



## Equilibrium and Kinetics Study of Reactive Blue 19 Dye from Aqueous Solution by a Rapid Adsorption Approach to Degradation

Elham Keshmirizadeh\*, Marzieh Shomeilzadeh

Department of Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran.

(Received 30 Mar. 2013; Final version received 17 Jul. 2013)

---

### Abstract

The present investigation assesses the application of ceric sulfate for the removal of the colorant reactive blue 19 (R.B19) from synthetic wastewater. The adsorption characteristics and dye removal efficiency of adsorbent have been determined by investigating factors such as effect of pH ( $\text{pH}_{\text{Optimum}} < 2$ ), effect of concentration of the dye (up to 1000 mg/L), dose of adsorbent (up to 0.7 g/L) and contact time (under 120 sec). Under the optimized conditions, the percentage of color removal efficiency increased up to 97%. Langmuir, Freundlich and Tempkin isotherm models have been used to evaluate the ongoing adsorption. Langmuir equation shows higher conformity than the other two. On the basis of pseudo first order, pseudo second order and intra particle diffusion kinetic equations, different kinetic parameters have been obtained. From the kinetic experiment data, it was found that the sorption process follows the pseudo second order.

**Keywords:** Removal of dye, Reactive blue 19, Cerium (IV) sulfate, Kinetic study.

---

### Introduction

At present, large amounts of highly colored wastewater are discharged from textile, printing, paper, and leather industries which use many kinds of artificial composite dyes. These dye-containing industrial wastewaters discharged into streams and river constitutes one of the major sources of water pollution [1].

The textile industry uses approximately 21-377 m<sup>3</sup> of water per ton of textile produced and thus generates large quantities of wastewater from different steps of dyeing and finishing process [2]. Reactive dyes are widely used because of their bright colors, those dyes in wastewaters have limited biodegradability in an aerobic environment. Most reactive dyes are stable to

---

\*Corresponding author: Dr. Elham. Keshmirizadeh, Assistance Prof., Department of Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran. Email: ekeshmirizadeh@yahoo.com, Tel: +98(937)7807397, P.O. Box: 31485-313, Iran, Fax: +9826-34418156.

light and to biological degradation [3]. The textile wastewater treatment is a very serious problem due to several reasons such as: high Total Dissolved Solids (TDS) content of the waste water, presence of toxic heavy metals such as Cr, As, Cu, Zn, etc., non-biodegradable nature of organic dye stuffs present in the effluent, and presence of free-chlorine and dissolved silica [4]. Physicochemical methods for the treatment of dye containing wastewaters, such as ultra-filtration, coagulation, flocculation floatation, reverse osmosis, hyper filtration, irradiation, precipitation, electrochemical treatment, and ion-pair extraction, adsorption by activated carbon, oxidation (with chlorine, hydrogen peroxide, and ozone), are effective in the removal of dyes [5-7].

However, none of these methods has been found to be very suitable because they are expensive and produce toxic pollutants, also conventional chemical processes such as precipitation with alum or ferrous sulfate generate large volumes of sludge, which creates problems of disposal [8-9].

For a single rare earth has little researched on wastewater treatment. According to rare earth application in wastewater treatment studies, in the process of adjusting pH, Ce (IV) and Ce (III) form hydroxide, Ce (IV) formed  $[\text{Ce}(\text{OH})_x \cdot n\text{H}_2\text{O}]^{(4-x)+}$  after hydrolyzation and Ce (III) obtained after Ce (IV) reduction formed  $[\text{Ce}(\text{OH})_x \cdot n\text{H}_2\text{O}]^{(3-x)+}$  after hydrolyzation,

especially Ce (OH)<sub>4</sub> has a larger surface area, it has high adsorption capacity of suspended solids in wastewater [10]. The present paper is aimed to investigate and develop a kind of rapid approach for color removal from aqueous solution using Ce(SO<sub>4</sub>)<sub>2</sub> system. Optimum conditions of de-colorization such as the dosage of ceric sulfate, time of de-colorization and pH were also determined. One kind of dye, reactive blue 19 (R.B19), was chosen for de-colorization. The equilibrium isotherm and kinetic characteristics of reactive dye adsorption on the above mentioned adsorbent were investigated using bench scale batch tests.

## Experimental

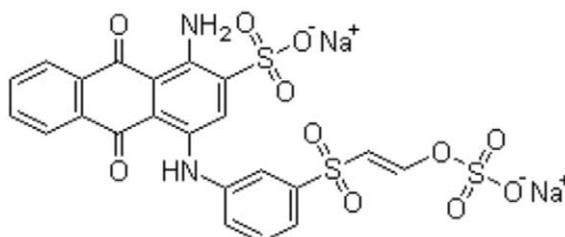
### Materials

Reactive blue 19 (R.B19) dye, (C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>11</sub>S<sub>3</sub>, MW:626.54), Purchased from Alvan-rang Company, Iran. It was used as received without further purification. The structure of the dye is presented in Fig 1. Reagent grade of Cerium (IV) sulfate (99%) obtained from Merck-Germany, used as adsorbent reagent. For preparation procedure of this system, Stock solution of Cerium (IV) sulfate was prepared in 25 g/L concentration from Ce(SO<sub>4</sub>)<sub>2</sub> powder and 1 mL concentrated acid sulfuric was added for better solubility. Note: the solubility of Ce(SO<sub>4</sub>)<sub>2</sub> in water is 9.84g/100mL, at 20°C. This solution was stirred for 30 min at 200 rpm.

### Methods

A stock solution of reactive blue (1000 mg/L) was prepared and suitably diluted to the required initial concentration 10-1000 mg/L. A calibration curve of absorbance vs. concentration was constructed using a UV

spectrophotometer (Hach Model: DR-2800) at maximum wavelength of 588 nm. All chemicals were of analytical reagent grade. All measurements are based on methods from standard method [11].



**Figure 1.** Structure of reactive blue19 dye (R.B19).

### Batch kinetic studies

Experimental kinetic data for R.B19 adsorption by Cerium (IV) sulfate were investigated at temperatures 298K. All the kinetic experiments were performed at optimum pH (pH<3) of solutions. Certain amount of Cerium (IV) sulfate (see Table 1) was contacted with 50 mL R.B19 solutions in a sealed flask agitated by a magnetic stirrer at 400rpm. A volume of 0.5mL was pipetted and all the samples were centrifuged at 5000rpm for 4 min, the residual concentration of dye in solution was measured specter photometrically. Percentage of Color Removal efficiency can be calculated by the following equation:

$$\% \text{ Color Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$C_0$  is initial, and  $C_e$  is residual dye concentration. The amount of R.B19 adsorbed on ceric sulfate was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)}{M} \quad (2)$$

$q_e$ :adsorption capacity(mg/g),  $M$ : dose of adsorbent(g/L).

### Result and discussions

The mentioned process was controlled by several operational parameters, In order to enhance the process performances, the influences of these parameters were studied as follows:

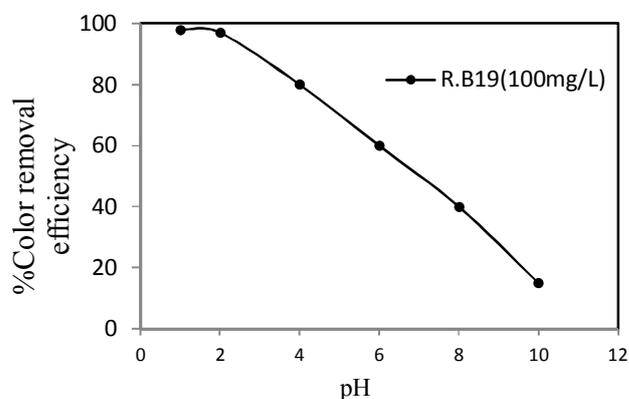
#### *Effect of important operating parameters: pH and dose of $Ce(SO_4)_2$*

The effect of % color removal efficiency on adsorption can be described versus on an important parameter such as pH. The pH dependence profile indicates that adsorption is very dependent over the entire pH range examined. The results show that optimum pH was below 2(Fig 2). Previous work indicated

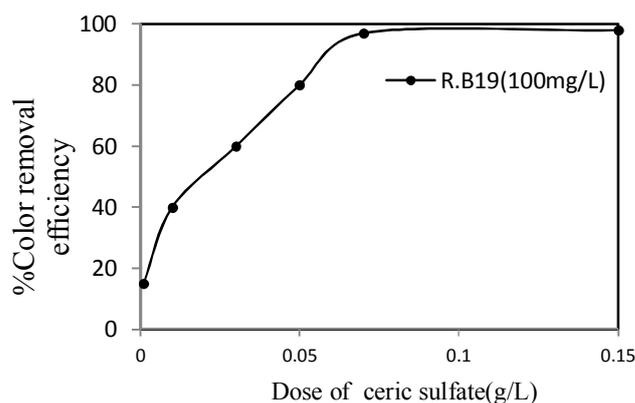
that optimum pH was near 0.5[10].The effect of ceric sulfate dosage on the color removal of R.B19 was investigated. The dosage of ceric sulfate was increased from 0.001 to 0.15g/L with a fixed amount of R.B19:100mg/L dosage. The results were shown in Fig 3.

It is evident that color removal efficiency gradually improved with increasing ceric sulfate dosage. About %98 of de-colorization was observed when ceric sulfate dosage was

above 0.07g/L but further increase in the dosage didn't produce higher removal rate, also Previous research didn't mention to the dosages of ceric sulfate [10].To investigate the effect of time on dye removal efficiency a series of experiments were carried out by solutions containing constant initial dye concentrations (10–1000 mg/L) by considering each optimized parameters represented in Table 1.



**Figure 2.** Percent of color removal efficiency versus pH for 100 mg/L solution of R.B19.



**Figure 3.** Percent of color removal efficiency versus dose of ceric sulfate for 100 mg/L solution of R.B19.

**Table 1.** Optimized operational parameters for various dye (R.B19) initial concentration.

Time of color removal (sec)	Dose of Ceric sulfate (g/L)	Adsorption capacity $q_e$ :(Eq2) (mg/g)	R.R19 Solution conc.[C <sub>0</sub> ] (mg/lit)	Residual dye conc. [Ce] (mg/lit)	% Color Removal Efficiency Eq(1)
1	0.02	384	10	0.40	96.00
5	0.05	972	50	1.39	97.22
10	0.07	1281	100	3.88	96.12
50	0.12	1543	200	7.09	96.45
60	0.17	1652	300	10.80	96.4
75	0.35	1377	500	18.02	96.39
120	0.70	1380	1000	33.63	96.63

### Adsorption Kinetics

To optimize the design of an adsorption system of R.B19 onto ceric sulfate, it was deemed necessary to establish the most appropriate correlations for the equilibrium data for each system. Therefore, several kinetic models including the pseudo first order, pseudo second order rate models and intra-particle diffusion models, were used to determine adsorption mechanism Eq. 3-5.

The linearized form of the pseudo first-order rate equation is given as [13-14]:

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right)\left(\frac{1}{t}\right) + \frac{1}{q_1} \quad (3)$$

$$\frac{t}{q} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (4)$$

$$q = k_p t^{0.5} + C \quad (5)$$

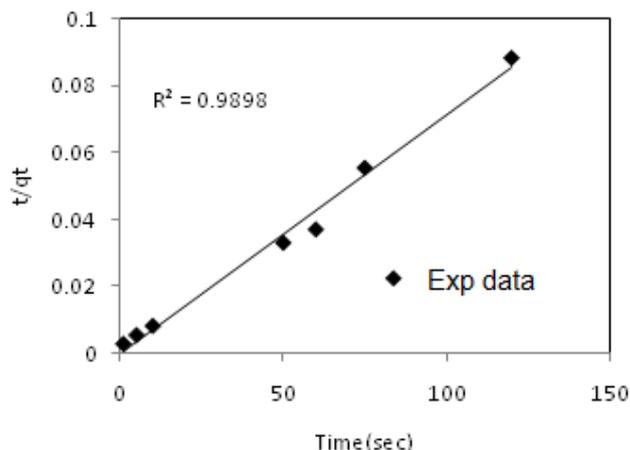
Where  $q_t$  is the amount of dye adsorbed (mg/g) on adsorbent at time  $t$ (sec),  $q_1$ : the maximum capacity(mg/g)for the pseudo first order

adsorption,  $k_1$  is the pseudo first order rate constant for the adsorption process (1/sec).

$q_2$ : the maximum adsorption capacity(mg/g) for the pseudo second order adsorption,  $k_2$  the rate constant of pseudo second order for the adsorption(g/(mg.sec)),  $k_p$ : the intraparticle diffusion rate constant (mg/(g.sec<sup>0.5</sup>)),  $C$ : the intercept for the intraparticle diffusion model (mg/g). The results were given in Table 2, all the parameter can be determined by slopes and intercepts of plots.

In many cases the first order equation does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [15].

In this study because of good correlation coefficient  $R^2 = 0.98$  was obtained by fitting the experimental data to Eq. 4, indicating that the adsorption process on the  $Ce(SO_4)_2$  is pseudo second order as shown in Figure 4 and Table 2.



**Figure 4.** Pseudo-second order kinetics model plot for the adsorption of R.B19 on ceric sulfate.

**Table 2.** Kinetic Parameters for R.B19 adsorption by Cerium (IV) sulfate.

parameters	Types of Kinetic		
	Pseudo 1 <sup>st</sup> Order	Pseudo 2 <sup>nd</sup> Order	Intra-particle diffusion
$q_1$ (mg/g):1600 $k_1$ (sec <sup>-1</sup> ):3	$q_2$ (mg/g):1428 $k_2$ (g/(mg.sec)):0.005	C(mg/g):716 $k_p$ (mg/(g. sec <sup>0.5</sup> )):87	
$R^2$	0.23	0.9898	0.57

#### Adsorption isotherms

An adsorption isotherm shows how the adsorbate molecules partition between the liquid and solid phases when the adsorption process reaches equilibrium conditions. Dye concentration plays an important role in affecting the adsorption capacity on ceric sulfate (Table 1). Several isotherm models are used in order to correlate the equilibrium adsorption data. The adsorption isotherms used here were the Langmuir, Freundlich and Tempkin, (Eq(6-8)), in linearized form separately [16-17].

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (6)$$

$$\ln q_e = \ln K_f + n \ln C_e \quad (7)$$

$$q_e = \frac{RT}{b_T} (\ln A_T) + \frac{RT}{b_T} (\ln C_e) \quad (8)$$

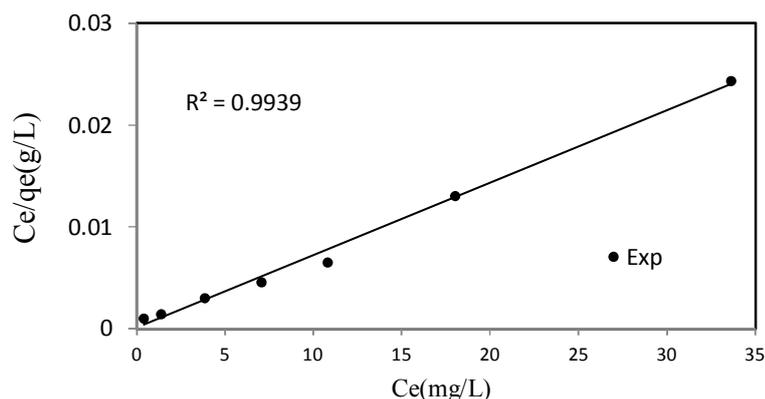
Where  $C_e$  is the equilibrium concentration of R.B19 (mg/L) in the solution,  $q_e$  is the equilibrium dye concentration (mg/g),  $b$ (L/mg) and  $Q_0$  signifies the maximum adsorption capacity (mg/g).  $K_f$  is roughly an indicator of the adsorption capacity (mg/g) and is heterogeneity factor (adsorption intensity).  $A$  (L/g) and  $b_T$ (J/mol) are the Tempkin constant. Linear regression was frequently used to determine the most fitted isotherm (Figure 5). The parameters together with the  $R^2$  values are shown in Table 3. As it is seen from Table 3, the correlation factors ( $R^2$ ) indicates that better applicability was obtained using linearized Langmuir than Freundlich isotherms and Tempkin isotherms. The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor ( $R_L$ ) given by the

following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

Where  $C_0$  is the initial dye concentration (mg/L).  $R_L$  values within the range  $0 < R_L < 1$

indicate favorable adsorption. In this study  $0.007 < R_L < 0.43$  indicating that on-going adsorption process is favorable for the dye using ceric sulfate as adsorbent.



**Figure 5** .The Langmuirplot for the adsorption of R.B19 on ceric sulfate. Condition: Initial pH<2 ( by H<sub>2</sub>SO<sub>4</sub>), Initial volume of dye = 50 mL, Mixing rate = 200 rpm.

**Table 3.** Equilibrium constants for R.B19 sorbtion by Cerium (IV) sulfate.

	Types of Isotherm		
	Langmuir	Freundlich	Tempkin
parameters	Q <sub>0</sub> :1428.5 b:0.128	K <sub>f</sub> :711.2 n:3.5	A:32.62 RT/b <sub>T</sub> :239.2
R <sup>2</sup>	0.993	0.718	0.727

## Conclusions

We studied the degradation of R.B19 in aqueous solution by ceric sulfate and found it to be an effective and fast way to treat synthetic textile wastewater. The experiments showed that the removal rate of Ce(IV) was affected by initial dye concentration, pH, dose of cerium (IV) sulfate. The adsorption characteristics and dye removal efficiency of adsorbent have been determined by investigating factors such as effect of pH (pH<sub>Optimum</sub> <2), effect of concentration of the dye (up to 1000mg/L), dose of adsorbent(

up to 0.7g/L) and contact time(under 120 sec). Under the optimized conditions, the percentage of color removal efficiency increased up to 97%.

More work is required to determine the mechanism for removal of R.B19 by ceric sulfate. In this study, Ce(IV) solution had a strong ability to remove color, Ce(IV) could forma larger surface area of sediment, which could adsorb and flocculate organic dye. The equilibrium isotherm and kinetic characteristics of reactive dye adsorption on the above mentioned adsorbent were

investigated using bench scale batch tests. The Langmuir adsorption isotherm model was used for the description of the adsorption equilibrium of R.B19 dye onto ceric sulfate. The data were in good agreement with Langmuir isotherm. The data agreed well with the pseudo second order kinetic model.

## References

- [1] N. Gupta, A. K. Kushwaha, M.C. Chattopadhyaya, *Arabian J. Chemistry*, In press, Doi: 10.1016/j.arabjc.2011.07.021, 1-10 (2011).
- [2] S. S. Kalra, S. Mohan, A. Sinha, G. Singh, *Advanced Oxidation Processes for Treatment of Textile and Dye Wastewater: A Review*, 2nd *International Conference on Environmental Science and Development* (2011).
- [3] G. Sreelatha, V. Ageetha, J. Parmar, P. Padmaja, *J. Chem. Eng. Data*, 56, 35 (2011).
- [4] S.Eswaramoorthi, K. Dhanapal, D.S. Chauhan, *Environmental Technology Awareness Series*, 22, 17 (2008).
- [5] J. F. Judkins, J.S. Hornsby, *J. Water Pollut. Control Fed.*, 50, 2446 (1978).
- [6] L. Tan, R.G.Sudak, *J. Am. Water Works Assoc.*, 84, 79 (1992).
- [7] Y.Al-Degs, M. A. M.Kharaisheh, S.J.Alen, M.N. Ahmad, *Water Res.*, 34, 927 (2000).
- [8] T.S. Shaffiqu, J. J. Roy, R. Aswathi, T. E. *Appl. Biochem. Biotechnol.*, 102-103: 315 (2002).
- [9] S.V. Mohan, J. Karthikeyan, *Advances in Wastewater Treatment Technologies*, pp. 272-289. In: Goel, P. K. (ed.) (1999).
- [10] Z.Jianjun, L.Bingwei, Y.Chenxuan, R.Xiangdong, *J. Rare. Earths.*, 28, 37 (2010).
- [11] APHA - AWWA, WPCF, "Standard Methods for the Examination of Water and Wastewater", 21th ed., American Public Health Association, Washington, DC (2005).
- [12] X.Li, Q.Xu, G.Han, W.Zhu, Z.Chen, X.He, X.Tian, *J. Hazard. Mat.*, 165, 469 (2009).
- [13] K. Li, X. Wang, *Bioresour. Technol.*, 10, 2810 (2009).
- [14] Y.S Ho, G. McKay, *Process. Biochem.*, 34, 451 (1999).
- [15] A. Gucek, S. Sener, S. Bilgen, M. A. Mazmanci, *J. Colloid Interf. Sci.*, 286, 53 (2005)
- [16] F.Colak, N.Atar, A.Olgun, *Chem. Eng. J.*, 150, 122 (2009).
- [17] R. Nadeem, M.H. Nasir, M.S. Hanif, *Chem. Eng. J.*, 150, 40 (2009).