Journal of Applied Chemical Research, 8, 1, 7-14 (2014)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

The Color Removal of Dye-Containing Wastewater by Cerium (IV) Sulfate from Aqueous Solutions

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Received 26 Aug. 2013; Final version received 24 Nov. 2013

Abstract

In this study a giant reagent such as Ce $(SO_4)_2$ was used for removing different initial dye concentration (10-1000 mg/l) of reactive red 31 (R.R31) less than two minutes in a laboratory scale whereas the percent of dye removal efficiency was %99.9. The Langmuir, Freundlich and Tempkin adsorption models were applied to describe the equilibrium isotherms. The Langmuir model agreed very well with experimental data ($R^2 > 0.99$). The kinetics of adsorption was evaluated by the pseudo first-order, second-order and intra particle models. The data agreed well with the pseudo first-order kinetic model. These results demonstrated that Ce $(SO_4)_2$ is an efficient reagent for removal of R.R 31 from aqueous solutions.

Key words: *Reactive red 31(R.R31), Cerium (IV) Sulfate, Dye-Containing Wastewater, Langmuir isotherm.*

Introduction

Dye pollutants from textile dye industries are an important source of environment contamination. Majority of colored effluents of various industries comprised of synthetic organic dyes, which are difficult to biodegrade [1-3]. Various man-made methodologies have been Investigated and employed for removal of these dyes from wastewater, for instance: Coagulation, biological treatments, micellar enhanced ultra-filtration, oxidation, ozonation, nano-filtration, ultra-filtration, adsorption onto agricultural solid waste, bentonites, various types of activated carbon or surfactant impregnated montmorillonite [4-6].

Rare earths application in wastewater treatment studies have generally focused on the following three aspects: it plays a catalytic or catalytic assistance in the degradation of organic matter or reducing harmful substances [1]; in adsorption or filtration material to strengthen a supporting role to play; on the

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rare earth compound flocculation agents and so on improved wastewater treatment agents. Unfortunately for a single rare earth has little researched on wastewater treatment [7-8].

At present, rare earths application in wastewater treatment has become more and more widely used, according to the fact that the Ce (IV) has the strong oxidation ability under acid condition. Results showed that oxidation-reduction reaction occurred between Ce (IV) and the organic compounds or other reducing substances in industrial wastewater, thereby the color reduced effectively. Ce (IV) formed [Ce (OH)x•nH$_2$O]$^{(4-x)+}$ after hydrolyzing and Ce (III) obtained after Ce (IV) reduction formed [Ce (OH)x•nH$_2$O]$^{(3-x)+}$, this hydrate had big specific surface area, could absorb the substances and removed toxic or harmful ions in industrial wastewater[8].

In this study, a wide range of R.R31 dye initial concentrations (10- 1000 mg/L) were investigated, whereas other studies worked on initial concentrations up to 100 mg/L. Also in this investigation some operational parameters corresponding to dye removal were optimized (Table1) and also equilibrium isotherms and kinetic study were investigated.

Experimental

Materials

Reagent grade of Cerium (IV) sulfate (99%) obtained from Sigma-Aldrich, Germany, used as adsorbent. Reactive Red 31 ($C_{30}H_{15}Cl N_7Na_5O_{15}S_4$, MW: 992.14), Purchased from Alvan-rang Company, Iran. It was used as received without further purification. The structure of the dye is presented in Figure 1. A stock solution of reactive red (1000 mg /L) was prepared and suitably diluted to the required initial concentration.

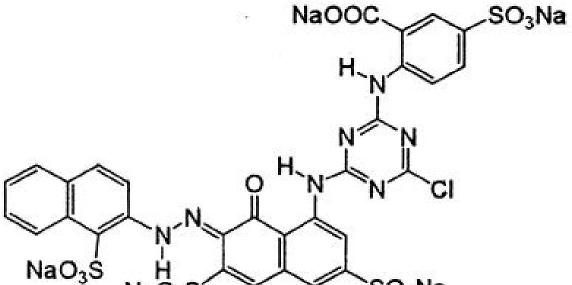

Figure 1. Structure of dye, reactive red31, (R.R31).

Method

A calibration curve of absorbance versus concentration was constructed using a UV spectrophotometer (Hach, Lange Model: DR-2800) at maximum wavelength of 522 nm. All chemicals were of analytical reagent grade. All measurements are based on methods from standard method [9].

Batch studies

A certain volume of synthetic aqueous dye solution was taken and adjusted to appropriate pH with sulfuric acid and sodium hydroxide solution, added a certain amount of cerium (IV) sulfate solution (up to 3.0 g/L). Experiments were carried out at room temperature (25°C). In each batch experiment 50 ml of R.R31 solution of known initial concentration (10-1000 mg/ L) was shaken at the constant agitation speed (200 rpm) with a required dose of cerium (IV) sulfate solution. After equilibrium, the final concentration or residual dye concentration was measured. The percentage removal of dye was calculated using the following relationship:

$$\%\text{Removal of dye}=\left(\frac{C_i-C_e}{C_i}\right)\times 100 \qquad (1)$$

where C_i and C_e are the initial and final (equilibrium) concentrations of dye (mg /L), respectively.

Results and discussion

Effect of important operating parameters:

In this study, the removal of R.R31 process was controlled by several operational parameters such as, reaction time, initial pH, initial dye concentration and dose of cerium (IV) sulfate. In order to enhance the process performances, the influences of these parameters were studied as follows (Table1).

Effect of pH

It has been established that the influent pH is an important parameter influencing the performance of the dye removal process. To examine its effect, the dye solution was adjusted to the desired pH for each experiment by adding sodium hydroxide or sulfuric acid solution. In all experiments, the results revealed that when pH of the dye solutions was under 2 there was maximum color removal efficiency.

Table 1. Properties of initial synthetic dye wastewater based on optimum operating conditions for removal of R.R31 by Ce $(SO_4)_2$. Conditions: pH<2, Volume of wastewater: 50 ml.

Initial dye concentration (mg/L)	Dose of Ce $(SO_4)_2$ (g/L)	Reaction time (Sec)	%Removal of dye(R.R31)
10	0.16	18	99.90
50	0.28	25	99.90
100	0.58	30	99.90
200	0.86	45	99.80
300	0.98	55	99.70
500	1.06	65	98.60
1000	1.30	75	97.00

Adsorption isotherms

In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations for the equilibrium data for each system. Three isotherm models of Langmuir, Freundlich and Tempkin were tested in the present study. The applicability of the isotherm equations is compared by judging the correlation coefficient, R^2. In the present study the results show that Langmuir theory can represent experimental data, the values of R^2 are observed to be in the range of 0.99 (Figure 2 and Table 2).

Langmuir model

The Langmuir adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution concentration. It suggests that when the sorbet occupies a site further sorption cannot take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighboring sites. The amount of solute adsorbed, C_e/q_e, is related to the equilibrium concentration of solute in solution, C_e, as follows [10]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (2)$$

Where Q_0 shows the monolayer sorption capacity (mg/g), b is the Langmuir constant (L/mg), C_e is equilibrium dye concentration in the solution (mg/L) and q_e represents amount of dye sorbed onto sorbent at equilibrium (mg/g). The plot of C_e/q_e versus C_e was employed to generate the intercept value of $1/(bQ_0)$ and slope of $1/Q_0$ (Figure 2). One of the essential characteristics of the Langmuir model can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter, R_L, defined as:

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

where C_o is the initial concentration of dye (mg/L). The value of RL indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The RL value in this study was found as 0.04 indicating that this sorption process is favorable, in this study R_L=0.057.

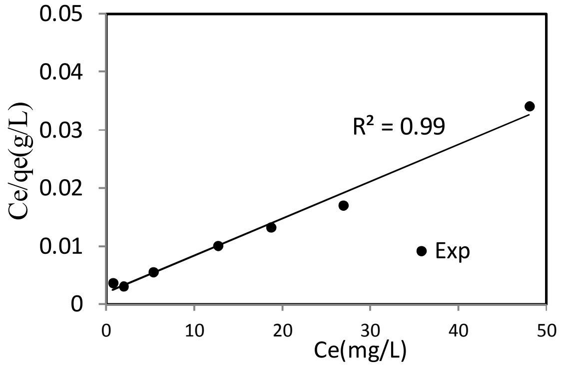

Figure 2. Langmuir isotherm for adsorption of R.R31 dye at PH<2 by $Ce(SO_4)_2$.

The Freundlich isotherm equation is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energies of adsorption and is given by the relation [11]:

$$q_e = K_f {C_e}^{1/n} \qquad (4)$$

Or in linear form is expressed as:

$$\log q_e = logK_f + \frac{1}{n} logC_e \qquad (5)$$

Where q_e is the amount of adsorbed per unit mass of the adsorbent(mg/g), C_e is the equilibrium concentration and 1/n and K_f are Freundlich constants.

These parameters give a measure of adsorbing capacity of the adsorbent and intensity of adsorption, respectively. Results are shown in Table 2, R^2=0.85, and the Langmuir isotherm was fitted better than the Freundlich and Tempkin isotherms.

Tempkin model

The Tempkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage of the adsorbate molecules over adsorbent surface [12]. The linear form of this isotherm can be given by:

$$q_e = \frac{RT}{b_T} \ln A_T C_e \qquad (6)$$

$$q_e = \frac{RT}{b_T} lnA_T + \frac{RT}{b_T} \ln C_e \qquad (7)$$

where A_T (L/g) and bT (J/mol) are the Tempkin constants. R: gas constant, T absolute temperature. A_T and b_T constants were determined from the slope and intercepts of the plots obtained by plotting qe versus lnCe (Table 2). Based on the linear regression correlation coefficient, R^2, the equilibrium data could be near interpreted by the Tempkin model, R^2=0.944.

Table 2. Adsorption equilibrium isotherm models parameters and statistical indices values of R.R31 by $Ce(SO_4)_2$ reagent.

Type of Isotherm	parameter	Value
Langmuir	R^2	0.997
	R_L	0.057
	Q_0	81.94
	b	0.279
Freundlich	R^2	0.851
	K_f	26.65
	1/n	0.2964
Tempkin	R^2	0.944
	A	1.281
	RT/b_T	3.364

Kinetic study

Adsorption kinetics is an important parameter for designing adsorption systems and is required for selecting optimum operating conditions for batch adsorption study. To investigate the adsorption kinetics of removing of R.R31 by cerium (IV)sulfate reagent, three different kinetics models, pseudo first-order, pseudo second-order rate models and intra-particle diffusion models, were used in this study [13].

The linear form of the pseudo first-order rate equation is given as:

$$ln(q_e - q_t) = lnq_e - K_1 t \qquad (8)$$

where, q_e is the amount of adsorbed dye at equilibrium (mg/g), q_t in(mg/g) is the amount of dye adsorbed at time t, min, and K1, is the rate constant of first-order sorption (1/min). A linear plot of log (q_e-q_t) against time (t) allows obtaining the rate constants. The rate constants for the pseudo first order model are calculated from the slopes and intercepts of the plots of Eq. 8. The results have shown that the experimental data do agree with the pseudo first-order rate equation. In Figure 3 the curve-fitting plot of the first order rate is illustrated (Figure 3 and Table 3).

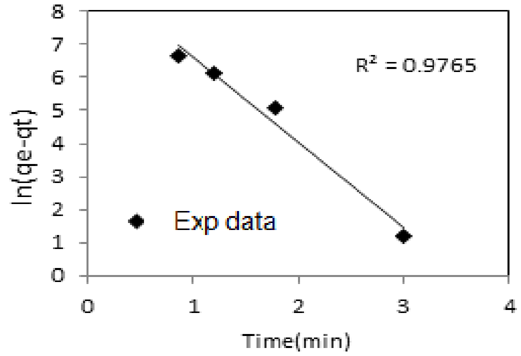

Figure 3. The pseudo first-order rate equation plot for removal of R.R31 by Ce $(SO_4)_2$ reagent.

The pseudosecond-order kinetic model is expressed as [14]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} (9)$$

where K_2 (g/(mg. min) is the rate constant of pseudo second-order adsorption. The slopes and intercepts of plots of t/q vs. t were used to calculate the second-order rate constant K_2 and qe. It is more likely to predict the behavior over the whole range of adsorption and is in agreement with the chemisorption mechanism being the rate-controlling step. The results show that the pseudo first-order (R^2= 0.976) was fitted better than the pseudo second-order (R^2=0.9) and intra-particle diffusion models (R^2=0.89).

The intra-particle diffusion equation is given as[15]:

$$q_t = K_d t^{0.5} + C \qquad (10)$$

Where q_t , is the amount dye adsorbed(mg/g) at time t, C is the intercept K_d, the intra-particle diffusion rate constant (mg/g $min^{0.5}$) can be obtained from the slope of the q_t versus $t^{0.5}$ plot. The parameters obtained for the three models are presented in Table 3.Good correlation coefficients were obtained by fitting the experimental data to Eq8, indicating that the adsorption process on the $Ce(SO_4)_2$ is pseudo first-order as shown in Figure 3.

Conclusion

In this research, the optimum operating conditions in solutions containing initial dye(R.R31) concentrations within (10-1000) mg/L were obtained to achieve a higher removal capacity(99.9-97%) by a giantrare earth reagent named Ce $(SO_4)_2$. The best optimized conditions were proposed are as follows: Optimized dose of Ce (SO4)2:0.16-1.3(g/L), Operating time: 18–75 sec, pH optimum<2.

In this work, Kinetic and equilibrium isotherms on degradation of Reactive Red 31 from aqueous solutions by cerium (IV) sulfate were studied.

Three isotherm models have been tested in the present study; Langmuir, Freundlich and Tempkin models. The applicability of the isotherm equations is compared by judging the correlation coefficient, R^2. The Langmuir model agreed very well with experimental data ($R^2 > 0.997$).

To investigate the adsorption kinetics of removing of RR31 by cerium (IV)sulfate reagent, three different kinetics models, pseudo first-order, pseudo second-order and intra-particle diffusion, were used in this study. The data agreed well with the pseudo first-order kinetic model. These results demonstrated that Ce $(SO_4)_2$ as a giant reagent is efficient for fast removal of R.R 31 from aqueous solution.

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