



EQUILIBRIUM AND THERMODYNAMIC STUDIES OF THIONINE ADSORPTION FROM AQUEOUS SOLUTION ONTO RICE HUSK

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In this study, the removal of thionine dye from aqueous solutions using low-cost materials as adsorbent by a batch system was investigated. Experiments were carried out as a function of contact time, initial concentration, pH and temperature. The equilibrium adsorption of thionine dye on rice husk adsorbent was analyzed by Langmuir, Freundlich and Temkin models. The results indicate that the Langmuir model provides the best correlation of the experimental data. Various thermodynamic parameters such as enthalpy ΔH° , entropy ΔS° and free energy ΔG° were evaluated. Thermodynamic parameters values revealed that the adsorption of thionine onto rice husk is endothermic, spontaneous, with an increased randomness in nature. The results revealed that the thionine is considerably adsorbed on rice husk and it could be an economical method for the removal of thionine from aqueous systems.

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Introduction

To remove dyes and other colored contaminants from wastewaters, several physical, chemical, physico-chemical and biological such as coagulation and flocculation, membrane separation, different advance oxidation processes, ozonations, electro-coagulation, and adsorption.¹⁻⁵ Among these methods, adsorption currently appears to offer the best potential for overall treatment methods have been developed.⁶

Adsorption is one of the promising alternative techniques used for the removal of dyes from water and wastewater,⁷ and activated carbon is the most widely used adsorbent.⁸ However, the production of activated carbon is complex and expensive, making this technology economically inefficient. Accordingly, the critical challenge of applying the adsorption method to dye removal is finding a low-cost adsorbent that is profoundly available with a high removal capacity so adsorption can successfully compete with other dye removal techniques. This is the driving force behind further studies attempting to find an efficient low-cost adsorbent. Waste materials have recently been viewed as potential low-cost adsorbents, and many reports have been published showing their ability to adsorb various contaminants including dyes.⁷⁻¹⁵ Rice husk, an agricultural waste, is proposed as a no-cost and profoundly accessible potential dye adsorbent.

Rice husk is agricultural waste, accounting for about one fifth of the annual gross rice, 545 million metric tons, of the world. Rice husk contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and

amidogen,¹⁶ which make the adsorption processes possible and it has been successfully used to remove colored components¹⁷ or metal ions.¹⁸

Due to the biological and chemical stability of dyestuffs in a number of conventional water treatment methods, adsorption is considered as an attractive and favorable alternate for the removal of dyes and other chemicals from wastewater streams.¹⁹⁻²³ For an efficient adsorption process, rapid removal of the pollutants as well as a high ultimate adsorption capacity of the adsorbent is needed.

The main purpose of the present study is the removal of thionine onto rice husk adsorbent from aqueous solutions under different experimental conditions. The effects of solution pH, dye concentration, contact time and solution temperature were studied for thionine removal. 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. Thermodynamics of the adsorption process have been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined.

Experimental

Adsorbent

The milled rice husk was obtained from rice farms in the north of Iran, Guilan, Iran and was used as an adsorbent. The milled rice husk sieved through the sieves, 50-80 mesh size particles. Then rice husk in above particle size rinsed with distilled water to remove dust and soluble impurities and was then dried at 70 °C for 12 hours in an oven before use (The heat treatment of rice husk was carried out for removing any volatiles such as moisture). The dried husks were stored in a desiccator until used.

Adsorbate

Thionine acetate was product of Sigma-Aldrich and was used as received without further purification (Fig. 1).

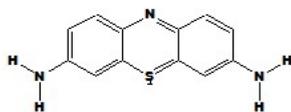


Figure 1. Chemical structure of thionine

A stock solution of dye was prepared by dissolving 0.025 g of it in 50 mL of double distilled water. Working solutions of different concentrations ($10\text{--}50\text{ mg L}^{-1}$) were prepared by further dilutions. The concentration of the dye thionine was determined using a UV-vis spectrophotometer (Janway 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 Metrohm pH meter (model 827) with a combined double junction glass electrode was used for showing pH values. pH adjustments were carried out using dilute NaOH and HCl solutions.

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 Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The pH of the solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The flasks were shaken for the required time period in a water bath shaker. For the thermodynamic study, the experiment was performed using 0.20 g rice husk added to 100 mL of thionine solution in 250 mL flasks at the different temperature. The flasks were shaken at 120 rpm for 60 min at pH 6. The initial thionine concentration used in this study was 20 mg L^{-1} . A mixture of 0.2 g of rice husks with 100 mL thionine solutions of 20 mg L^{-1} concentrations was shaken at 120 rpm for 60 min at $25\text{ }^{\circ}\text{C}$. The initial pH of the solution was adjusted to 6. All experiments were performed in duplicate. The filtrate samples were analyzed for the determination of the final concentration of thionine by using an UV-vis spectrophotometer (Janway 6100) set at a wavelength of 598 nm, maximum absorbance. The thionine concentration retained in the adsorbent phase was calculated according to:

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

where

C_0 and C_e are the initial and the equilibrium concentrations (mg L^{-1}) of thionine solution, respectively; V is the volume (L), and W is the weight (g) of the adsorbent.

Results and discussions

Effect of pH

The effect of pH on the removal efficiency of thionine was studied at different pH ranging from 2.0 to 12.0 and results are shown in Fig. 2. It can be seen that adsorption of thionine was minimum at solution pH 2 and increased with pH up to 6.0 and then remained nearly constant over the initial pH ranges of 6–12. The observed low absorption rate of thionine on the rice husk at $\text{pH} < 6$ may be because the surface charge becomes positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. To decrease in acidity of the solution, the functional groups on the adsorbent surface become deprotonated resulting in an increase in the negative charge density on the adsorbent surface and facilitate the binding of dye cation.

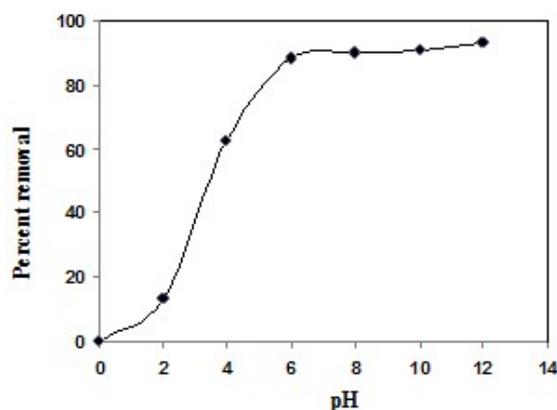


Figure 2. Effects of pH on thionine dye removal at various concentrations (adsorbent dosage: 0.20 g; contact time: 120 min; temperature: $25\text{ }^{\circ}\text{C}$).

The increase in dye removal capacity at higher pH may also be attributed to the reduction of H^+ ions which compete with dye cations at lower pH for appropriate sites on the adsorbent surface. However with increasing pH, this competition weakens and dye cations replace H^+ ions bound to the adsorbent surface resulting in the increased dye uptake.

Effect of Adsorbent Dose

Fig. 3 shows the effect of adsorbent dose (rice husk) on the removal of thionine ($C_0=20\text{ mg L}^{-1}$) at $25\text{ }^{\circ}\text{C}$. It can be seen that the thionine removal increases with increase rice husk up to 0.40 g, thereafter remained fairly constant despite an increase in the amount of the rice husk to 0.4 g. At the equilibrium time, the % removal increased from 34.67 to 80% for an increase in rice husk dose from 0.05 to 0.40 g. The increase in % removal was due to the increase of the available sorption surface and availability of more adsorption sites.

Table 1: Thermodynamic parameters for the adsorption of thionine onto rice husk

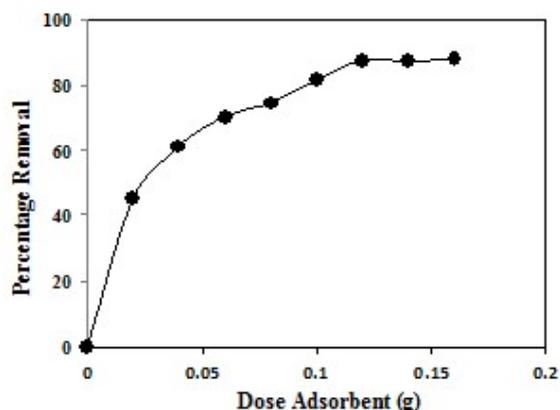
Initial thionine concn. (mg L ⁻¹)	ΔH° , kJ mol ⁻¹	ΔS° , J mol ⁻¹ K ⁻¹	ΔG° , kJ mol ⁻¹			
			15 °C	25 °C	35 °C	45 °C
20	21.940	86.711	-3.319	-4.073	-4.794	-5.607

Table 2. Isotherm models constants and correlation coefficients for adsorption thionine onto rice husk.

Adsorbent	Langmuir Isotherm			Freundlich isotherm			Temkin isotherm		
	a (mg g ⁻¹)	B (L mg ⁻¹)	R^2	K_F	n	R^2	A (L g ⁻¹)	B	R^2
Rice Husk	8.67	0.55	0.99	2.85	2.22	0.94	5.19	3.11	0.96

Effect of contact time on dye removal

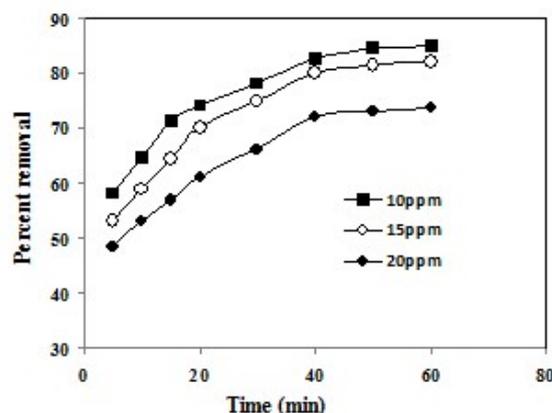
Adsorption of thionine was measured at given contact times for the different initial thionine concentrations from 10 to 20 mg L⁻¹. From Fig. 4, the plot reveals that the percent thionine removal is higher at the beginning; this is probably due to a larger surface area of the rice husk being available at the beginning for the adsorption of thionine. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Most of the maximum percent thionine removal was attained after about 90 min of shaking time at different concentrations. The increasing contact time increased the thionine adsorption and it remained constant after equilibrium was reached in 40 min for different initial concentrations.

**Figure 3.** Effects of contact time of the dye removal at various concentrations (adsorbent dosage: 0.2 g; pH: 7.0; temperature: 25 °C).

Effect of initial dye concentration

The effect of the initial concentration in the range of 5 to 30 mg L⁻¹ on adsorption was investigated and is shown in Fig. 5. It is evident from this figure that the percentage thionine removal decreased with the increase in initial concentration of thionine. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of thionine between the aqueous phase and the solid phase. The increase in initial dye concentration also enhances the interaction between thionine and rice husk. Therefore, an increase in the initial concentration of the enhances the adsorption uptake of the. This is due to the increase in the driving

force of the concentration gradient produced by the increase in the initial thionine concentration. While the percentage thionine removal was found to be 89.59% for a 5 mg L⁻¹ initial concentration, this value was 59.10% for 30 mg L⁻¹.

**Figure 4.** Influence of rice husk dosage on thionine removal under different solution concentration (contact time: 120 min; pH: 7.0; temperature: 25°C).

Thermodynamic studies

The thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations.²⁴

$$\Delta G^\circ = -RT \ln K \quad (2)$$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{T} \quad (3)$$

where K_C is the distribution coefficient for adsorption and is determined as:

$$K = \frac{C_{Ae}}{C_e} \quad (4)$$

where

C_{Ae} is the equilibrium dye concentration on the adsorbent (mg L⁻¹) and

C_e is the equilibrium dye concentration in solution (mg L⁻¹).

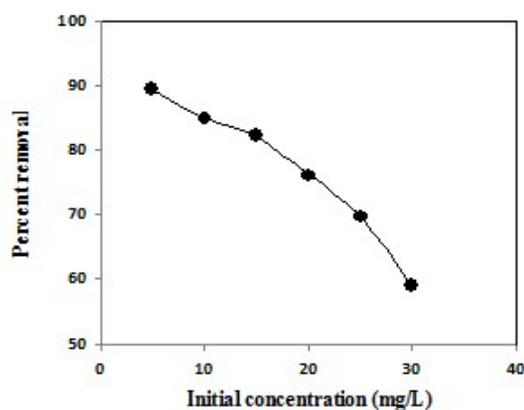


Figure 5. Effect of initial concentration thionine on its sorption onto rice husk (adsorbent dosage: 0.20 g; contact time: 120 min; temperature: 25 °C).

In order to explain and confirm the mechanism of thionine adsorption onto rice husk, the thermodynamics of adsorption were evaluated using ΔG° , ΔH° and ΔS° , given by Eqs. (2) and 3). As seen in Table 1, the value of ΔG° for all tested temperatures was calculated to be negative, which suggests that the adsorption of thionine onto rice husk is spontaneous and indicates that rice husk has a high affinity for the adsorption of thionine from solution under experimental conditions.²⁵ Values of ΔG° between -20 and 0 kJ mol^{-1} indicate a physical adsorption process,²⁶ thus, the results of thermodynamic investigation reconfirmed the hypothesis of physisorption of thionine onto rice husk. Furthermore, the values of ΔH° and ΔS° in the present experiment were 21.94 J mol^{-1} and 86.71 $\text{J mol}^{-1} \text{K}^{-1}$, respectively. A positive value of ΔH° proves the adsorption phenomenon is endothermic.²⁷ Also, the positive value of ΔS° (86.71 $\text{J mol}^{-1} \text{K}^{-1}$) reflects the affinity of the treated rice husk for thionine and an increased randomness at the solid-solution interface during adsorption.^{28, 29}

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 thionine sorption isotherm followed the linearized Freundlich model, as shown in Fig. 6. The relation between the thionine uptake capacity q_e (mg g^{-1}) of adsorbent and the residual thionine concentration C_e (mg L^{-1}) at equilibrium is given by

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where the intercept, $\ln K_F$, is a measure of adsorbent capacity, and the slope $1/n$ is the sorption intensity.

The isotherm data fit the Freundlich model well ($R^2=0.94$). The values of the constants K_F and $1/n$ were calculated to be 2.85 and 0.45, respectively. Since the value of $1/n$ is less than 1, it indicates a favorable adsorption. The Freundlich isotherm is more widely used, but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

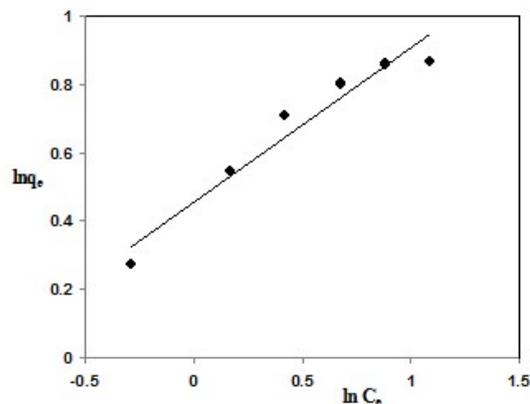


Figure 6. Freundlich adsorption isotherm thionine-rice husk system.

The Langmuir equation relates the solid phase adsorbate concentration (q_e) or uptake to the equilibrium liquid concentration (C_e) as follows:

$$q_e = \frac{abC_e}{1 + bC_e} \quad (6)$$

where a and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant can be seen from Fig. 7. The isotherm data fits the Langmuir equation more poorly ($R^2=0.99$) than the Freundlich and Temkin equations. The values of a and b were determined from Fig. 7 to be 8.67 mg g^{-1} and 0.55 L mg^{-1} , respectively.

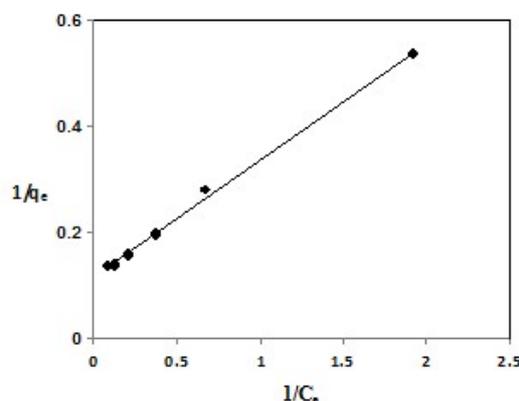


Figure 7. Langmuir adsorption isotherm thionine-rice husk system.

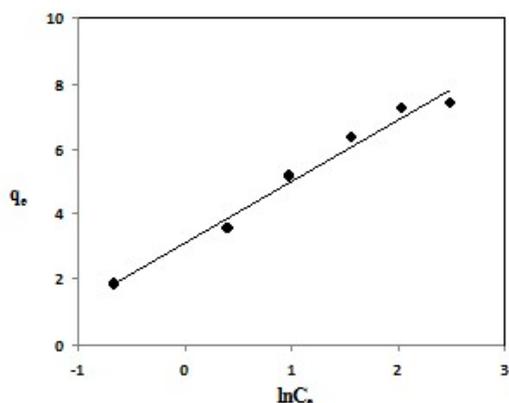


Figure 8. Temkin adsorption isotherm thionine-rice husk system.

The Temkin isotherm has been used in the following form:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

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. (7). 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 Fig. 8 and were found to be 5.19 L g^{-1} and 1.88 , respectively. The correlation coefficient of 0.96 obtained showed that adsorption of thionine also followed the Temkin model.

The Langmuir isotherm is obeyed better than the Freundlich and Temkin isotherms, as is evident from the values of the regression coefficients. The resulting values of the parameters K_F , n , a , b , A , B , R^2 , for all the experiments in solutions with pH equal to 6.0 for maximum removal of thionine are presented in Table 2.

Conclusion

The results of this study indicate that the rice husk adsorbent can be successfully used for the adsorption of thionine dye from aqueous solutions. Adsorption is a strong choice for removal of dye from wastewater. The adsorption of thionine on rice husk reached equilibrium in 40 minutes. The equilibrium sorption data fitted the Langmuir isotherm model better than the Freundlich and Temkin models. The negative values of ΔG° and positive ΔH° obtained indicated that the thionine dye adsorption process is a spontaneous and an endothermic. Rice husk showed high adsorption capacities and it can be successfully used for treatment of thionine containing wastewater. Since this method involves less capital cost and is highly efficient, it is practically feasible for developing countries.

The results of this investigation will be useful for the removal of cationic dyes from industrial effluents.

Acknowledgements

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References

- Faria, P. C. C., Orfao, J. J., Pereira, M. M. F. R., *Water Res.*, **2004**, *38*, 2043.
- Qin, Q., Liu, J. Ma., K., *J. Hazard. Mater.*, **2009**, *162*, 133.
- Namasivayam, C., Radhika, R., Suba, S., *Waste Manage.*, **2001**, *21*, 381.
- Mall, D. V. C., Srivastava, N. K., *Dyes Pigm.*, **2006**, *69*, 210.
- Jain, R., Gupta, V. K., Sikarwar, S., *J. Hazard. Mater.*, **2010**, *182*, 749.
- Muthukumar, M., Sargunamani, D., Selvakumar, N., Venkata Rao, J., *Dyes Pigm.*, **2004**, *63*, 127.
- Gupta, V. K., Suhas, *J. Environ. Manage.*, **2009**, *90*, 2313.
- Wu, F. C., Tseng, R. L., Juang, R. S., *J. Colloid Interface Sci.*, **2005**, *283*, 49.
- Rafatullah, M., Sulaiman O., Hashim, R., Ahmad, A., *J. Hazard. Mater.*, **2010**, *177*, 70.
- Song, S., Fan, J., He, Z., Zhan, L., Liu, Z., Chen, J., Xu, X., *Electrochim. Acta.*, **2010**, *55*, 3606.
- Deniz, F., Saygideger, S. D., *Bioresour. Technol.*, **2010**, *101*, 5137.
- Safa, Y., Nawaz Bhatti, H., *Chem. Eng. J.*, **2011**, *167*, 35.
- Tehrani-Bagha, A. R., Nikkar, H., Mahmoodi, N. M., Markazi, M., Menger, F. M., *Desalination* **2011**, *266*, 274.
- Moussavi, G., Khosravi, R., *Chem. Eng. Res. Design*, **2011**, *89*, 2182.
- Vargas, A. M. M., Cazetta, A. L., Martins, A. C., Moraes, J. C. G., Garcia, E. E., Gauze, G. F., Costa, W. F., Almeida, V. C., *Chem. Eng. J.*, **2012**, *181*, 243.
- Dong, Y., Han, Z., Liu, C., Du, F., *Sci. Total Environ.*, **2010**, *40*, 2245.
- Dogan, M., Ozdemir, Y., Alkan, M., *Dyes Pigm.*, **2007**, *75*, 701.
- Suna, D., Zhang, X., Wu, Y., Liu, X., *J. Hazard. Mater.*, **2010**, *181*, 335.
- Tan, I. A. W., Ahmad, A. L., Hameed, B. H., *Desalination*, **2008**, *225*, 13.
- Nakbanpote, W., Goodman, B. A., Thiravetyan, P., *Colloid Surf. A: Physicochem. Eng. Aspects*, **2007**, *304*, 7.
- Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y., Zou, L., *Bioresour. Technol.*, **2008**, *99*, 2938.
- Naiya, T. K., Bhattacharya, A. K., Das, S. K., *Environ. Prog. Sustain. Ener.*, **2009**, *28*, 538–546.
- Mohapatra, M., Khatun, S., Anand, S., *Chem. Eng. J.*, **2009**, *155*, 184.
- Anirudhan, T. S., Radhakrishnan, P. G., *J. Chem. Thermodyn.*, **2008**, *40*, 702.
- Crini, G., *Dyes Pigments*, **2008**, *77*, 415.

- ²⁶Almeida, C. A. P., Debacher, N. A., Downs, A. J., Cottet, L.C., Mello, A. D., *J. Colloid Interface Sci.*, **2009**, 332, 46.
- ²⁷Cheung, W. H., Szeto, Y. S., McKay, G., *Bioresour. Technol.*, **2007**, 98, 2897.
- ²⁸Liu, Y., Liu, Y. J., *Sep. Purif. Technol.*, **2008**, 61, 229.
- ²⁹Jain, S., Jayaram, R. V., *Desalination* **2010**, 250, 921.

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