

ADSORPTION OF CONGO RED USING Mg/Al HYDROTALCITE

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ABSTRACT

Mg/Al hydrotalcite and Mg/Al hydrotalcite intercalated with polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ (1:1) was synthesized and used as adsorbent colored-dye i.e. Congo red. Adsorption was conducted using batch system. The factor that influencing adsorption such as kinetic, thermodynamic, and pH was investigated. The results showed that kinetically adsorption of Mg/Al intercalated polyoxometalate was faster than Mg/Al hydrotalcite before intercalation. On the other side, thermodynamically adsorption using Mg/Al hydrotalcite is higher than Mg/Al hydrotalcite intercalated polyoxometalate. Probably due to high molecular size of Congo red can decreased the adsorption ability of Mg/Al hydrotalcite after intercalated.

Keywords: hydrotalcite, polyoxometalate, intercalated, Congo red, adsorption

INTRODUCTION

Hydrotalcite has general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2](A^{n-})_x/nH_2O$. This layer materials contains divalent and trivalent metal cation with high flexibility cation exchange and easily synthesized in laboratory (Zhao, *et.al*, 2011). Application of hydrotalcite can be achieved optimally by modification of these material.

The modification of hydrotalcite for various applications is interesting due to ion exchange ability such as sensors, membranes, adsorbents, catalysts, and ion exchanges (Duan *et.al*, 2011).

Modification of hydrotalcite can be achieved by intercalation using anion such as sulfate, carbonate, or nitrate. These anions are cations with small size (Asif *et.al*, 2017). In order to increase the ability of hydrotalcite as adsorbent, the use of macroanion is vital. Macroanions are rarely obtained in the nature or laboratory. Thus synthesis of macroanions for intercalant of hydrotalcite is intriguing research. Lesbani *et.al* (2008, 2015) was used polyoxometalates as macroanion for starting materials of ionic crystals and as catalysts. The advantages of polyoxometalate are high acidity, redox properties, high solubility depending on counter ions, and various structures such as Keggin, Dawson, Anderson, and Lacunary types. Among these polyoxometalates, Keggin type is commonly used in many applications due to stability of these compound. Polyoxometalates were applied as intercalant in many layer double hydroxides materials like hydrotalcite (Jia *et.al*, 2015, Liu *et.al*, 2016).

In this research, hydrotalcite and hydrotalcite intercalated Keggin type polyoxometalate of $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was used as adsorbent of Congo red. In the previous research, optimization of intercalation process of hydrotalcite was conducted using polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ (Palapa and Said, 2016). Congo red is an anionic azo dye having IUPAC

name as 1-naphthalesulfonic acid, 3, 3'-[4,4'-biphenylenebis(azo)] bis (4-amino disodium) salt (Bhoi, 2010). The adsorption process of hydrotalcite intercalated polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ is intended to determine the effect of pH, kinetic, and thermodynamic parameters by measuring residual concentration and adsorbed amount using UV-Vis spectrophotometer.

EXPERIMENTAL SECTION

Materials

The chemicals used are qualified materials such as sodium metasilicate, sodium tungstate, hydrochloric acid, potassium hydroxide, potassium chloride, diethyl ether, sodium hydroxide, sodium carbonate, magnesium nitrate, Congo red dye and aquadest.

Methods

Synthesis of hydrotalcite, polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$, and hydrotalcite intercalated $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ has been reported previously (Palapa and Said, 2016).

Application of Hydrotalcite intercalated by Polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ as adsorbent of Congo red dye

1. pH

pH reaction of Congo red adsorption on hydrotalcite intercalated was studied by varying the initial pH of Congo red solution. 0,1 g of hydrotalcite and hydrotalcite intercalated each added into 50 mL of Congo red dye solution 50 mg/L shaker until 10 minutes using a horizontal shaker. The initial pH of Congo red was set at 3, 4, 5, 6, 7, 8, 9 and 11 with the addition of 0,1 M NaOH and 0,1 M HCl. Then the Congo red was separated and the residual concentration after the adsorption process was measured using a UV-Visible spectrophotometer.

2. Kinetic

0,1 g of hydrotalcite and hydrotalcite intercalate each added into 50 mL of Congo red dye solution 50 mg/L shaker with variations in absorption time varied start from 10, 20, 30, 40, 50,

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60, 70, 80, 90, 100, 110 and 120 minutes using a horizontal shaker. The solution of the adsorbed Congo red dye substance was separated by filtration and then measured its concentration by using UV-Vis spectrophotometer. The adsorption rate can be calculated using the Langmuir Equation 1.

3. Thermodynamic

Thermodynamic adsorption of the Congo red dye into hydrotalcite and hydrotalcite intercalated of experiment series as carried out through a series of experiments by varying the concentration and the adsorption temperature. 0,1 g hydrotalcite intercalated by polyoxometalate added 50 mL of Congo red dye solution varied concentration 50, 60, 70, 80 and 90 mg/L while stirred using a horizontal shaker for 30 min at varying temperatures 30, 40, 50, 60 and 70°C. As the control, in different containers as much as 0,1 g of hydrotalcite added into 50 mL Congo red dye solution varied of concentration 10, 20, 30, 40 and 50 mg/L. The solution was filtered and Congo red separated from the adsorbent was measured using a UV-Visible spectrophotometer.

Data Analysis

Hydrotalcite and hydrotalcite intercalated by polyoxometalate were characterizations using FT-IR, XRD, and TG-DTA. The result was applied as adsorbent Congo red dye. The adsorption process was studied by the kinetic and thermodynamic parameter. The kinetics of adsorption was studied by varied of time and adsorption rate was calculated with Langmuir equation:

$$\ln\left(\frac{C_0}{C}\right) = k_1 \frac{t}{C} + K \quad (1)$$

Where :

C_0 = Initial concentration of Congo red

C = Concentration of Congo red after the time

t = Time of adsorption

K = The adsorption equilibrium constant

Thermodynamic Parameters was studied by varied of concentration Congo red dye, adsorption capacity and adsorption energy calculated using Langmuir eq:

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \quad (2)$$

$$E = -RT \ln K \quad (3)$$

Where :

C = The Congo red concentration after adsorption reaches equilibrium

m = Mol of Congo red adsorption 0,1 g hydrotalcite

K = Equilibrium constant

b = Adsorption capacity

E = Adsorption Energy

R = Boltzmann constant

T = Temperature

Whereas to find the coefficient value of adsorbate distribution is used the equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

Where :

K_d = Coefficient distribution adsorption find the coefficient value of adsorbate distribution (q_e/C_e)

ΔH = Enthalphy

ΔS = Enthrophy

R = Boltzmann constant

T = Temperature

The bonds formed between the adsorbate and the adsorbent was studied by FT-IR spectrophotometer.

RESULTS AND DISCUSSION

Characterization of intercalated layered double hydroxide with $H_4[\alpha-SiW_{12}O_{40}].nH_2O$ was presented by Palapa and Said (2016) in previous published article. In this results, adsorption of congo red process was systematically reported.

Effect of Initial pH Adsorption of Congo red Dye by Hydrotalcite Mg/Al Intercalated Polyoxometalate $H_4[\alpha-SiW_{12}O_{40}].nH_2O$

pH adsorption of hydrotalcite and hydrotalcite intercalated to Congo red is shown in Figure 1. Hydrotalcite has optimal pH at pH 9 with adsorbed concentration of 48,893 ppm with addition of 0.05 mL of hydrochloric acid. The insertion double layer hydroxyl has an optimum pH at pH 8 with an adsorbed concentration of 47.529 ppm with addition of 0.10 mL of sodium hydroxide. Previously controls for Congo red dyes without adsorbents showed that Congo red to become unstable due to the influence of pH, this is indicated by the color change in Congo red.

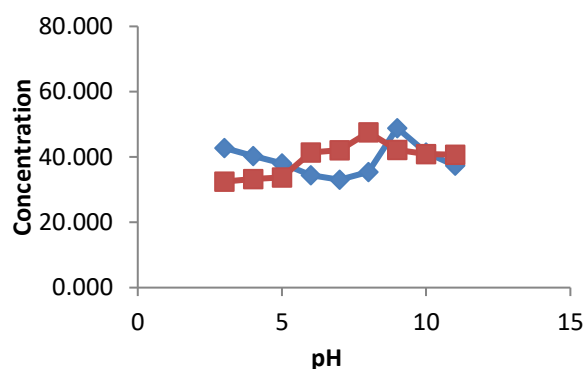


Figure 1. Effect of adsorption pH of hydrotalcite and hydrtalcite intercalated amount of adsorbed Congo red

Effect of Congo red Adsorption of Time by Hydrotalcite and Hydrotalcite Intercalated

Hydrotalcite intercalated can absorb more adsorbate than hydrotalcite at the same time. At the optimum time of adsorption at 70 min it is seen that the amount of Congo red dye

stuff adsorbed by 1.5 times the adsorbent without insertion process. This is because the hydrotalcite intercalated has a larger basal spacing of 9.81 Å than the previous value of 7.4 Å. The hydrotalcite intercalated and hydrotalcite curves before the insertion process are presented in Figure 2.

The data obtained in Table 1 show that the hydrotalcite intercalated adsorbent has a higher adsorption rate than the hydrotalcite before intercalated it causes the hydrotalcite intercalated adsorbent to have a greater reactive rate than the hydrotalcite before intercalated.

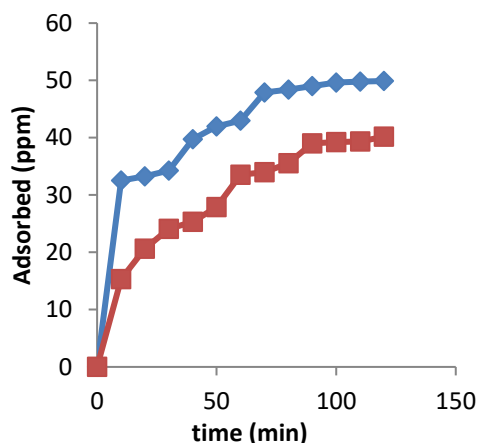


Figure 2. Effect of Congo red Adsorption of Time by Hydrotalcite and Hydrotalcite Intercalated

Table 1. Adsorption rate values for hydrotalcite and hydrotalcite intercalated

Adsorbent	Parameter	
	k_1 (Sec ⁻¹)	R ²
hydrotalcite	13,64	0,984
Hydrotalcite intercalated	51,38	0,999

Effect of Concentration and Temperature Adsorption Congo red Dye by Hydrotalcite and Hydrotalcite Intercalated

Adsorption temperature data by hydrotalcite adsorbent and hydrotalcite intercalated. Figures 3 and 4 show the results of the effect of adsorption temperature on the adsorbed Congo red amount of hydrotalcite adsorbent and the hydrotalcite intercalated. Figures 3 and 4 show the effect of temperature and concentration of Congo red dye by a hydrotalcite adsorbent and hydrotalcite intercalated shows that the larger the temperature the greater the amount of adsorbed Congo red, the greater the concentration. Then the amount of Congo red adsorbed will increase as well Hydrotalcite adsorbent (control) presented in Figure 3.

The adsorption capacity and adsorption energy of the Congo red dye adsorption process by hydrotalcite and the hydrotalcite intercalated Table 2 explains that the adsorption energy value (E) of Congo red adsorption by hydrotalcite intercalated at

visible concentration variations. The greater the temperature the more decreasing the adsorption energy (E). This indicates that the adsorption process occurring at the varied temperature undergoes an exothermic condition which means the process releases energy. This state suggests for chemistry states (chemical adsorption) (Vimoses et al, 2009). The determination of the adsorption capacity (b) is determined by the equation 2 which expresses the adsorbent's ability to adsorption the Congo red presented in Table 2. The table shows when the temperature increases, the larger the adsorption capacity.

The subsequent thermodynamic parameters of enthalpy (ΔH) and entropy (ΔS) of the Congo red dye adsorption process by the hydrotalcite and hydrotalcite intercalated are presented in Table 3. The table shows the entropy (ΔS) of Congo red adsorption by hydrotalcite intercalated indicates the degree of irregularity that occurs where large entropy values indicate that the smaller the concentration the degree of irregularity or greater entropy. In addition to the enthalpy value (ΔH) of Congo red adsorption by the hydrotalcite intercalated presented in Table 3 indicates a decrease as concentration increases.

Study of Adsorption Congo red Dye by Hydrotalcite and Hydrotalcite Intercalated

The Congo red adsorption interaction study by hydrotalcite adsorbent and the hydrotalcite intercalated was carried out to determine the changes occurring in the adsorbent prior to the adsorption process and after the adsorption process. The change of each adsorbent is seen through characterization using FT-IR spectrophotometer. Figure 5 and 6 show the FT-IR spectrum, before and after the Congo red adsorption process.

Figure 5 shows the comparison of the double layer hydroxy spectrum prior to adsorption and double layer hydroxy after adsorbing Congo red differences in each bonding vibration. Figure 5 after adsorbing Congo red indicates the wave number of 3000-3500 cm⁻¹ indicated that there is a vibration peak of -OH and NH whereas for Fig. 10 before adsorbing a strong and widespread vibration Congo red is a vibration of -OH only. The presence of Congo red vibrations is amplified by a peak at 1635 cm⁻¹ which is slightly dilated with low intensity this is due to the bend vibration of OH which coincides with the vibration of the azo structure (N = N) which is characteristic of Congo red (Zvezdova, 2014). When compared to Figure 20 before adsorbing the Congo red wave numbers at 1653 cm⁻¹ with high enough intensity and sharpness indicates only OH bend vibration.

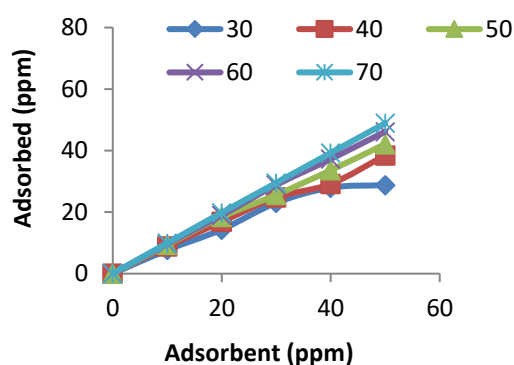


Figure 3. Adsorption Congo red dye varied of concentration and temperature by hydrotalcite

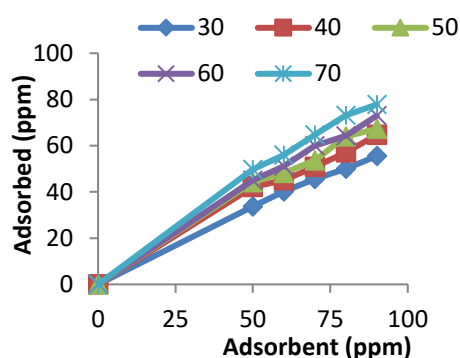


Figure 4. Adsorption Congo red dye varied of concentration and temperature by hydrotalcite intercalated

The Congo red color has a $S = O$ vibration shown in Figure 20 after adsorbing Congo red at the peak of vibration with a very low intensity at 1072 cm^{-1} wave numbers. In addition, the aromatic $C = C$ vibration appears at 1481 cm^{-1} wave numbers. The symmetric stretching vibration of the $N-O$ nitrate of the double layer hydroxyl compound with reduced intensity of the double layer hydroxyl before the adsorption process is present at the wave number 1371 cm^{-1} and the vibration of the 1419 cm^{-1} wave number indicates the buckling of $C-N$ (Kaur and Rajvir, 2016).

Tabel 2. The adsorption capacity and adsorption energy of the Congo red dye adsorption process by hydrotalcite and the hydrotalcite intercalated

Adsorbent	$^{\circ}\text{C}$	b (mg/g)	E (kJ/mol)
Hydrotalcite	30	0.548	7.670
	40	1.880	7.033
	50	2.865	6.180
	60	8.130	5.720
	70	22.222	0.799
Hydrotalcite intercalated	30	1.295	10.752
	40	2.092	1.826
	50	4.525	10.675
	60	3.861	3.684
	70	9.091	3.861

The double layer hydroxyl adsorbent inserted with the $\text{H}_4[\alpha\text{SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ polyoxometalate compound before and after the Congo red adsorption process is shown in Figure 6. Figure 6 shows the hydroxyl of the double layer inserted prior to the adsorption process shown by the FT-IR spectrum in Fig. 6 before the Congo red adsorption process shows a wider and larger peak when compared to Figure 6 of the double layer hydroxy insertion after the adsorption process has a peak showing the characteristic of the Congo red, There is a widened and strong peak which is a vibration of $-OH$ and NH at wave numbers $3000\text{--}3600 \text{ cm}^{-1}$. At the same wavelength region the adsorbent before the insertion process has a widened peak which is the vibration of the OH alone is shown in Fig. 6. Figure

6 hydroxyl layer of hamper after Congo red adsorption process at wave number 2924 cm^{-1} there is a peak of aromatic benzene vibration from Congo red, peak Vibration for azo structure $N = N$ and OH buckling is present at wave number 1635 cm^{-1} , aromatic $C = C$ vibration at wave number 1481 cm^{-1} , for vibration of NO bend is at wave number 1373 cm^{-1} and vibration $S = O$ is at number Wave 1072 cm^{-1} . The presence of a characteristic peak of Congo red dyestuff vibration indicates that Congo rally absorbed into the adsorbent surface resulting in changes in the FT-IR spectrum before and after the adsorption process.

Tabel 3. The subsequent thermodynamic parameters of enthalpy (ΔH) and entropy (ΔS) of the Congo red dye adsorption process by the hydrotalcite and hydrotalcite intercalated

Adsorben	Co	R^2	ΔH	ΔS
layered double hydroxide	10	0,9280	84,511	0,281
	20	0,9330	76,114	0,251
	30	0,8910	64,059	0,212
	40	0,9100	70,810	0,227
	50	0,9780	84,387	0,265
Intercalated layered double hydroxide	50	0,9030	40,838	0,136
	60	0,9290	38,967	0,1277
	70	0,9380	39,200	0,127
	80	0,9060	39,20	0,118
	90	0,9780	28,242	0,091

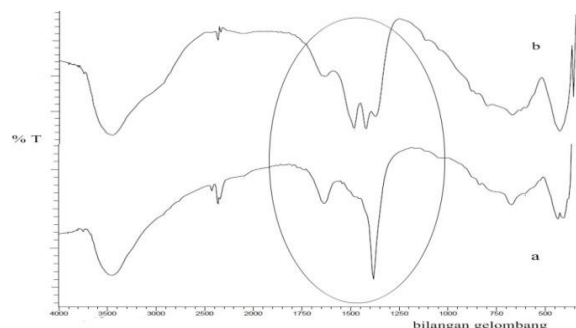


Figure 5. FT-IR spectrum of Hydrotalcite and hydrotalcite intercalated

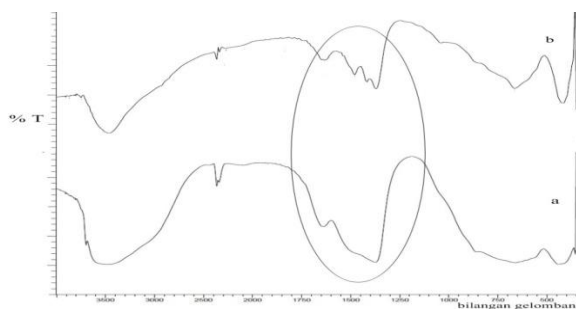


Figure 6. FTIR spectrum of double layer hydroxide inserted polyoxometalate, which adsorp Congo red (A), and double layer hydroxide insertes polyoxometalate.

CONCLUSION

Adsorption process of Congo red dye by double layer hydroxy and double layer hydroxy inserted polyoxometalate $H_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$ (1:1) showed adsorption rate of 13.64 and 51.38 min^{-1} . While the adsorption thermodynamic parameters for both adsorbents showed an increase in adsorption capacity along with increasing temperature. Other thermodynamic parameters such as enthalpy and entropy decrease with increasing dye concentration. The effect of pH indicates that the optimum pH for the double layer hydroxy compound is at pH 9, and the polyoxometalate-insulated double-hydroxied hydroxy is at pH 8.

REFERENCES

- Asif, M., Haitao, W., Shuang, D., Aziz, A., Zhang, G., Xiao, F., Liu, H. (2017). Metal Oxide Intercalated Layered Double Hydroxide Nanosphere: With Enhanced Electrocatalytic Activity Towards H_2O_2 For Biological Applications. *Sensor and Actuators B: Chemical*, 239, 243-252.
- Bhoi, K. S., 2010. Adsorption Characteristic of Congoed Dye onto PAC and GAC Based on S/N Ratio. *Thesis*. India: National Institute of Technology Rourkela.
- Duan, X., Lu, J., Evans, D.G. (2011). Assembly Chemistry of Anion-Intercalated Layered Materials. *Modern Inorganic Synthetic Chemistry*, Chapter 17, 375-404, Elsevier.
- Frost, L., Ray, Musumeri, W. A., Bostrom, W., Jones, W., Kooli, F., 1997. Insertion of Electrochemically Reduced Keggin Anion Into LDH. *J. Matter Chem.* 7(9) : 1937-1939.
- Jia, Y., Fang, Y., Zhang, Y., Miras, H.N., Song, F.-Y. (2015). Classical Keggin Intercalated Into Layered Double Hydroxides: Facile Preparation and Catalytic Efficiency in Knoevenagel Condensation Reactions. *Chemistry A European Journal*, 21, 14862-14870.
- Kaur, R., and Rajvir, H. K., 2016. Electrochemically Degredation of Congo red from Aquos Solutions. *Portugalle Acta.* 3(3) : 185-196.
- Lesbani, A., Kawamoto, R., Uchida, S., Mizuno, N. (2008). Control of Structures and Sorption Properties of Ionic Crystals of $A_2[Cr_3O(OOCC_2H_5)_6(H_2O)_3]_2[\alpha-SiW_{12}O_{40}]$ (A = Na, K, Rb, NH_4 , Cs, TMA). *Inorganic Chemistry*, 47, 3349-3357.
- Lesbani, A., Fitriliana., Mohadi, R. (2015). Conversion of Cyclohexanone to Adipic Acid Catalyzed by Heteropoly Compounds. *Indonesian Journal of Chemistry*, 15, 64-69.
- Liu, K., Xu, Y., Yao, Z., Miras, H.N., Song, Y.-F. (2016). Polyoxometalate-Intercalated layered Double Hydroxides as Efficient and Recyclable Bifunctional Catalysts For Cascade Reactions. *Chem. Cat. Chem.*, 8, 929-937.
- Said, M., & Palapa, N. (2017). Adsorption of Congo Red Using Mg/Al Hydrotalcite. *Science & Technology Indonesia*, 1(1), 25-28.
- Vimoses, Vipasiri., Lei, Shaomin., Jin, Bo., Chow., and Saint, C., 2009. Kinetic Study and Equilibrium Isotherm Analysis of Congo red.
- Xie, W., Reng, Hong., Chem, L., 2006. Calcined Mg/Al Hydrotalcite as Solid based Catalysis for Methanolysis of Soybean Oil. *Journal of Molecular Catalysis.* 246 : 24-32.
- Yang, S., Huang, Y., and Li Yu., 2011. Catalytic Application of $H_4SiW_{12}O_{40}/SiO_2$ in Synthesis of Acetals and Ketals. *Advanced Materials Research*, 284-286: 2374-2379.
- Zhao, S., Xu, J., Wei, M., and Song, F. Y., 2011. Synergistic Catalysis by Polyoxometalate-Intercalated Layered Double Hydroxide: Oximation of Aromatic Aldehyd. *Green Chem.* 13 : 384-388
- Zvezdova, Dilyana., 2014. Preparation, Characterization and Adsorption Properties of Chitosan Nanoparticles for Congo red as a Model Anionic Direct Dye. *Nacni trudove na Rusendei University.* 53(10) : 83-87