

# Removal of Reactive Orange 13 (RO13) onto Rice Husk in Aqueous Solution

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## Abstract

*The present study shows that rice husk which is easy to get can be used as a low-cost adsorbent. Rice husk can remove harmful Reactive Orange 13 (RO13) from aqueous solution. In dyeing industries RO13 is used in a large quantity and when those industries dispose the untreated effluent to the open water it creates serious water pollution. Rice husk can remove the dye stuff from the aqueous solution and may help to keep water comparatively clean and safe. This study helps to know that rice husk as natural adsorbent can remove dyes by adsorption process and the process was endothermic in nature. Adsorption process was spontaneous too. Experimental data shows the nature of adsorption was physical in type and feasible.*

**Key Words:** Adsorption; Adsorbent; Reactive Orange 13; Removal; Spontaneous;

## 1 Introduction

Chemical pollution of waste water via a huge range of pollutants is an important environmental problem now-a-days. Huge amount of synthetic dye are now using in textile industry [1]. The textile wastewaters possess high color and other substances [2]. Without proper treatment, discharge of dye wastewaters into water bodies affect aquatic environment by reducing light penetration and photosynthesis, and being hazardous and toxic to aquatic life [3,4]. This contaminated water also harmful to human because of its carcinogenic nature [5]. There are many traditional methods for removing dyes include removal, electrocoagulation, ozonation,

ultrafiltration, reverse osmosis, flocculation, oxidation, ion-exchange, etc. [6]. Adsorption has been found to be satisfactorily efficient for the removal of colour in terms of ease of operation, initial cost, simplicity of design [7] and sludge free process [8]. Many research groups applied this removal method for removal of different pollutants [9-18]. Activated carbon is commonly used adsorbent for colour removal, because of its capability for efficiently adsorbing a wide range of different types of adsorbate. But activated carbon is expensive. Many low-cost adsorbents have been investigated on dye removal, such as fly ash [19-21] bottom ash, clay, zeolite, calcine alunite [22] etc .

In this study untreated rice husk was used as a low-cost adsorbent to adsorb a dye from aqueous solution. The influence of pHs, solution temperature, concentration effect, ionic strength effect, desorption and reuse were studied in batch mode. Various models were tested to investigate the removal kinetics and equilibrium removal behavior.

## 2 Experimental

### 2.1 Materials

Rice husk was collected from local market and crushed to powder by grinder. The Reactive Orange 13 (RO13) was obtained from Sigma-Aldrich Germany and was used without purification. The chemical structure of RO13 is shown in Fig: 1.

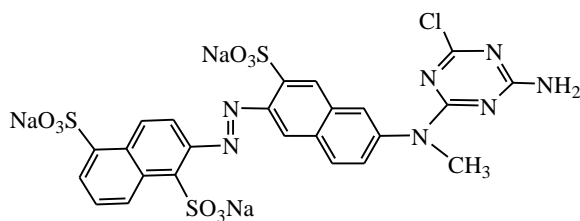


Figure: 1 Chemical Structure of RO13

All other reagents and solvents were commercially available and highest grade of purity; hence they were used without purification. Deionized water was prepared by passing distilled water through a deionizing column (Branstead, Syboron Corporation, boston. USA).

## 2.2 FTIR Spectra

The Fourier transformation infrared (FTIR) spectra of Reactive orange13 (RO13) and rice husk before and after removal of amaranth (RO13) were recorded in the frequency range 400-4000cm<sup>-1</sup> using FTIR spectrometer (IR Prestige-21 FTIR Spectrophotometer, Simadzu, Japan).

## 2.3 Batch removal experiments

Batch removal experiments were carried out to determine the extent of removal at various pH, concentrations, ionic strengths and temperatures.

## 3 Results and discussion

### 3.1 Point of zero charge measurements

Point zero charge of rice husk was found to be 5.85.

### 3.2 FTIR Analysis

The FTIR spectrum (Figure is not shown) displays peak at 3440.1 cm<sup>-1</sup> for the intramolecular hydrogen bonding aromatic -OH and -O-H stretching, peak at 1622.7 cm<sup>-1</sup> and

1555.4 cm<sup>-1</sup> for -C=C stretching of aromatic rings, 1466.5 cm<sup>-1</sup> and 1394.6 cm<sup>-1</sup> -C-H stretching of alkyl acetals, peak at 1329.8 cm<sup>-1</sup> and 1187.5 cm<sup>-1</sup> for -C-N stretching due to amines, peak at 845.2 cm<sup>-1</sup>, 799.9 cm<sup>-1</sup>, 763.3 cm<sup>-1</sup> for -C-H stretching, 617.8 cm<sup>-1</sup> -C-Cl stretching.

The FTIR spectra of Rice husk (before removal) (Figure is not shown) peaks at 3414.67 cm<sup>-1</sup> for surface -OH stretching, peak at 2923.37 cm<sup>-1</sup> for aliphatic C-H stretching, peak at 2852.62 cm<sup>-1</sup> for aldehyde C-H stretching, peak at 1653.98 cm<sup>-1</sup> for unsaturated group like alkene, peak at 1560.17 cm<sup>-1</sup> for aromatic C-NO<sub>2</sub> cm<sup>-1</sup> stretching, peak at 1077.57 cm<sup>-1</sup> for Si-O stretching [23].

The FTIR spectra of Rice husk (after removal) (Figure is not shown) the peaks at 3414.67 cm<sup>-1</sup> for surface -OH stretching shifted to 3422.55cm<sup>-1</sup>, peak at 2923.11 cm<sup>-1</sup> for aliphatic C-H stretching, peak at 2852.66 cm<sup>-1</sup> for aldehyde C-H stretching, peak at 1653.33 cm<sup>-1</sup> for unsaturated group like alkene, peak at 1560.38 cm<sup>-1</sup> for aromatic C-NO<sub>2</sub> cm<sup>-1</sup> stretching, peak at 1077.57 cm<sup>-1</sup> for Si-O stretching shifted to 1050.77cm<sup>-1</sup>, sharp peak at 1253.62 cm<sup>-1</sup>, 1185.99 cm<sup>-1</sup> and 1140.66 cm<sup>-1</sup> in reactive orange 13 (RO13) for S=O stretching is absent in the FTIR spectra of rice husk after removal.

FTIR analysis suggested that there is some sort of interaction among OH and Si-O groups of rice husk and -SO<sub>3</sub>H groups of dyes.

### 3.3 Effect of pH on the removal process

The pH is an important parameter for removal studies that affects not only the removal capacity but also the color and solubility of the adsorbate solutions. The effect of pH on the removal of RO-13 by rice husk was studied in aqueous solution within pH range 2-8 as shown in Fig: 2. The rate of uptake of RO-13 on rice husk indicated that about 120 min was taken to

reach the equilibrium time for all pHs. However the data was taken for 180 min. to make sure that full equilibrium was established. Before the equilibrium time, it was observed that the initial rate of removal ( $h$ ) of RO-13 increases significantly with decreasing solution pH. Lower initial rate of removal observed at basic pH values is due to competition between the excess hydroxyl ions and the negatively charged RO-13 ions for the sorption sites.

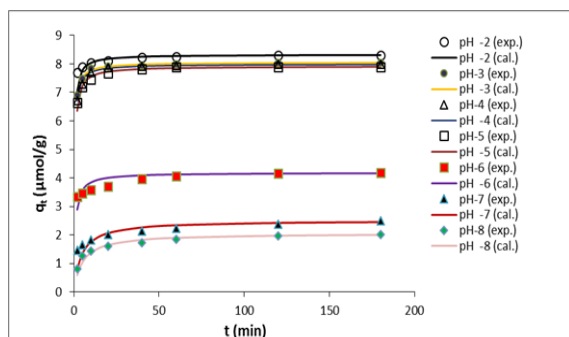


Figure: 2 Effect of pH on dye removal

Hence the pH of aqueous solution plays an important role on the initial rate of RO-13 removal onto rice husk powder. We know removal of cations is favored at  $\text{pH} > \text{pH}_{\text{PZC}}$ , while the removal of anions is favored at  $\text{pH} < \text{pH}_{\text{PZC}}$ . After 180 min. of removal, the equilibrium sorption capacity ( $q_e$ ) was found to be  $8.31 - 2.02 \mu\text{mol/g}$  at pH 2-8. These results suggest that the initial rate of removal ( $h$ ) as well as the equilibrium removal capacity of rice husk is suitable at pH- 2 among the observed pH ranging from 2-8 and the initial concentration of RO-13 solution was  $34.22 \mu\text{mol/L}$ . Similar result observed in the case of adsorption of reactive red 198 onto  $\text{ZnCl}_2$  activated pistachio hull waste [24]. The percentage of removal was illustrated in Table -1 which indicated the percentage of removal decreased with the increase in pH.

### 3.4 Effect of initial dye concentration on the removal process

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases [25]. Concentration effect was evaluated by taking different initial dye concentrations ( $91.44 - 1500 \mu\text{mol/L}$ ) at pH-2 of the dye solution and a constant system at temperature  $30^\circ\text{C}$ . It was observed that increase in the initial dye concentration leads to an increase in the removal capacity of the dye onto rice husk. It was found that as the initial dye concentration was increased relative to a fixed sorbent dosage, the extent of removal increased (Figure is not shown) as the initial dye concentration was increased, the amount absorbed ( $q_t$ ) increased for RO-13. Similar phenomenon were also observed in the removal of reactive black 5 (RB5) onto chitosan in aqueous solution.

This result suggests that the rate of removal for lower initial dye concentration was faster than that of higher one. The removal capacity ( $q_e, \text{exp}$ ) increases with increasing the initial dye concentration. The rapid uptake of dye particles at the beginning is due to the occurrence of solute transfer only due to sorbate and sorbent interactions with negligible interference due to solute-solute interactions. The percentage of removal was illustrated in Table: 1 which indicated the percentage of removal decreased with the increase in concentration of dye solution.

### 3.5 Effect of ionic strength on dye removal

The effects of ionic concentration on the removal kinetics are observed under various ionic strength ( $0.01\text{M}$ ,  $0.05\text{M}$ ,  $0.10\text{M}$ ,  $0.15\text{M}$  and  $0.20\text{M}$ ) of KCl solution and other fixed operating conditions (concentration  $62.33 \mu\text{mol/L}$ , and at pH-2 of the dye solution).

The result indicated that the higher the KCl concentration is, the lower the removal capacity (Figure is not shown) (Table:1) since the addition of KCl reduces the electrostatic interaction between rice husk and dye. The addition of salts allows the neutralization of the negative sites of dye molecules which help to lower the attraction force between surface of rice husk and dye molecule results decrease the removal.

### 3.6 Effect of temperature on the removal process

Temperature is an important parameter that can influence the equilibrium and rates of sorption processes. The effects of temperature on the removal kinetics of RO13 onto rice husk were observed in aqueous solution at pH 2 and initial concentration of dye solution was 35.11 μmol/L. The results are shown in Fig: 7. which indicates the removal increased with increasing solution temperatures. Adsorption onto Rice husk increased from 8.31 to 8.36 μmole/g by increasing the temperature of the solution from 303 to 318K, indicating that the process is endothermic. Similar endothermic nature observed in the case of adsorption of acid red 37 onto the modified laccase-modified red mud [26]. This may be attributed to increased mobility of the reactive dye molecules at higher temperature. This may be due to the fact that increasing the temperature may produce a swelling effect within the initial structure of rice husk. Dye removal increased with temperature (Table: 1).

Table: 1 % of removal of reactive orange 13 (RO13) by 0.1g rice husk at various pH, concentrations of RO13 aqueous solution

At various pH, Initial concentration of RO13 solution 34.22 μmol/L

pH	% of removal of Dye
2	97.40

3	94.16
4	93.51
5	92.53
6	49.03
7	29.22
8	23.70

At various concentrations (μmol/L)

Concentration μmol/L	% of removal of Dye
91.44	97.33
388.89	68.57
666.67	65.00
1044.44	52.13
1500.00	36.30

Table-1 % of removal of reactive orange 13 (RO13) by 0.1g rice husk at various ionic strength and temperature of RO13 aqueous solution

At various ionic strength (M), Initial concentration of RO13 solution 62.33 μmol/L

M	% of removal of Dye
0.01	97.33
0.05	96.61
0.10	96.43
0.15	96.08
0.20	95.72

At various temperature (°C), Initial concentration of RO13 solution 34.11 μmol/L

Temp. (°C)	% of removal of Dye
30	97.39
35	97.72
40	98.05
45	98.37

### 3.7 Rate Constant Studies

To study the rate constant The pseudo-first-order, Pseudo-Second-Order Kinetic and Elovich Kinetic Models were used. The removal rate constant  $k_1$  was determined from the slope of the plot of  $\log(q_e - q_t)$  vs  $t$ . The values of  $k_2$  and  $q_e$  was determined from the intercept and slope of the plot of  $t/q_t$  versus  $t$  respectively (Figures are not shown). The Elovich coefficients can be calculated from the plot of  $q_t$  vs  $\ln t$ . It is found that the experimental data fitted well to the second-order kinetics than that for the pseudo-first-order and Elovich kinetics model. Similar type of kinetic was shown in the adsorption of acid red 27 on TiO<sub>2</sub>-P25 nanoparticles [27].

### 3.8 Adsorption mechanism

To determine the rate limiting intraparticle diffusion and film diffusion models were used. It was found that none of the linear plots at any concentration pass through the origin which means both intraparticle diffusion and film diffusion may involve in the rate limiting steps of the removal onto rice husk. The above conclusion suggests that all three mechanisms: intrinsic surface reaction, film mass transfer and intraparticle diffusion are rate-limiting steps.

### 3.9 Activation Parameters of the removal process

The activation energy ( $E_a$ ) for the sorption RO-13 dye on rice husk can be estimated by using Arrhenius equation.

$$\ln k = \ln k_0 - \frac{E_a}{RT}$$

When  $\ln k_2$  is plotted versus  $1/T$  (Figure is not shown), a straight line with slope ( $-E_a/R$  is obtained). The values of  $E_a$  is presented in Table: 2.

Low activation energies (5–40 kJ/mole) are characteristics for physisorption, while higher

activation energies (40–800 kJ/mole) suggest chemisorption. The values of  $E_a$  from the slopes of the plots are 18.50 kJ/mole for RO-13 dye. Which indicating the rate-limiting step in the removal process, might be a physically controlled type. To calculate the thermodynamic parameters such as enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ) and free energy of activation

( $\Delta G^\ddagger$ ) the equation

$$\ln(k_2/T) = -\Delta H^\ddagger /R(1/T) + \ln(k_B/h_p) + \Delta S^\ddagger$$

was used. The slope and y-intercept of the plot  $\ln(k_2/T)$  versus  $1/T$  (Figure is not shown). The value of  $\Delta H^\ddagger$  was found to be 15.92 kJ/mole, which is consistent with endothermic nature of the diffusion process. The value of  $\Delta S^\ddagger$  was estimated to be -215.29 J/mole/K, which reflects no significant change occurs in the internal structure of the absorbent material during removal. Negative value of  $\Delta S^\ddagger$  is familiar in removal. The positive value of  $\Delta G^\ddagger$  (Table: 2) indicate the presence of an energy barrier in the removal process which is supported by many previous work.

Table: 2 Activation Parameters

Name of dye	Parameters	
Reactive Orange (RO-13)	$E_a$	18.50 (kJ/mol)
	$\Delta H^\ddagger$	15.92 (kJ/mol)
Temperature ( $^\circ\text{C}$ )	$\Delta S^\ddagger$	-215.29 (J/mole/K)
		(kJ/mol)
		81.15
	$\Delta G^\ddagger$	82.23
		83.31
		84.38

### 3.10 Adsorption isotherms

Tempkin isotherm, Freundlich adsorption isotherm and Langmuir Isotherm Model were used. By plotting equilibrium removal

capacity ( $q_e$ ) of rice husk versus equilibrium concentration of dye in aqueous phase ( $C_e$ ) (Figures are not shown). It shows removal capacity increases with increasing temperature. This observation agrees with the temperature effect. The rise in removal capacity is due to the increase in collision frequency between adsorbent and adsorbate, which results in the enhanced removal onto the surface of the adsorbent. This enhancement may be due to the creation of new reaction sites or increased rate of inparticle diffusion of adsorbate molecules into the pores of the adsorbent at higher temperature.

Experimental data shows that the Langmuir removal isotherm provides a good description of data for RO-13 dye over the whole temperature range studied in single systems since  $R^2$  values from Langmuir isotherms are always greater than that of Freundlich isotherms and Tempkin isotherm. Thus, it can be concluded that monolayer removal is occurred in this study. This also suggests that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. Thus, the equilibrium constants or binding constants ( $a_L$ ) obtained from Langmuir isotherms are used to calculate the thermodynamic parameters for the removal process. Similar result was observed in the case of adsorption of methylene blue on hybrid-SiO<sub>2</sub> alginate [28].

### 3.11 Thermodynamic parameters

To determine the thermodynamic parameters like  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  following equations were used

$$\Delta G = -RT \ln K$$

and

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

The values of  $\Delta H$ ,  $\Delta S$  were calculated from the slope and y-intercept of Van't Hoff plot of  $\ln a_L$  vs.  $1/T$  (Fig: 3). Generally a value of  $\Delta H$  in between 5-40 kJ/mol is consistent with electrostatic interaction between removal sites and adsorbing ion (physical removal) while a value ranging from 40-800 kJ/mol suggests chemisorption.

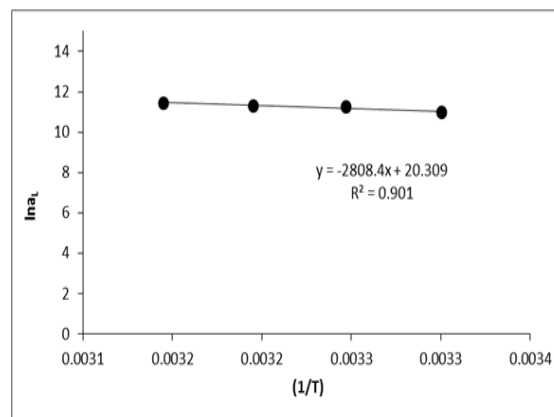


Figure: 3 Thermodynamic Parameters

The results showed the changes in enthalpy  $\Delta H$  for the removal of RO-13 by rice husk were 23.35kJ/mol. A positive enthalpy change ( $\Delta H$ ) suggests that the interaction of dye adsorbed by rice husk is endothermic which is supported by the increasing removal of the dye with the increasing in temperature while a negative removal standard free energy change ( $\Delta G$ ) and a positive standard entropy change ( $\Delta S$ ) indicate (Table: 3) that the removal reaction is a spontaneous process.  $\Delta H$  for physical removal ranges from 4 to 40 kJ/mol, compared to that of chemical removal ranging from 40 to -800 kJ/mol.

The negative values of Gibb's free energy changes ( $\Delta G$ ) indicate that the removal process is spontaneous and more favorable at high temperature. These behaviors seem to be explained by the ionic nature of the dye-rice husk interaction. The positive value of  $\Delta S$  suggests that both enthalpy and entropy are

responsible for making the  $\Delta G$  negative so that the removal process is spontaneous. The positive value of  $\Delta S$  also indicates that the randomness increases at the solid--solution interface during the removal of dye onto the rice husk.

Table: 3 Thermodynamic Parameters

Temperature ((K)	303	308	313	318
$\Delta G$ (kJ/mole)	-27.69	-28.94	-30.69	-31.49
$\Delta H$ (kJ/mole)	23.35			
$\Delta S$ (J/mole/K)	168.85			
$R^2$	0.901			

### 3.12 Desorption studies

Desorption studies help to understand the nature of removal and recycling of the spent adsorbent and the dye. RO13 desorbs in alkaline solution which suggests the ion exchange mechanism involved in the removal. This desorption study supported that the removal process was physical type in nature.

### 3.13 Reuse

This step is performed to test the feasibility of Rice husk as a reusable adsorbent. Certain concentration of dye solution was agitated with certain amount of the adsorbent powder for the equilibrium time. After shaking the supernatant dye solution was discarded and the adsorbent was separated and allow to wash with deionized water and then dried. Then it was taken in to a shaking bottle with 0.1M NaOH solution and was agitated for the equilibrium time and adsorbent was separated and allow to wash with deionized water and then dried. For reuse study 0.1g of that was taken in to a shaking bottle with 25ml of 1044.44 $\mu$ mol/L of dye solution also maintained pH2 and batch removal process was followed. It is found that Rice husk can be used as reusable absorbent.

## 4 Conclusion

Present study shows that the rice husk can be used as an adsorbent for the removal of Reactive Orange (RO-13) from its aqueous solution. FTIR analysis suggested that OH and Si-O groups of rice husk and  $-\text{SO}_3\text{H}$  groups of dyes are mainly involved in removal. The amount of dye sorbed was found to vary with pH, initial dye concentration, contact time, ionic strength and temperature. The amount of dye uptake ( $\mu\text{mol/g}$ ) was found to increase with increase in contact time, initial dye concentration and solution temperature, and found to decrease with increase in ionic strength. The results demonstrate a highly significant linear relationship between  $t/q_t$  Vs  $t$  in this study with high correlation coefficients. This suggests that the removal system studied belongs to the second-order kinetic model. Thermodynamic activation parameter shows that the process is endothermic. The negative value of the Gibbs energy change of the removal indicates that the removal is spontaneous. The positive value of the enthalpy change of the removal shows that the removal is endothermic process. Thus, raising the temperature leads to higher Reactive Orange (RO-13) removal at equilibrium. This study showed that rice husk has a high potential to adsorb RO-13 from aqueous solutions. Therefore, it can effectively be used as an adsorbent for the removal of Reactive Orange (RO-13) from waste waters.

## References:

- [1] S.K. Alpat, O. Ozbayrak, S. Alpat, H. Akcay, *J. Hazard. Mater.* 151, 213–220, **2008**.
- [2] P. Janos, H. Buchtova, M. Ryznarova *Water Res.* 37, 4938–4944. **2003**.
- [3] A. Aguedach, S. Brosillon, J. Morvan, E.K. Lhadi, *Appl. Catal. B*, 57, 55–62, **2005**.

- [4] A.R. Dincer, Y. Gunes, N. Karakaya, E. Gunes, *Bioresource Technol.*, 98, 834–839, **2007**.
- [5] Hameed, B.H., D.K Mahmoud and A.L. Ahmad. *J.Hazard. Mater.*, 158,65-72, **2008**.
- [6] Nevine Kamal Amin, *Elsevier Desalination*. 223,152-161, **2008**.
- [7] O. Yavuz, AH. Aydin, *Polish Journal of Environmental Studies*. 15(1),155-161, **2006**.
- [8] Sajjala Sreedhar Reddy, Bijjam Kotaiah, Nanaga Siva Prasad Reddy, *Chem. Soc. Ethiop*. **2008**,22:369-378, *International Research Journal of Pure & Applied Chemistry*, 4(5): 568-577, 2014 577,**2008**.
- [9] K. Ravikumar , S. Ramalingam ,S. Krishnan , K. Balu , *Dyes Pigment*, 70,18–26, **2006**.
- [10] M. Auta ,BH. Hameed, *Chem Eng. J.*, 175,233–243,**2011**.
- [11] Y. Liu , J Wang ,Y Zheng ,A Wang, *Chem. Eng. J.* 184,248–255. **2012**.
- [12] S Chatterjee ,A Kumar , S Basu , S Dutta, *Chem Eng J.*, 181:289–299, **2012**.
- [13] M.N Rashed, *Int.J. Environ. And Waste Management*, 7(1/2),175-191, **2011**.
- [14] F. Rozada, M. Otero, A. Moran, A.I. Garcia, *Biosou. Technol.* 99,6332-6338,**2009**.
- [15] S. Rio, F.B Catherine, L.C Laurence, C. Philippe and L.C. Pierre, *Chemosphere*, 58,423-437, **2005**.
- [16] M.J. Martin. A. Artola, M.D. Balaguer and M. Rigola, *J. Chem. Technol. Biotechnol.*, 77,825-833,**2002**.
- [17] O. Gulnaz, A. Kayaa, F. Matyar and B. Arikan, *J. Hazard. Mater.*,108,183-188, **2004**.
- [18] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, *Dyes and Pigments*, 57,55-65, **2003**.
- [19] Z. Eren, F.N. Acar *J. Hazard. Mater.*, 143, 226– 232, **2007**.
- [20] S. Wang, Z.H. Zhu, *J. Hazard. Mater.*126, 91–95, **2005**
- [21] M. Rachakornkij, S. Ruangchuay, S. Teachakulwiroj *J. Sci. Technol.* 26 (1), 13–24 (in Thai),**2004**.
- [22] M. Ozacar, I.A. Sengil, *J. Hazard. Mater.*, 98, 211–224,**2003**.
- [23] T.K. Saha, N. C. Bhoumic, S. Karmaker, M.G. Ahmed, H. Ichikawa, Y. Fukumori, *Clean-Soil,Air, Water*, 39 (100), 984-993, **2010**.
- [24] E. Bazrafshan, F. Kord mostafapour, A. Hossain Mahvi, *Int. J. Environ. Health Engineering*, 2(6),38-45, **2013**.
- [25] T. K. Saha, N.C. Bhoumik, S. Karmaker, M. G. Ahmed, H. Ichikawa, Y. Fukumori, *Clean: Soil.Air, Water*, 39, 984-993, **2011**.
- [26] H. Nadaroglu, E. Kalkan and N. Celebi, *Annual Research & Review in Biology*, 4(17),2730-2754,**2014**.
- [27] A. Mohammad, Bhenajady, S. Yavari, N. Modirshahla, *Chem.Ind. Eng.* 20(1),97-107,**2014**.





[28] J A Barron Zambrano, A J Lopez-Perez,  
A avila Ortega, D Munoz Rodriguez, C Carrera  
Figueiras, IOP Conf. Series: *Materials Science  
and Engineering*,45,012018,**2003**.  
DOI:10.1088/1757-899X/45/1/012018.