

## Removal of an Anionic Dye from Wastewaters by Adsorption on Modified Rice Husk and Sugarcane Bagasse

Hamid Dezhampanah<sup>1\*</sup>, Amineh Mousazadeh<sup>1</sup> and Issa Mousazadeh<sup>2</sup>

<sup>1</sup>Laboratory of Physical Chemistry, Department of Chemistry, Faculty of science, University of Guilan, P. O. Box 41335-1914, Rashat 0098, Iran

<sup>2</sup>Shahid Rajaei Technical and Vocational University, Tarbiat moallem Ave., lahijan, Postal code: 4416777158, Po. Box: 1478, Guilan, Iran

\*Corresponding Author: [h.dpanah@guilan.ac.ir](mailto:h.dpanah@guilan.ac.ir)

### Abstract

*In this study, the removal of sunset yellow dye from aqueous solutions using low-cost materials as adsorbents such as modified Rice husk (MRH) and sugarcane bagasse (SB) by a batch system were investigated. Experiments were carried out as a function of contact time, initial concentration, pH and adsorbent dosages. The equilibrium adsorption of sunset yellow dye on adsorbents was analyzed by Langmuir, Freundlich and Temkin models. The results indicate that the Freundlich model provides the best correlation for sunset yellow-MRH system and the Langmuir model provide the best correlation for sunset yellow-SB system and also pseudo-second-order model was best applicable to the sorption data. The results revealed that the sunset yellow is considerably adsorbed on modified rice husk and sugarcane bagasse and it could be an economical method for the removal of sunset yellow from aqueous systems.*

**Keywords:** Rice husk, Thermodynamic, sunset yellow, Isotherm, Adsorption

### 1. Introduction

Dyes are type of organic compounds that can provide bright and lasting color to other substances [1]. Various types of inorganic and organic substances are used for dyeing. Organic dyes are generally difficult to treat, because their decomposition produces hazardous metabolites and products [2]. Synthetic dyes have been increasingly used in the textile, leather, paper, rubber, plastic, cosmetics, pharmaceuticals, and food industries [3]. In most of the applications more than 50% of the dye used is usually lost in wastewater [1- 4]. Among various types of environmental pollutions water pollution is of major concern and for its occurrence dye-based industries are the main cause and foremost. Dyes are released into the environment, entering into aquatic ecosystem, deteriorating the water quality and there by affecting the flora and fauna [5].

Diverse techniques, including adsorption, flocculation, oxidation and electrolysis, have been employed for removal of dyes from wastewaters. Among these methods, adsorption is

superior since it is more efficient and economical than others [6]. The adsorption process is one of the effective methods for removal of dyes from waste effluent. The process of adsorption has an edge over the other methods due to its sludge-free clean operation and completely removes dyes, even from diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But, commercially available activated carbon is very expensive. Furthermore, regeneration using solution produces small additional effluent while regeneration by refractory technique results in a 10–15% loss of adsorbents and its uptake capacity [7].

Sunset yellow (also known as FD&C Yellow No. 6) is a colorant used in drug dosage forms such as tablets and capsules. It is also approved for use in foods and cosmetics. FD&C Yellow No. 6, a water-soluble, monoazo dye, imparts a reddish-yellow color to medicinal dosage forms. Animals studies have not reported a carcinogenic (cancer-causing) potential for FD&C Yellow No. 6. [8]

Rice husk and sugarcane bagasse are easily available low cost agricultural wastes biomass [6-10]. Both of them are composed of silica, cellulose, hemi cellulose and lignin. It is an efficient biosorbent material for metals cation and dyes [11-13]. The chemical modification of sorbents with acids or bases was reported in the literature in order to enhance their adsorption capacity [11-13].

The main purpose of the present study is the removal of Sunset yellow onto modified rice husk and sugarcane bagasse adsorbent from aqueous solutions under different experimental conditions. The study includes an evaluation of the effects of various operational parameters such as initial dye concentration, adsorbent dose, contact time, and pH on the dye adsorption process. The equilibrium sorption behavior of the adsorbents has been studied using the adsorption isotherm technique. Experimental data have been fitted to various isotherm equations to determine the best isotherm to correlate the experimental data.

## **2. Experimental**

### **2.1. Adsorbent**

The milled rice husk and sugarcane bagasse were obtained from farms in the north of Iran, Guilan. Then, it was used as an adsorbent. Both of adsorbent sieved through the sieves, 50-80 mesh size particles. Then adsorbents in above particle size rinsed with distilled water to remove dust and soluble impurities. The rice husk modified by mixing 5 wt. % HCl at room temperature. Finally the treated rice husk and sugar cane bagasse were dried in an oven at 70 °C over night and stored and labeled as (MRH) and (SB).

### **2.2. Adsorbate**

The azo dye sunset yellow CFC was product of Sigma-Aldrich and was used as received without further purification (Figure 1). A stock solution of dye was prepared by dissolving 0.011 g of it in 250 mL of double distilled water. Working solutions of different concentrations (10–50 mg/ L) were prepared by further dilutions. The

concentration of the dye sunset yellow was determined using a UV-vis spectrophotometer (WTW 6100) at a wavelength corresponding to the maximum absorbance of the dye. Calibration curve was plotted based on the absorbance versus concentration of the dye solution at the maximum wavelength of the dye using Beer's law. A WTW pH meter (model 740) with a combined double junction glass electrode was used for showing pH values. pH adjustments were carried out using dilute NaOH and HCl solutions.

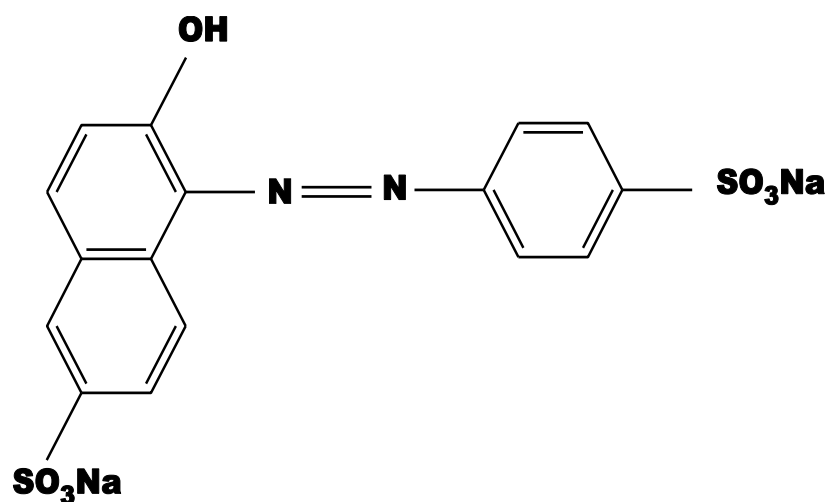


Figure 1. Chemical structure of sunset yellow

### 2.3. Adsorption Experiment

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature, and adsorbate concentration. The experiments were carried out in 250 mL Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature, and adsorbate concentration. The experiments were carried out in 100 mL beaker and the total volume of the reaction mixture was kept at 50 mL. The pH of the solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The beakers were shaken for the required time period in a mechanical shaker. For the thermodynamic study, the experiment was performed using 1.1 g rice husk added to 50 mL of sunset yellow solution in 100 mL beakers at the different temperature. The flasks were shaken for 30 min at pH 2. The initial sunset yellow concentration used in this study was 10 mg/L. All experiments were performed in duplicate. The filtrate samples were analyzed for the determination of the final concentration of sunset yellow by using an UV-vis spectrophotometer (WTW 6100) set at a wavelength of 481 nm, maximum absorbance. The sunset yellow concentration retained in the adsorbent phase was calculated according to:

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

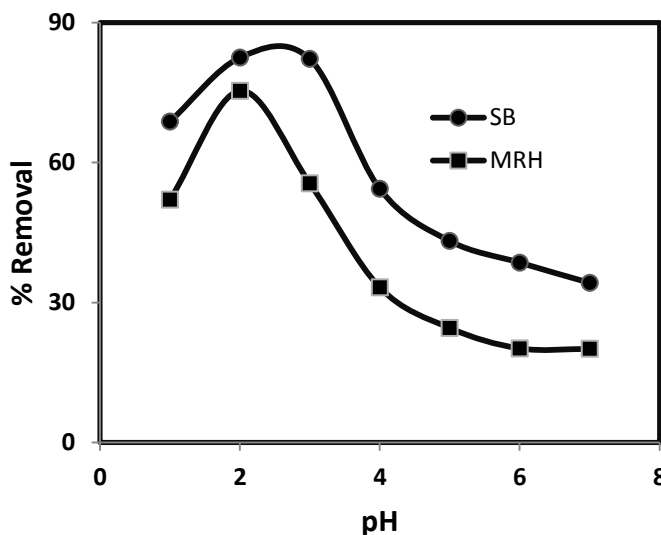
where  $C_o$  and  $C_e$  are the initial and the equilibrium concentrations (mg/L) of thionine solution, respectively;  $V$  is the volume (L), and  $W$  is the weight (g) of the adsorbent.

### 3. Results and Discussions

#### 3.1. Effect of pH

The effect of pH on the removal efficiency of sunset yellow was studied at different pH ranging from 2.0 to 7.0 and results are shown in Figure 1. The results obtained are presented in Figure 1, which describes maximum adsorption of around 83% and 75% for MRH and SB, respectively, at pH 2.0. Hence, all the succeeding investigations were performed at pH 2.0 for both adsorbents.

At the lower pH adsorbents surface become protonated so the amount of dye adsorbed increase due to electrostatic attraction between positively charge surface and the negatively charge dye molecules. On the other hand increasing the pH above 2 a negatively charged surface sites on the adsorbent didn't favour the adsorption of sunset yellow dye anions due to electrostatic repulsion. In conclusion the removal of sunset yellow is drastically affected by increasing the pH value.

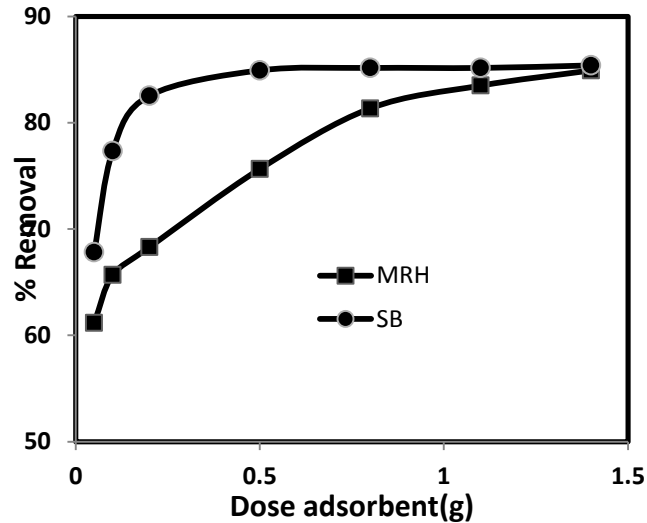


**Figure 2. Effects of pH on sunset yellow dye removal at various concentrations MRH (adsorbent dosage: 0.50 g; contact time: 30 min; temperature: 25°C) and SB (adsorbent dosage: 0.20 g; contact time: 30 min; temperature: 25°C)**

#### 3.2. Effect of Adsorbent Dose

Figure 3 shows the effect of adsorbent dose (MRH and SB) on the removal of sunset yellow at 25°C. The percentage removal increased with adsorbents dosage up to certain

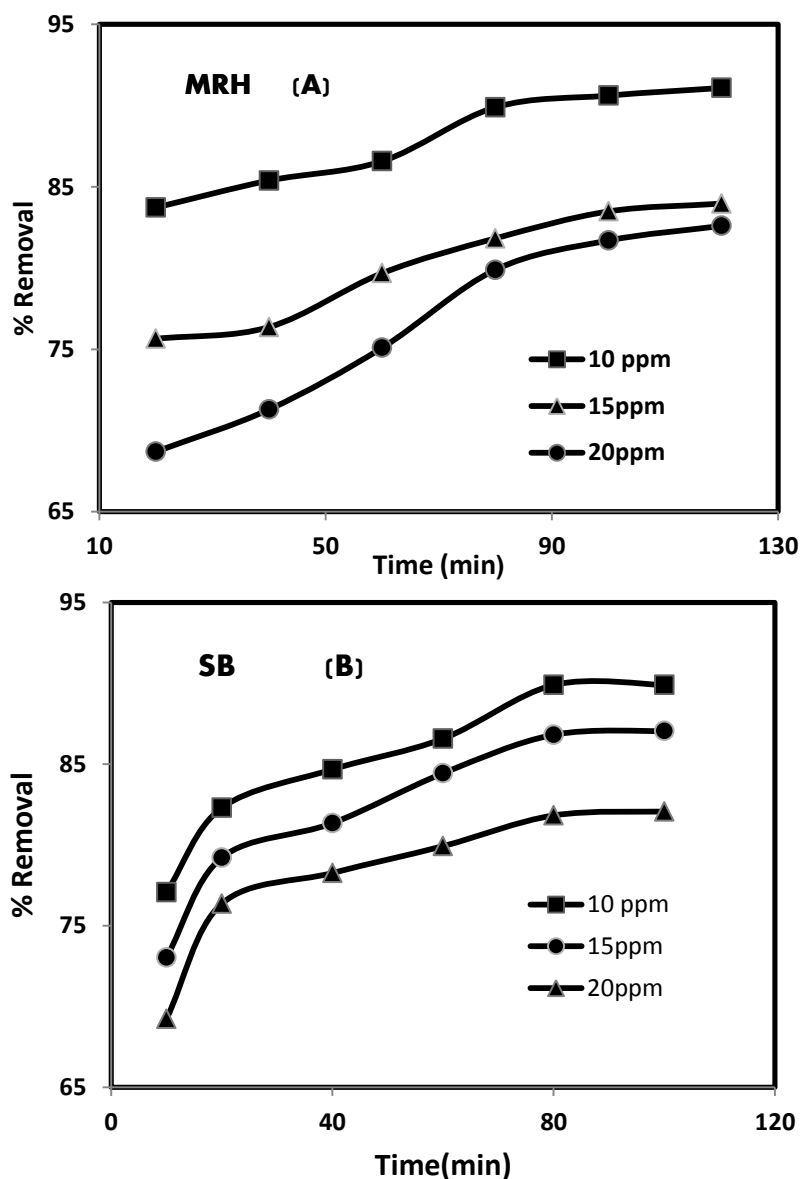
limit then it reached a constant value. At the equilibrium time the % removal increase from 61.16 to 84.92 for modified rice husk and 67.81 to 85.39 doses for sugarcane bagasse as dosages from 0.05 to 1.4 g. An increase in the adsorption with increase in adsorbent dosage can attribute to greater surface area and the availability of more adsorption surface sites.



**Figure 3. Influence of adsorbents dosage on sunset yellow removal under different solution concentration MRH (contact time: 20 min; pH: 2.0; temperature: 25°C) SB (contact time: 30 min; pH: 2.0; temperature: 25°C)**

### 3.3. Effect of contact time on dye removal

Adsorption of sunset yellow was measured at given contact times for the different initial sunset yellow concentrations from 10 to 20 mg/L. From Figure 4 the plot reveals that as the contact time increases, rate of adsorption first increases and then becomes almost constant. The high rate of sunset yellow adsorption onto MRH occurred with in the first 60 min of the process and the equilibrium state was reached after 100 min. and for SB occurred with in the first 20 min of the process and the equilibrium state was reached after 80 min. At the initial stage the rate of adsorption was fast due to the higher availability of vacant surfaces. At the beginning the dye is adsorbed by the exterior surface of the modified rice husk, the adsorption rate is fast when the exterior adsorption surface saturate the dye enters into the pores of the adsorbent and is adsorbed by the interior surface of the particles.

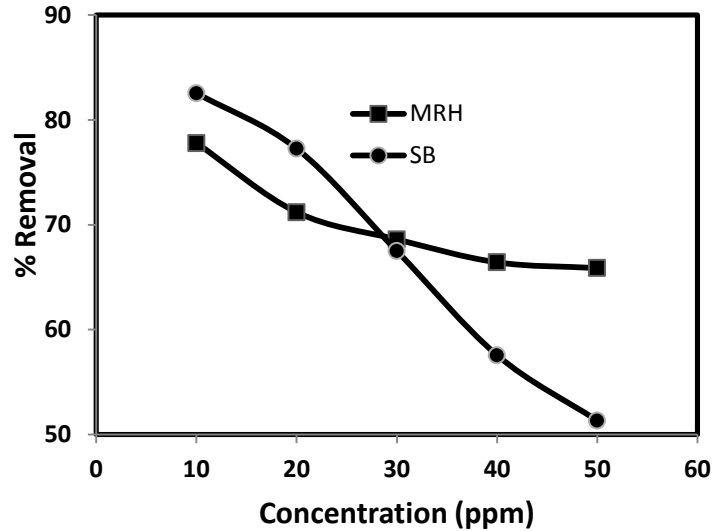


**Figure 4. Effects of contact time of the dye removal at various concentrations**  
A; MRH (adsorbent dosage: 1.1 g; pH: 2.0; temperature: 25°C). B; SB  
(adsorbent dosage: 0.5 g; pH: 2.0; temperature: 25°C)

### 3.4. Effect of initial dye concentration

The effect of initial dye concentration in the range of 10 to 50 ( $\text{mg L}^{-1}$ ) was investigated and is shown in Figure 5. It is observed that with increasing concentration of the dye from 10 to 50 ( $\text{mg L}^{-1}$ ) the percentage removal decreases from 78 to 65% for MRH. and 82 to 51% for SB. This is so because the initial dye concentration provides the driving force to overcome the resistance to mass transfer of dye between the aqueous and solid phase. The increase in initial dye concentration also enhances the interaction between adsorbents and sunset yellow. Therefore, an increase in initial concentration of sunset yellow enhances the adsorption

uptake of sunset yellow. This is due to increase in the driving force of the concentration gradient.



**Figure 5. Effect of initial concentration sunset yellow on its sorption onto adsorbents**

**(adsorbent dosage: 0.50 g; contact time: 30 min; temperature: 25 °C).**

**(adsorbent dosage: 0.20 g; contact time: 30 min; temperature: 25 °C).**

### 3.5. Adsorption isotherms

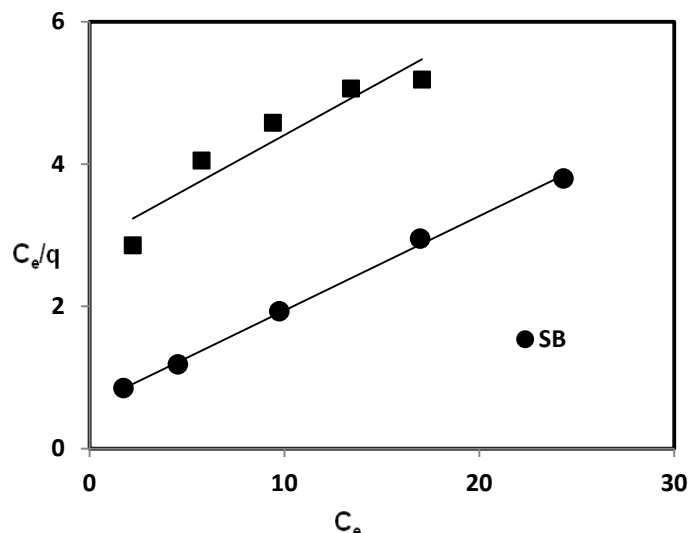
The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purpose. The adsorption capacity of this system was investigated with the Freundlich, Langmuir and Temkin adsorption isotherms.

The sunset yellow sorption isotherm followed the linearized Freundlich model, as shown in Figure 6. The relation between the sunset yellow uptake capacity  $q_e$  (mg/g) of adsorbent and the residual sunset yellow concentration  $C_e$  (mg/L) at equilibrium is given by

The adsorption data for adsorption over MRH and SB were also found to be fitted to the linear form of the Freundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Fig. 6 was used to calculate the Freundlich constants  $K_F$  and  $n$  for MRH and SB, respectively, and their values are given in Table 1.



**Figure 6. Langmuir adsorption isotherm A; sunset yellow-MRH system B; sunset yellow-SB system**

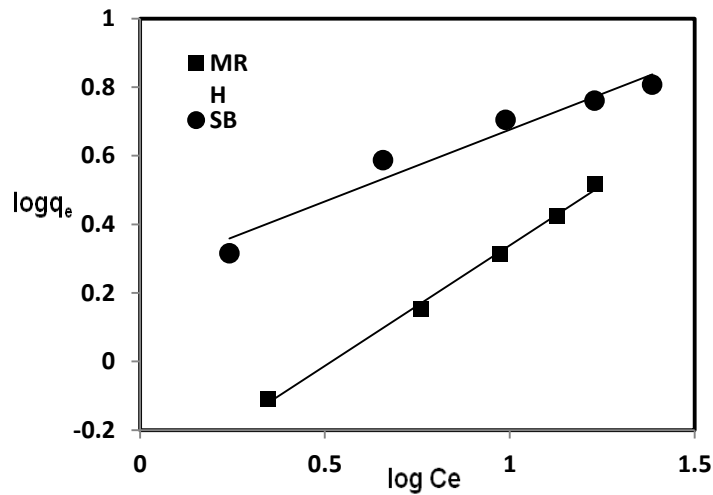
The Langmuir isotherm has been used by many workers to study the sorption of a variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of the isotherm was analyzed in the light of the model:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (3)$$

where  $q_e$  is the amount adsorbed (mol/g) and  $C_e$  is the equilibrium concentration of the adsorbate (mol L<sup>-1</sup>).  $Q_0$  and  $b$  are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When  $\frac{1}{q_e}$  is plotted

against  $\frac{1}{C_e}$ , a straight with slope  $\frac{1}{bQ_0}$  is obtained, which shows that the adsorption of sunset yellow follows the Langmuir isotherm (Figure 7) for both the adsorbents. Langmuir constants are calculated and the values of these constants at 25°C are given in Table 1.





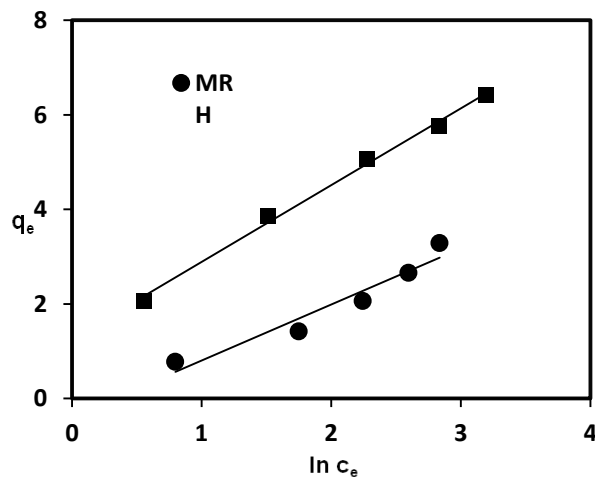
**Figure 7. Freundlich adsorption isotherm A; sunset yellow-MRH system B; sunset yellow-MRH system**

The Temkin isotherm has been used in the following form:

$$q_e = B \ln A + B \ln C_e \quad (4)$$

where  $B = RT/b$ ,  $T$  is the absolute temperature in Kelvin and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).  $A$  is the equilibrium binding constant and  $B$  is corresponding to the heat of sorption.

The sorption data can be analyzed according to Eq. (4). Therefore, a plot of  $q_e$  versus  $\ln C_e$  enables one to determine the constants  $A$  and  $B$ . The values of the Temkin constants  $A$  and  $B$  were determined from Figure 8 and were found to be  $0.73 \text{ L/g}$  and  $1.18$  for MRH and  $2.17 \text{ L/g}$  and  $1.62$  for SB, respectively.



**Figure 8. Temkin adsorption isotherm A; sunset yellow-MRH system B; sunset yellow-SB system**

**Table 1. Isotherm models constants and correlation coefficients for adsorption sunset yellow onto MRH and SB**

Isotherm models	MRH	SB
	10 (mg L <sup>-1</sup> ); 0.5 g	10 (mg L <sup>-1</sup> ); 0.2g
Langmuir		
q <sub>m</sub> (mg g <sup>-1</sup> )	6.630	7.530
b (L mg <sup>-1</sup> )	0.052	0.216
R <sup>2</sup>	0.891	0.998
Freundlich		
K <sub>F</sub>	0.433	1.810
n	1.430	2.390
R <sup>2</sup>	0.997	0.955
Temkin		
A(L g <sup>-1</sup> )	0.728	2.170
B	1.18	1.62
R <sup>2</sup>	0.932	0.996

From data of Table 1 showed the Freundlich isotherm and Langmuir isotherm are obeyed better than other isotherms for MRH and SB, respectively, as are evident from the values of the regression coefficients.

### 3.6. Adsorption kinetic

Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, characteristic constants of sorption were determined using intraparticle diffusion, pseudo-first order equation and pseudo-second order equation.

A linear form of pseudo-first order model:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (5)$$

where q<sub>e</sub>, q<sub>t</sub> and k<sub>1</sub> are the amount of dye adsorbed at equilibrium (mg g<sup>-1</sup>), the amount of dye adsorbed at time t (mg g<sup>-1</sup>) and the equilibrium rate constant of pseudo-first order kinetics (min<sup>-1</sup>).

Linear form of pseudo-second order model, was illustrated as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model as:

$$Q_T = K_{id} t^{\frac{1}{2}} + C \quad (7)$$

where k<sub>id</sub> is the intraparticle diffusion rate constant. Values of C give an idea about the thickness of the boundary layer, *i.e.*, the larger intercept the greater is the boundary layer effect. According to this model, the plot of uptake should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and shows that the intraparticle diffusion

is not the only rate limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously.

To understand the applicability of the intraparticle diffusion, pseudo-first order and pseudo-second order models for the dye adsorption onto two adsorbents, linear plots of  $q_t$  versus  $t^{1/2}$ ,  $\log(q_e - q_t)$  versus contact time (t) and  $t/q_t$  versus contact time (t) are plotted. The values of  $k_{id}$ , C,  $k_1$ ,  $k_2$ , and R<sup>2</sup> (correlation coefficient values of all kinetics models) and the calculated  $q_e$  ( $(q_e)_{Cal.}$ ) are shown in Table 2:

The linearity of the plots (R<sup>2</sup>) demonstrates that the intraparticle diffusion and pseudo-second order kinetic models play a significant role in the uptake of the dye by modified rice husk and sugarcane bagasse (Table 2). In addition, the experimental  $q_e$  ( $(q_e)_{Exp.}$ ) values agree with the calculated ones ( $(q_e)_{Cal.}$ ), obtained from the linear plots of pseudo-second order kinetics (Table 2).

**Table 2. kinetic parameters for the adsorption of sunset yellow onto MRH and SB**

Kinetic models	MRH		SB	
	10 mg L <sup>-1</sup>	20 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	20 mg L <sup>-1</sup>
Pseudo-first order				
$K_1$ (min <sup>-1</sup> )	0.034	0.033	0.025	0.035
$q_e$ (exp) (mg g <sup>-1</sup> )	0.082	0.146	0.146	0.142
R <sup>2</sup>	0.804	0.862	0.961	0.934
Pseudo-second order				
$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.713	0.380	0.417	0.515
$q_e$ (exp) (mg g <sup>-1</sup> )	0.424	0.849	0.920	0.838
R <sup>2</sup>	0.999	0.999	0.999	0.999
$q_e$ (cal) (mg g <sup>-1</sup> )	0.412	0.825	0.899	0.818
Intra particle diffusion				
$K_{id}$	0.004	0.008	0.016	0.012
$C_i$	0.363	0.726	0.746	0.708
R <sup>2</sup>	0.999	0.966	0.963	0.990

#### 4. Conclusion

The results of this study indicate that the modified rice husk and sugarcane bagasse adsorbents can be successfully used for the adsorption of sunset yellow dye from aqueous solutions. Adsorption is a strong choice for removal of dye from wastewater. The adsorption of sunset yellow on MRH reached equilibrium in 100 minutes but this adsorption onto sugar cane bagasse reached equilibrium sooner. The equilibrium sorption data fitted the Freundlich isotherm model better than the Langmuir and Temkin models at sunset yellow- MRH system and for another system the Langmuir isotherm is much better. The kinetics data indicated that the adsorption kinetics of dyes on both of adsorbents followed the pseudo-second order. Results obtained from this study showed that MRH and SB was very effective at removing sunset yellow dye from the aqueous solution in a static batch system. Since rice husk and sugarcane bagasse, an agricultural solid waste, is freely, abundantly and locally available, the sorbent is expected to be economically viable for wastewater treatment. Since this method involves less capital cost and is highly efficient, it is practically feasible for developing countries.

#### Acknowledgements

We gratefully acknowledge the Research Council of University of Guilan for supporting this work.

## References

- [1] J. R.Gong, Y. Sun, J. Chen, H. Liu and C. Yang, *Dyes Pigments*, vol. 67, (2005), pp. 175.
- [2] A. Abbas, R. Rehman, S. Mortaza, U. Shafique, A. Zahid and R. Ayud, *J. Chem. Soc. Pak.*, vol. 34, no. 5, (2012), pp. 134.
- [3] R. Gong, Y. Jin, J. Chen, Y. Hu and j. Sun, *Dyes pigments*, vol. 73, (2007), pp. 332.
- [4] A. El-A. A. Said, A. A. M. Aly, M. M. A. El-Wahab, S. A. Soliman1, A. El-Hafez1, V. Helmeý and M. N. Goda, *Resources and Environment*, vol. 2, (2012), pp. 92.
- [5] P. Sharma, H. Kaur, *Appl Water Sci.*, vol. 1, (2011), pp. 135.
- [6] T. G. Chuah, A. Jamasiah, I. Azni and S. Katayon, *Desalination*, vol. 175, (2005), pp. 305.
- [7] W. Zhang, H. Li, X. Kan, L. Dong, H. Yan, Z. Jiang, H. Yang, A. Li and R. Cheng, *Bioresource Technology*, vol. 117, (2012), pp. 40.
- [8] J. Huff, *Environ. Health Perspect. FD&C Yellow*, vol. 6, no. 45, (1982), pp. 209.
- [9] S. Wang, Y. Boyjoo, A. Choueib and Z.H. Zhu, vol. 39, (2005), pp. 129.
- [10] Y. Safa and H. N. Bhatti, *African Journal of Biotechnology*, vol. 10, no. 16, (2011), pp. 3128.
- [11] Y. Safa and H. N. Bhatti, *Chemical Engineering Journal*, vol. 167, no. 35, (2011), pp. 41.
- [12] A. A. Said, A. G. Ludwick and H. A. Aglan, *Bioresource Technol.*, vol. 100, (2009), pp. 2219.
- [13] R. Gong, Y. Jin, J. Chen, Y. Hu and j. Sun, *Dyes pigments*, vol. 73, (2007), pp. 332.