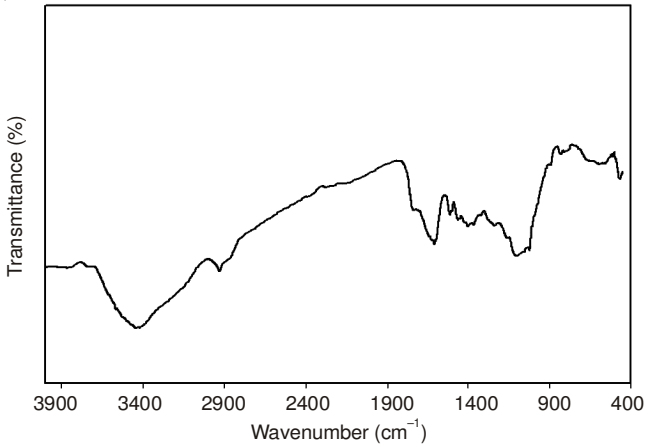


Fig. 2. FTIR spectrum of basic modified rice husk

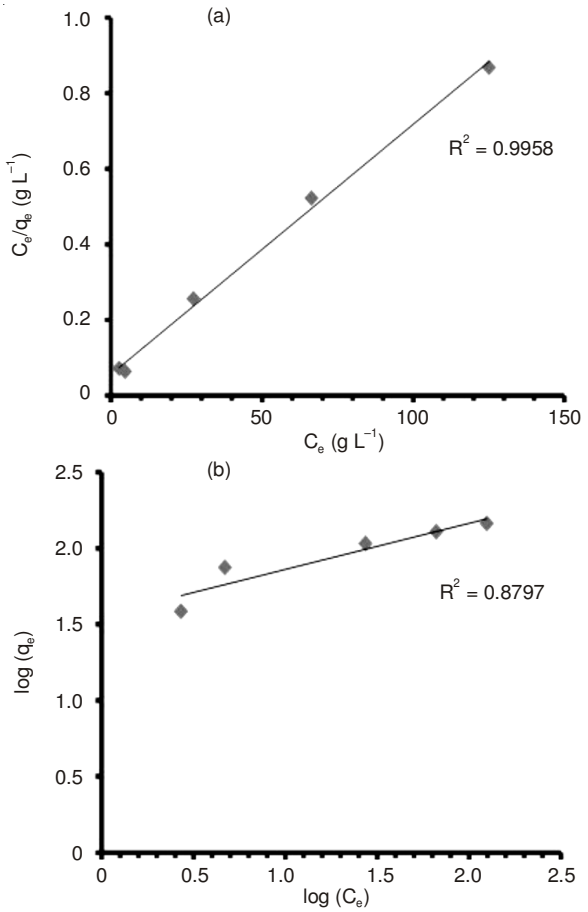


Fig. 3. Adsorption model of Langmuir isotherm (a) and Freundlich isotherm (b)

Langmuir was applied to evaluate the adsorption behavior based on monolayer adsorption without transmigration of malachite green to the plane of surface. The linear form of Langmuir's isotherm model is given by the following eqn. 2:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \left(\frac{1}{Q_0}\right)C_e \qquad (2)$$

where C_e is the equilibrium concentration of the adsorbate malachite green (mg L^{-1}), q_e the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}) and Q_o and b are Langmuir constants related to the adsorption capacity and rate of adsorption, respectively (Table-1). The homogeneous surface of adsorbent was indicated by the information from the Langmuir isotherm model. This allowed the malachite green to adsorb on the surface of basic modified rice husk as the monolayer coverage. The maximum capacity of basic modified rice husk (Q_0) in this study was higher than that value reported for activated carbon from basic treated rice husk[16], activated carbon from coconut coir[17] and treated ginger waste[2]. Moreover, our value was much higher than alkaline treated husk of rice from India[18]. The different capacities may from the different varieties of rice (Jasmine and other rice). It has been reported that activated carbon from ground nut shell showed higher value than our study[19].

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS FOR MALACHITE GREEN ADSORPTION ONTO BASIC MODIFIED RICE HUSK AT 40 °C

Langmuir isotherm	Value
Q_o (mg g^{-1})	151.52
b (mg^{-1})	0.117
R^2	0.9958
R_L	16.8E-03
Freundlich isotherm n	3.308
K_F [(mg g^{-1})(mg^{-1})$^{1/n}$]	36.18
R^2	0.8797

Freundlich isotherm, which based on the heterogeneous surface energies, was also applied to characterize the adsorption behavior of malachite green onto basic modified rice husk. The linear equation of Freundlich isotherm model was given by the following eqn. 3:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \qquad (3)$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate malachite green and K_F and n are Freundlich constants and an intensity of adsorption. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of malachite green adsorbed onto basic modified rice husk for a unit equilibrium concentration. The slope 1/n ranging between 0 and 1, is a measurement of adsorption intensity or surface heterogeneity. The more heterogeneous is observed as its value gets closer to zero[20].

Generally, the value of 1/n is below unity, indicating a normal Freundlich isotherm. On the other hand, if the 1/n above unity, it indicates the cooperative adsorption[21]. The plot of log q_e *versus* log C_e gives straight lines yield the slope of '1/n' (Fig. 3b), which shows that the adsorption of malachite green also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated as summarized in Table-1.

The values for the parameters obtained from both isotherm models and the related correlation coefficients were used to consider the applicable model. According to the data in Table-1, the Langmuir model showed a better correlation ($R^2 = 0.9958$) than the Freundlich model ($R^2 = 0.8797$) due to the higher correlation coefficient.

Bath adsorption kinetics: The adsorption kinetics study describes the rate of dye uptake. The adsorption of malachite green to basic modified rice husk may be obeyed the pseudo-first order or pseudo-second order kinetics[22]. Pseudo-first-order kinetic equation was expressed in the form:

TABLE-2
KINETIC PARAMETERS FOR MALACHITE GREEN ADSORPTION ONTO BASIC MODIFIED RICE HUSK AT 40 ºC

Initial concentration (mg L^{-1})	q_e, exp (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q_1, cal (mg g^{-1})	k_1 (h^{-1})	R_1^2	q_2, cal (mg g^{-1})	k_2 [g(mg h)$^{-1}$]	R_2^2
100	38.72	40.16	0.1004	0.9702	39.21	0.0059	0.9999
200	76.40	95.23	0.4142	0.8679	78.74	0.0012	0.9979
300	111.50	108.69	0.0326	0.8857	112.35	0.0019	0.9996
400	135.78	129.87	0.0090	0.1422	136.98	0.0015	0.9989
500	155.12	147.05	0.0147	0.4255	156.25	0.0012	0.9987

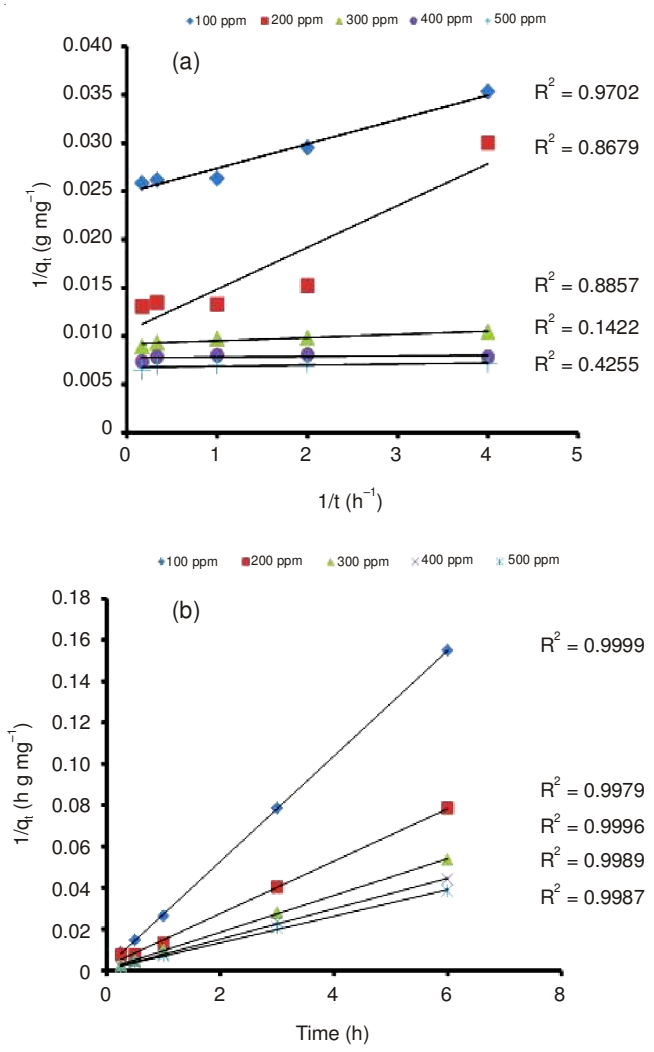


Fig. 4. Pseudo-first order sorption kinetics (a) and pseudo-second order sorption kinetics (b) of malachite green onto basic modified rice husk

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right)\left(\frac{1}{t}\right) + \frac{1}{q_1} \quad (4)$$

Pseudo-second order kinetic model can be written by the following equation:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_2^2}\right) + \frac{t}{q_2} \quad (5)$$

where q_t is the amount of malachite green adsorbed on the adsorbent at various times t, q_1 the maximum adsorption capacity (mg g^{-1}) for the pseudo first order adsorption, k_1 the rate constant (h^{-1}) of the pseudo first order model for the adsorption process, q^2 maximum adsorption capacity (mg g^{-1}) for the pseudo second order adsorption, k_2 the rate constant of the pseudo second adsorption (g mg^{-1} h^{-1}). The values of q_1, q_2, k_1, k_2 and correlation coefficient of malachite green were calculated from these plots and are shown in Table-2. The correlation coefficient (R_1^2) for pseudo first order adsorption are between 0.1422 and 0.9702 while the correlation coefficient (R_2^2) for pseudo second order adsorption are between 0.9979 and 0.9999. In addition, the maximum adsorption capacity for the pseudo second order adsorption (q_2) is closer to the observed values (q_e, exp) than the maximum adsorption capacity for the pseudo first order adsorption (q_1). From the results, the adsorption behaviour of malachite green onto basic modified rice husk would likely follow the pseudo second order kinetic model[22].

Conclusion

Basic modified rice husk showed the cracked structure with porous surface, which would provide the adsorption with malachite green. In addition, the functional group in the basic modified rice husk would facilitate the interaction toward malachite green. Based on the equilibrium data, the Langmuir isotherm showed higher correlation for dye adsorption than by the Freundlich adsorption isotherm. The isotherm constants were calculated successfully and used to compare the adsorptive capacities of basic modified rice husk. Based on the study, rice husk could be an alternative adsorbent for removing the organic dye from aqueous solution through the modification by alkaline treatment. Agricultural waste had a potential to utilize as an alternative adsorbent. This implied the economic treatment to remove dye from textile industries.

ACKNOWLEDGEMENTS

The Faculty of Applied Science and Engineering, Khon Kaen University, Nong Khai Campus, was acknowledged for all facilities. The adsorption testing was contributed invaluably by the research assistant, Mr. Suthee Chorwong. Financial support was the project to develop the new researcher, Khon Kaen University.

REFERENCES

1. C. O'Neill, F.R. Hawkes, D.L. Hawkes, N.D. Lourenço, H.M. Pinheiro and W. Delée, *J. Chem. Technol. Biotechnol.*, **74**, 1009 (1999).
2. R. Ahmad and R. Kumar, *J. Environ. Manage.*, **91**, 1032 (2010).
3. S. Srivastava, R. Sinha and D. Roy, *Aquat. Toxicol.*, **66**, 319 (2004).
4. S. Arellano-Cardenas, S. Lopez-Cortez, M. Cornejo-Mazon and J.C. Mares-Gutierrez, *Appl. Surf. Sci.*, **280**, 74 (2013).
5. R.F.P. Nogueira, M.R.A. Silva and A.G. Trovo, *Sol. Energy*, **79**, 384 (2005).
6. F. Sayilkan, M. Asilturk, P. Tatar, N. Kiraz, E. Arpac and H. Sayilkan, *J. Hazard. Mater.*, **144**, 140 (2007).

7. J. Zhang, Y. Li, C. Zhang and Y. Jing, *J. Hazard. Mater*., **150**, 774 (2008).
8. P. Pengthamkeerati, T. Satapanajaru and O. Singchan, *J. Hazard. Mater*., **153**, 1149 (2008).
9. G. Annadurai, R. Juang and D. Lee, *J. Hazard. Mater*., **92**, 263 (2002).
10. B.H. Hameed, R.R. Krishni and S.S. Sata, *J. Hazard. Mater*., **162**, 305 (2009).
11. A.H. Mahvi, A. Maleki and A. Eslami, *Am. J. Appl. Sci*., **1**, 321 (2004).
12. B.S. Ndazi, S. Karlsson, J.V. Tesha and C.W. Nyahumwa, *Composites*, **38**, 925 (2007).
13. A.M. Yeneneh, S. Maitra and U. Eldemerdas, *J. Appl. Sci*., **11**, 3555 (2011).
14. S. Chakraborty, S. Chowdhury and P. Das Saha, *Carbohydr. Polym*., **86**, 1533 (2011).
15. S.B. Daffalla, H. Mukhtar and M.S. Shaharun, *Int. J. Chem. Environ. Eng.*, **3**, 192 (2012).
16. I.A. Rahman, B. Saad, S. Shaidan and E.S. Sya Rizal, *Bioresour. Technol*., **96**, 1578 (2005).
17. Y.C. Sharma and S.N. Upadhyay, *Energy Fuels*, **23**, 2983 (2009).
18. S. Chowdhury, R. Mishra, P. Saha and P. Kushwaha, *Desalination*, **265**, 159 (2011).
19. R. Malik, D.S. Ramteke and S.R. Wate, *Waste Manage*., **27**, 1129 (2007).
20. F. Haghseresht and G. Lu, *Energy Fuels*, **12**, 1100 (1998).
21. K. Fytianos, E. Voudrias and E. Kokkalis, *Chemosphere*, **40**, 3 (2000).
22. H. Tang, W. Zhou and L. Zhang, *J. Hazard. Mater*., **209-210**, 218 (2012).