**J. Iranian Chem. Res.**
5 (1) (**2012**) 13-18
ISSN 2008-1030

# Isothermal and thermodynamic studies of the adsorption of safranine on MCM-41

Ghazaleh Koutchakzadeh [*], Zohreh Derikvand

*Department of Chemistry, Korram Abad Branch, Islamic Azad University, Korram Abad, Iran*
[*] *E-mail: gh_kouchakzadeh@yahoo.com*

**Received 10 August 2011**
**Received in revised form 5 March 2012**
**Accepted 10 March 2012**

The uses of MCM-41 as adsorbent have been studied as an alternative substitution of activated carbon for the removal dyes. This adsorbent was prepared at laboratory by authors. Adsorption of safranine on MCM-41 was studied to examine adsorption thermodynamics. In this study was investigated the effect of procces parameters like *p*H, initial dye concentration, temperature and adsorbent mass. MCM-41, as adsorbent, is characterized by high surface area and high pore volume to adsorbed dye very well. In this study, both Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. Langmuir model being has found to provide the best fit of experimental data. Results of thermodynamic evaluation indicated that adsorption reaction was spontaneous because Gibs energy was negative. This reaction was exothermic with negative enthalpy and reducing entropy.

**Keywords:** MCM-41; Safranine; Langmuir isotherm; Freundlich isotherm; Equilibrium adsorption

## 1. INTRODUCTION

Dyes are used in various fields widely. The control of water pollution has become of increasing importance in recent years. The release of dyes into the environment constitutes only a proportion of water pollution. Removal of dyes from waste water by adsorption method have many advantages, such as, simply designed, easy to handle and inexpensive. The adsorption process is one of the effective methods for removal dyes from the wastewater. Adsorption can produce high quality products while also being a process that is feasible economically.

In this study we have selected MCM-41 as adsorbent for removal dye from aqueous solutions. It provides exciting opportunities for fundamental study applied studies on mesoporous materials. Such material is characterized by high surface area, high pore volume, as well as parallel and ideally shaped pore structures without the complications of a network. The cylindrical pore structure and high degree of pore symmetry found in ordered mesoporous silica are ideal for testing various existing adsorption and diffusion models [1]. In the literature, the studies on the adsorption and transport of MCM-41 were concentrated on gases [2-7] with very few investigations dealing with the liquid-phase system [8-10]. Recently, Ho et al. (2003) have shown that materials prepared by grafting amino- and carboxylic-containing functional groups onto MCM-41 might be a useful adsorbent for the removal of Acid blue 25 and Methylene blue dyes from wastewater and these adsorbents can be regenerated by simple washing with alkaline or acid solution to recover the adsorbents and adsorbed dyes.

Activated carbon as adsorbent has unquestionably been the most popular and widely used adsorbent in wastewater treatment employment throughout the world. But activated carbon is a costly material. Therefore searching for low cost adsorbent materials is of great importance for the wastewater treatment. In this work we test the ability of adsorption a mesopourous such as MCM-

41 for removal dye from aqueous solution. In addition, equilibrium isotherm, thermodynamic parameters, effect of *p*H and temperature were also investigated.

## 2. EXPERIMENTAL

### 2.1. Preparation of adsorbent

Mesoporous MCM-41 has been successfully prepared using different synthesis procedures and conditions. Here, the MCM-41 has been successfully prepared using different synthesis procedures and conditions. For preparation MCM-41, Fumed silica (8 g, Merck) was added to a solution of sodium hydroxide (2g, Merck) in distilled water (150 mL) in a baker at 80 °C. The resulting mixture continuously stirred until a clear solution was obtained. Then cethyltrimethyl ammonium bromide (CTAB) (3 g, Merck) was slowly added to this solution under vigorous stirring at room temperature. The resulting gel was additionally stirred for 2 h. The obtained gel was transferred into a teflon-line stainless steel autoclave for a hydrothermal treatment at 100 °C for 3 days. The resulting solid product was recovered by filtration and washing with deionized water for several times. The obtained white solid was dried in air at 100 °C for 5 h. Finally, the sample was calcined at 600 °C for 16 h in air.

### 2.2. Dye solution preparation

Safranine was used as dye and it was obtained from Merck. Safranine solution was prepared in double distilled water. Dye concentration was determined by using of absorbance values measured before and after the treatment, in 480 nm with JENWAY UV-Vis spectrometer (Model 6505). Experiment was carried out at initial *p*H values ranging from 2 to 7, initial *p*H was controlled by addition of sodium hydroxide or hydrochloric acid, to the buffer of acetic acid, buric acid and phosphoric acid.

### 2.3. Adsorption experiment

20 mL of dye solution of known concentration and pH was added to 0.03 g MCM-41 in 100 mL water bath mechanical shaker for 100 minute to reach equilibrium.

### 2.4. The effect pH

As shown in Fig.1 adsorption of safranine on the MCM-41 is dependent to pH. The amount of dye adsorbed increases with increase in pH. The dye adsorption was significantly changed at pHs 4 to 6. The lowest percentage of dye removal was recorded at pH 2 and 3. At the pH range up to 6, the percentage of removal dye was almost remains constant**.** As the pH of the solution decreases (more acidic), the number of negatively charged adsorbents site increased. This will not favorite the adsorption of the positively charge dyes. As the pH value increased up to 6, the efficiency of the dyes removal is slightly become lessen.

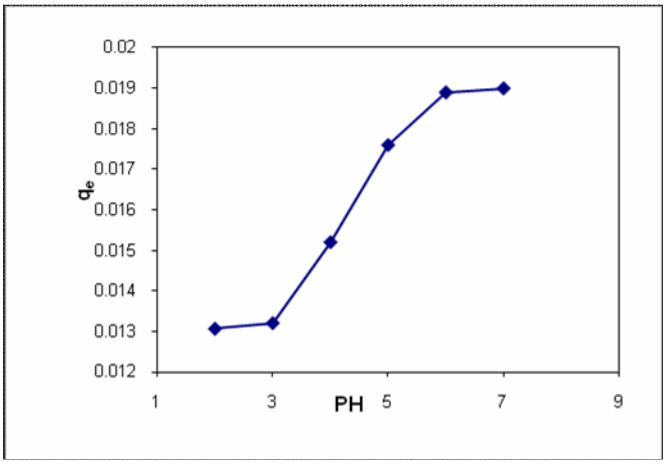

**Fig. 1.** Effect of pH on adsorption.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of initial dye concentration

The results show that the percentage of dye removal was low. The highest dye removal was measured for initial dye concentration of 20 mg $L^{-1}$. By increasing initial concentration dye removal was decreased. For safranine with initial concentration of 20, 30, 40 and 45 mg $L^{-1}$ at pH=7 were 72.30, 71.86, 68.17 and 68.00 %, respectively.

### 3.2. Equilibrium studies

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium study in adsorption gives the capacity of adsorbent; it is described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium [11]. In order to investigate the adsorption isotherm, two equilibrium models, Langmuir and Freundlich, were analyzed [12].

### 3.3. Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites with in the adsorbent 13]. The linear forms of Langmuir equation is given as:

$$\frac{1}{q_e} = \frac{1}{qb}\left(\frac{1}{C_e}\right) + \frac{1}{q}$$

where $C_e$ is the equilibrium concentration of the adsorbate ($mgL^{-1}$), $q_e$ is the amount of adsorbate adsorbed per unite mass of adsorbent ($mgg^{-1}$), q and b are Langmuir constants, q is the $q_e$ for a complete monolayer($mgg^{-1}$) and b is a constant related to the affinity of the binding sites and energy of adsorption. The constants can be evaluated from the intercept and the slope of the linear plots of $1/q_e$ versus $1/C_e$ (Fig. 2). The relative parameters and regression coefficients were listed in Table 1 [14].

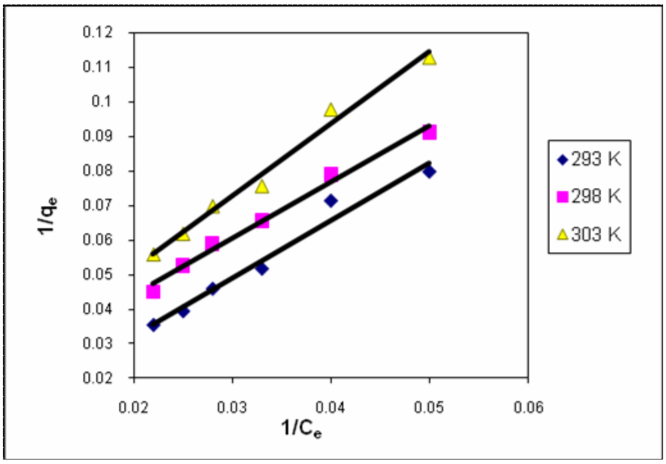

**Fig. 2.** Plot of $1/q_e$ vs. $1/C_e$ for safranine adsorption.

### 3.4. Freundlich isotherm

Empirical Freundlich equation based on a monolayer adsorption that often it used for heterogeneous surface energy system. The Freundlich equation in linear form is given as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

where $K_f$ and n are the Freundlich constants [15]. $K_f$ and n can be determined from the linear plot of log $q_e$ vs. log $C_e$ (Fig. 3). Isotherms evaluation showed that the Langmuir type is better than the Freundlich type, with good correlation coefficient for Langmuir isotherm.

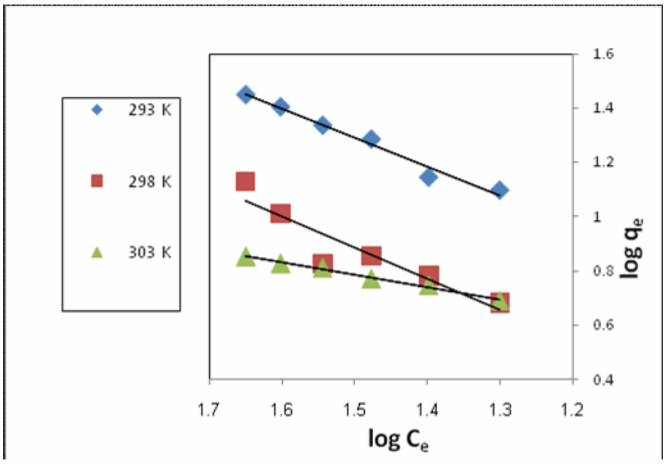

**Fig. 3.** Plot of log $q_e$ vs. log $C_e$ for safranine adsorption.

**Table 1.** Parameters for the application of Langmuir and Freundlich model to the adsorption safranine on MCM-41 using linear regression

| | Freundlich | | Langmuir | | | |
|---|---|---|---|---|---|---|
| T (K) | b | q | R | $K_f$ | 1/n | R |
| 293 | $9.5\times10^{-4}$ | 625.0 | 0.98 | 0.5 | 1.061 | 0.99 |
| 298 | $7.2\times10^{-3}$ | 85.5 | 0.99 | 0.14 | 1.15 | 0.93 |
| 303 | $4.9\times10^{-3}$ | 98.0 | 0.99 | 1.28 | 0.453 | 0.99 |

### 3.5. Effect of temperature

The effect of temperature on adsorption of safranine by MCM-41 was shown in Table 2, it was found that in the experimental temperature rang, with the increasing temperature, adsorptive quantity of dye removal was decreasing, so the process of dye is exothermic [16].

**Table 2.** The adsorption quantity of safranine on to MCM-41 at different temperature

| | 293 | 298 | 303 |
|---|---|---|---|
| $q_e$ for 25 ppm | 0.224 | 0.182 | 0.168 |
| $q_e$ for 45 ppm | 0.437 | 0.306 | 0.215 |

### 3.6. Thermodynamic evaluation

Thermodynamic parameters such as change in standard free energy, ΔG°, enthalpy, ΔH°, and entropy, ΔS°, were determined using the apparent equilibrium constant, $K_c^{'}$, of adsorption. $K_c^{'}$ was defined as:

$$K'_c = \frac{C_{ad}}{C_e}$$

where $C_{ad}$ (mg $L^{-1}$) is the amount adsorbed on solid at equilibrium time and $C_e$(mg $L^{-1}$) is the equilibrium concentration. ΔG° can be calculated using the relation that has given below:

$$\Delta G^0 = -RT Ln K_c^{'}$$

ΔH° and ΔS° were evaluated as:

$$\Delta H^{\circ} = -R\left[\frac{dLnK_c^{'}}{d\left(\frac{1}{T}\right)}\right]$$

$$LnK_c^{'} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where R, 8.314 J $mol^{-1}K^{-1}$, is the universal gas constant, T, K, is the absolute solution temperature. By plotting a graph of ln $K'_c$ vs. 1/T, the values of ΔH° and ΔS° can be estimated from the slope and intercept (Table 3).

**Table 3.** Thermodynamic parameters of safranine adsorption on MCM-41.

| T(K) | ΔG°(KJ/mol) | ΔH° (KJ/mol) | ΔS° (KJ/mol) |
|---|---|---|---|
| 293 | -7.765 | | |
| 298 | -2.189 | -200.7 | -0.661 |
| 303 | -1.180 | | |

The negative values of ΔG° indicated the spontaneous nature of the adsorption. The negative value of ΔH° indicated the exothermic nature of the process. The negative value of ΔS° shows adsorbed molecules to be almost fixed on active sites on MCM-41.

## 4- CONCLUSION

Adsorption of safranine on MCM-41 and effects of interaction between dye molecules and MCM-41 and potential of MCM-41 for dye removal were examined. MCM-41 is able to adsorbed safranine from aqueous solutions. The adsorption time of equilibrium is about 60 minute. It was noted that an increase in the temperature resulted the decrease of the adsorption. The highest dye removal was found for 20 mg $L^{-1}$ dye concentration. The equilibrium adsorption isotherm was followed two equilibrium models, Langmuir and Freundlich isotherms; consequently correlation coefficient for fitting the Langmuir equation was significantly better than Freundlich equation. Thermodynamics of safranine-MCM-41 system indicates the spontaneous and exothermic process of dye adsorption.

## REFERENCES

[1] L.Ch. Juang, Ch. Wang, Ch. Kung Lee, Chemosphere 64 (2006) 1920-1928.
[2] E.W. Hansen, F. Courivaud, Karlsson, A.S. Kolboe, M. Stöcker; Micropore. Mesopore. Mater. 22 (1998) 309-320.
[3] V.R. Choudhary, K. Mantri, Micropore. Mesopore. Mater. 40 (2000) 127-133.
[4] X. Hu, S. Qiao, X.S. Zhao, G.Q. Lu, Ind. Eng. Chem. Res. 40 (2001) 862-867.
[5] X.S. Zhao, G.Q. Lu, X. Hu; Colloid Surf. A: Physicochem. Eng. Aspects 179 (2001) 261-269.
[6] J.S. Oh, W.G. Shim, J.W. Lee, J.H. Kim, H. Moon, G. Seo, J. Chem. Eng. Data 48 (2003) 1458-1462.
[7] J.W. Lee, W.G. Shim, H. Moon, Micropore. Mesopore. Mater. 73 (2004) 109-119.
[8] J. Liu, X. Feng, G.E. Fryxell, L.Q. Wang, A.Y. Kim, A.Y. Gong, Adv. Mater. 10 (1998) 61-65.
[9] R.I. Nooney, M. Kalyanaraman, G. Kennedy, E.J. Maginn, Langmuir 17 (2001) 528-533.
[10] M. Ghiaci, A. Abbaspur, R. Kia, F. Seyedeyn-Azad, Purif. Technol. 40 (2004) 217-229.
[11] R.P. Han, J.H. Zhang, W.H. Zou, J. Shi, H.M. Liu, J. Hazard. Mater. 125 (2005) 266-271.
[12] A. Esmaili, S. Ghasemi, J. Biotechnology 7 (2008) 2034-2037.
[13] I. Langmuir, J. Am. Chem. Soc. 38 (1916) 2221-2295.
[14] R. Ahmad, R. Kumar, J. Iranian Chem. Res. 1 (2008) 85-94.
[15] H.M.F. Freundlich, Phys. Chem. 57 (1906) 385-470.
[16] R.P. Han, H.K. Li, Y.H. Li, J.H. Zhang, H.J. Xiao, J. Shi, J. Hazard. Mater. 137 (2006) 1569-1576.