CHEMICAL ENGINEERING TRANSACTIONS

VOL. 62, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Fei Song, Haibo Wang, Fang He

**ISBN** 978-88-95608- 60-0; **ISSN** 2283-9216

DOI: 10.3303/CET1762005

# Analysis of Congo Red Adsorption Capability of the Mn-Modified Diatomite

Yunhong Zhong

Department of Alcohol and Food Engineering, Sichuan Technology and Business College, Dujiangyan 611830, China
yunhongzhong321@126.com

Nowadays the dyeing wastewater has brought about increasingly serious environmental issues, and the methods of wastewater treatment both at home and abroad mainly include the adsorption, the flocculant, photocatalytic degradation, ultrafiltration and electrochemical methods, etc. Among them, the adsorption method has been widely applied to treatment of the dyeing wastewater due to its advantages such as simple operation, low cost and no secondary pollution, etc. The diatomite, with a relatively large surface area and strong adsorption capacity, is an excellent natural environmental adsorbent with negative charge on its surface when in solution. But it needs further modified so as to strengthen its limited adsorption capacity. This paper, using the diatomite as the raw material, studies the characteristics of the Mn-modified diatomite which has been prepared with the oxidation method after precipitation and the results show that the Mn-modified diatomite is covered with Mn oxide particles. It has found the optimal adsorption condition by studying Congo red adsorption of the Mn-modified diatomite mainly with static adsorption experiment. Moreover, it studies the impact of the adsorbent quantity, solution pH value, dye concentration as well as temperature on the adsorption effect and explores the kinetic behavior in which the Mn-modified diatomite adsorbs Congo red. The study shows that Mn-modified diatomite owns excellent removal effect to Congo red. And through kinetics analysis of the adsorption process, it has been found that Congo red adsorption of the Mn-modified diatomite conforms to the Langmuir isotherm, Freundlich linear model and pseudo-second-order kinetic equation.

## 1. Introduction

There're various organic matters in the industrial wastewater that are difficult to treat and tend to accumulate in the environment (Omahony et al., 2002), thus threatening the health of various creatures and human (Aksu and Tezer, 2000). Among it the dyeing wastewater emitted by the chemical companies occupies a relatively high percentage in the industrial mixed wastewater, and the diimide dyeing wastewater has been regarded by the researchers as a kind of organic wastewater harder to treat compared with most other dyeing wastewater (Yermiyahu et al., 2002). To strengthen the dyeing wastewater treatment is of important significance to alleviate the problem of critical water shortage (Bhatnagar et al., 2005), protect the environment, maintain ecological balance & human health (Chen and Zhao, 2009), and achieve the strategical goal of sustainable development. Therefore, it is of realistic significance to select Congo red, representative of the diimide dye, as the study object.

Currently the wastewater treatment include mainly the adsorption, floccutant, ultrafiltration, photocatalytic and electrochemical methods (Chakrabarti et al., 2009; Yang, 2017; Wu and Fan, 2017; Tian et al., 2017), among which the adsorption method has been widely applied to the dyeing wastewater treatment due to its advantages such as high efficiency & speed, easy adaptation and operation, etc.. And the new wastewater treatment technology developed in recent years - the modified filtering material filtration technology - has displayed better adsorption capacity than normal one in that it can adsorb heavy-metal ions, toxic cations & anions, total organic carbon, bacteria, and virus in the wastewater, thus owning wider prospect in wastewater treatment (Senthil, 2010).

As both the diatomite and Mn oxide own similar channel structure, large specific surface area (Samiey and Dargahi, 2010), good adsorption and ion exchange capability(Mazeau and Wyszomirski, 2012), loading the Mn oxide onto the surface of the diatomite with chemical method can give full play to the advantages of both,

Please cite this article as: Yunhong Zhong, 2017, Analysis of congo red adsorption capability of the mn-modified diatomite, Chemical Engineering Transactions, 62, 25-30 DOI:10.3303/CET1762005

thus improving their dyeing wastewater treatment capability. Therefore, by preparing the Mn-modified diatomite with the method of oxidation-reduction using the diatomite as the carrier (Majeda and Khraisheh, 2004), this paper focuses on analysis of the optimal conditions and influencing factors during Congo red adsorption at the same time of exploring its adsorption mechanism, thus providing scientific basis for the development and usage of effective, reasonable, cheap and appropriate adsorption materials.

## 2. Experiment

### 2.1 Test Reagent and Equipment

Test reagent: Hydrochloric acid, sodium hydroxide, Congo red
According to the references, load Mn oxide onto the surface of the diatomite to prepare Mn-modified diatomite as the adsorbent in the experiment.
Test Equipment: 752 UV spectrophotometer; TB-215D electronic balance; 800 electronic centrifuge; JSM-6510LV model scanning electronic microscope; Nicolet-6700 insitu infrared spectrometer; 868 model pH meter; ZHWY-100C incubator shaker, etc..

### 2.2 Test Method

1) Determinate Congo red (Attallah et al., 2013)concentration by testing the absorbance of its solution; Prepare standard Congo red solution of various concentrations; At 498 nm, determinate the solution concentration using the distilled water as blank solution, and through linear regression obtain the standard curvilinear equation: $y=0.032x+0.001$, $R^2=0.999$.
This paper mainly studies Congo red adsorption of the Mn-modified diatomite with static adsorption experiment.

## 3. Results Exploration

### 3.1 Surface Features of the Mn-Modified Diatomite Adsorbent

*Table 1: Percentage of elements in the Mn-modified diatomite*

| Element | O | Na | Mg | Al | Si | K | Mn | Fe | Total |
|---|---|---|---|---|---|---|---|---|---|
| Mass percent | 64.31 | 3.95 | 0.61 | 1.99 | 26.57 | 0.13 | 1.77 | 0.67 | 100.00 |
| Atomic percent | 76.07 | 3.25 | 0.48 | 1.40 | 17.90 | 0.06 | 0.61 | 0.23 | |

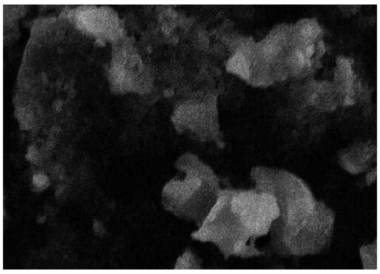

*Figure 1: SEM of the Mn-modified diatomite*

From Table 1 and Figure 1 it can be known that Mn was already loaded onto the diatomite surface covered after modification with Mn oxide particles, which, forming many micropores with the diatomite, widened the surface area and facilitated the improvement of adsorption capacity, which is the foundation of excellent adsorption effect.
According to the infrared spectrum of the Mn-modified diatomite during the test as shown in Figure 2, at 1629 cm-1 and 3436 cm-1 lie respectively the spectral band of the H-O-H bending vibration and -OH asymmetrical stretching vibration of the adsorbed water; At 1091 cm-1 lies the skeleton vibration absorption peak of the Si-O bond; at 474 cm-1, 619 cm-1, and 793 cm-1 there're absorption spectral band for the asymmetrical bending vibration of the Si-O-Si bond inside the silicon-oxygen tetrahedron, and among them the absorption peak at 474 cm-1 indicates the presence of amorphous SiO2, the major content of the diatomite. The additional 2922 cm-1 absorption peak on the spectrum is that of bending vibration after the diatomite was covered by Mn oxide, indicating the presence of the bonded interactions between the Mn oxide and the diatomite.

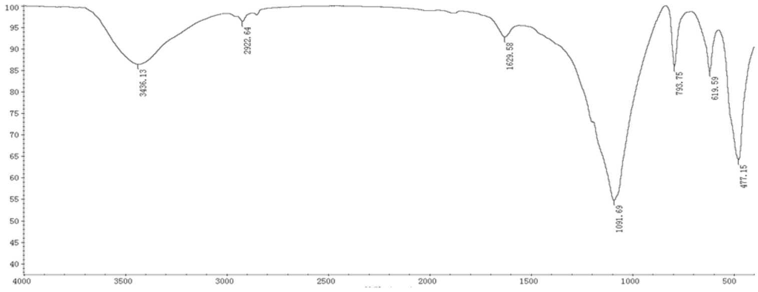


*Figure 2: Infrared spectrum of the Mn-modified diatomite*

### 3.2 Study on Congo Red Adsorption Performance of the Mn-Modified Diatomite

According to the impact of the adsorbent quantity on the adsorption effect as shown in Figure 3, when the adsorbent quantity increased from 1g/L to 9g/L, Congo red unit adsorption quantity decreased from 16.13 mg/g to 5.34 mg/g while its removal rate increased from 33.16% to 96.2%, indicating that Congo red unit adsorption quantity decreases with the increasing of the adsorbent quantity while the removal rate increases with it. Therefore, considering the treatment cost, 4g/L should be taken as the optimal test usage of the Mn-modified diatomite.

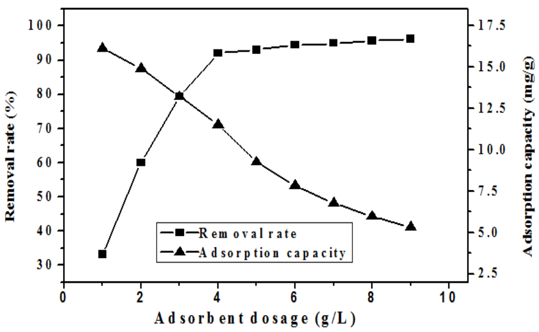


*Figure 3: Impact of the Mn-modified diatomite quantity on the adsorption effect*

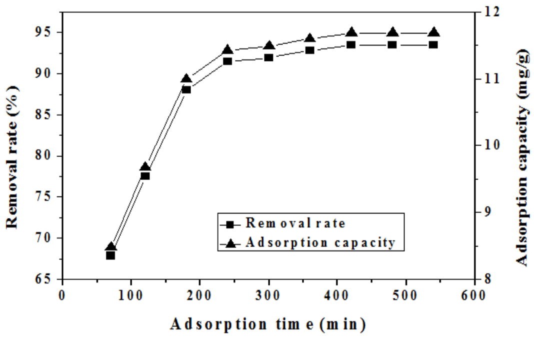


*Figure 4: Impact of the adsorption time on the adsorption effect*

Concerned with impact of the adsorption time on the adsorption effect, as shown in Figure 4, during the primary 180 min, the Mn-modified diatomite can rapidly adsorb Congo red dye with an removal rate of over 85%; Afterwards the adsorption rate decreased obviously and the adsorption capacity increased gradually; Then it went through the slow adsorption phase and reached the final dynamical adsorption equilibrium. The adsorption reached basic equilibrium after around 7h (420 min) when the removal rate reached 93.5% and the unit adsorption quantity reached 11.69mg/g. So in future adsorption experiment, 8h (480 min) should be taken as the time of adsorption equilibrium.

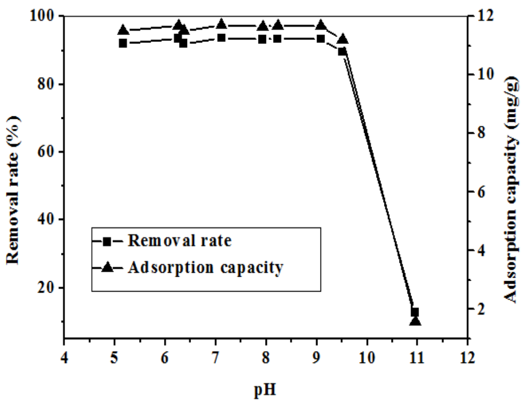


*Figure 5: Impact of the initial solution pH value on the adsorption effect*

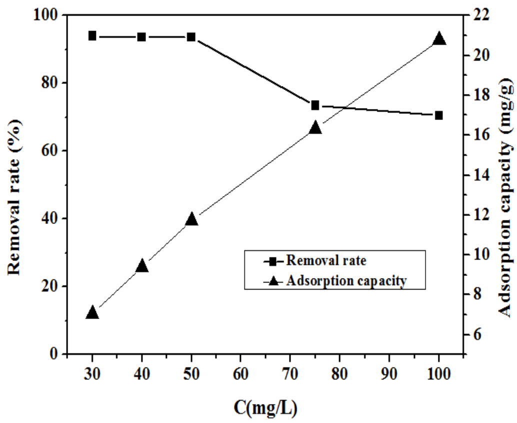


*Figure 6: Impact from the initial mass concentration of Congo red on the adsorption effect*

As for the impact of the initial solution pH value on the removal rate, as shown in Figure 5, when the pH value fell between 5-10, the Mn-modified diatomite showed good adsorption effect to Congo red. Therefore, the Mn-modified diatomite is applicable to treating industrial dyeing wastewater of various acidity. In the test the pH value, being adjustable, was 6.36 at that time.
In terms of the impact from the initial concentration of dye on the adsorption effect, as shown in Figure 6, with the increasing of the initial concentration $c_0$, Congo red removal rate of the Mn-modified diatomite decreased while the unit adsorption capacity increased, indicating that the initial concentration of Congo red solution imposed significant influence during adsorption. Through comprehensive consideration, 50mg/L should be selected as the initial concentration of Congo red solution.

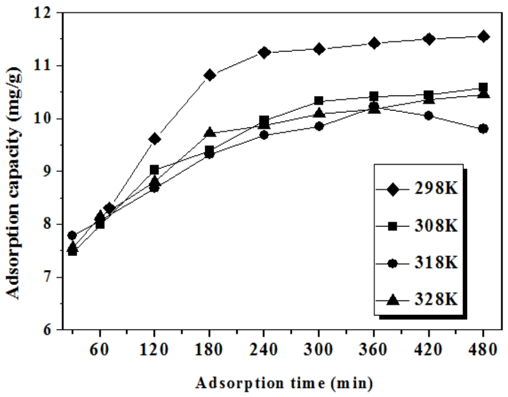


*Figure 7: Impact of the temperature on the adsorption effect*

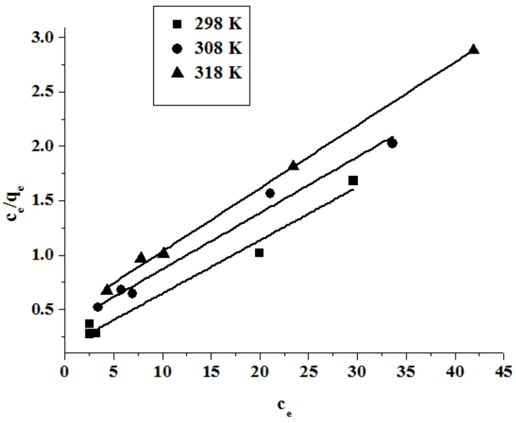


*Figure 8: Langmuir Adsorption Isotherm of the Mn-modified diatomite*

As for the effect of the solution temperature on the adsorption effect, as shown in Figure 7, with the increasing of the reaction temperature, Congo red adsorption capacity of the Mn-modified diatomite decreased and at 298K the unit adsorption quantity was higher than at other temperatures. This indicates on one hand that the adsorption is a process of heat release when the rising temperature will suppress the adsorption and on the other hand that at high temperature, the desorption rate is higher than the adsorption rate. Therefore, the adsorption temperature should be set at 298K in the experiment.

### 3.3 Primary Probe into Congo Red Static Adsorption Mechanism of the Mn-Modified Diatomite

Based on Figure 8, it can be calculated that the maximum adsorption capacity of the Mn-modified diatomite was 20.42mg/g at 298K, 19.35mg/g at 308K, and 17.23 mg/g at 318K, i.e. with the increasing of the temperature, the saturated adsorption capacity decreased, indicating that high temperature does no good to dye adsorption of the Mn-modified diatomite; Through calculation, the $R_L$ fell between 0-1 at different temperatures, indicating easy Congo red adsorption of the Mn-modified diatomite; And $R^2$ fell between 0.9759-0.9976, showing adsorption of the Mn-modified diatomite conforms to the Langmuir adsorption isotherm.

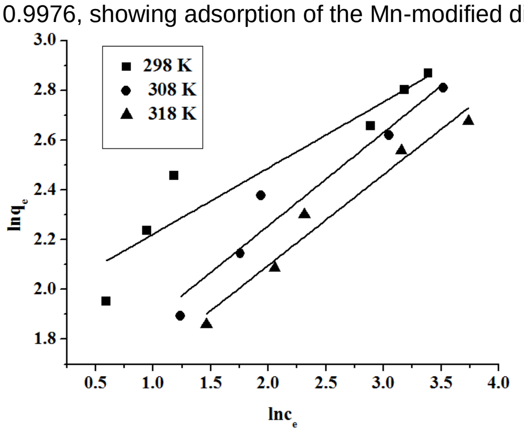


*Figure 9: Freundlich adsorption isotherm of the modified diatomite*

*Table 2: Langmuir and Freundlich isothermal parameters of the modified diatomite*

| T | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| (K) | b(Lmg$^{-1}$) | $q_e$(exp)(mg/g) | $R^2$ | $K_F$ | n | $R^2$ |
| 298 | 0.318 | 20.42 | 0.9759 | 7.079 | 3.766 | 0.8655 |
| 308 | 0.146 | 19.35 | 0.9820 | 4.515 | 2.669 | 0.9292 |
| 318 | 0.128 | 17.23 | 0.9976 | 3.931 | 2.743 | 0.9549 |

From the Freundlich isotherm in Figure 9 and Table 2 it can be known that at temperatures of 298K, 308K and 318K the $K_F$ value of the diatomite fell above 3 and $R^2$ fell between 0.8655-0.9549, conforming to the Freundlich adsorption isotherm.

### 3.4 Analysis of the Adsorption Kinetics Mode

From Figure 10 and Table 2-3 it can be known that with the increasing of temperature, the saturated adsorption capacity of the modified diatomite decreased that was obtained through fitting of the pseudo-first-order kinetics model, indicating that high temperature is adverse to the dye adsorption of the modified diatomite.

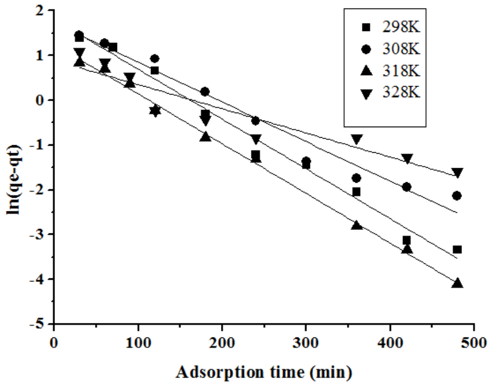


*Figure 10: Linear fitting of the pseudo-first-order equation (modified diatomite)*

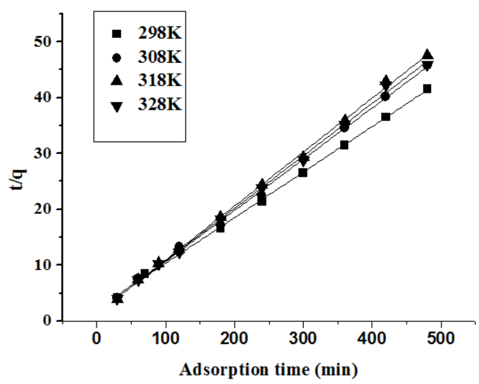


*Figure 11: Linear fitting of the pseudo-second-order equation (modified diatomite)*

*Table 3: Adsorption kinetic parameters of the modified diatomite at various temperatures*

| $C_0$(50mg/L) | $q_e$(exp) | Level 1 dynamic model | | | Level 2 dynamic model | | |
|---|---|---|---|---|---|---|---|
| T(k) | (mg/g) | $k_1$(min$^{-1}$) | $q_e$(mg/g) | $R^2$ | $k_2$(g.mg$^{-1}$.min$^{-1}$) | $q_e$ (mg/g) | $R^2$ |
| 298 | 11.55 | 0.0111 | 6.09 | 0.9848 | 0.00307 | 12.25 | 0.9991 |
| 308 | 10.59 | 0.00886 | 5.65 | 0.9643 | 0.00577 | 10.90 | 0.9982 |
| 318 | 10.11 | 0.0111 | 3.50 | 0.9965 | 0.00735 | 10.35 | 0.9987 |
| 328 | 10.52 | 0.00539 | 2.43 | 0.8676 | 0.00654 | 10.63 | 0.9982 |

Note: $q_e$(exp) is the adsorption capacity obtained from test and $q_e$ is that obtained through simulated fitting

From Figure 11 and Table 3 it can be known that Congo red adsorption effect of the modified diatomite was improved a lot. And the maximum adsorption capacity of the modified diatomite obtained through fitting of the pseudo-second-order kinetics model was more close to the equilibrium adsorption capacity obtained in the test, indicating the pseudo-second-order kinetics model owns higher goodness of fit than the pseudo-first-order one.

## 4. Conclusions

This paper studies the surface features of the Mn-modified diatomite which was prepared with oxidation after precipitation and analyzes Congo red static adsorption of the modified diatomite, then explores the adsorption mechanism. The results show that the prepared modified diatomite owns good adsorption effect and contains low Mn, thus reducing the cost. The research result is expected to be applied to pollution prevention and treatment of the dye wastewater. Below conclusions can be reached in this paper:

1)The adsorption effect is influenced to a certain extent by the input amount, adsorption time, solution pH value, initial concentration, and reaction temperature of the Mn-modified diatomite. With little impact from the solution pH value, the adsorption capacity of the diatomite has been greatly increased after modification and reaches the expected experiment effect, showing that the Mn-modified diatomite can be applied to treating dyeing wastewater of various acidity.

1) Congo red adsorption of the Mn-modified diatomite conforms to the Langmuir and Freundlich adsorption isotherm. With the increasing of the temperature, Congo red adsorption capacity of the modified diatomite decreased, indicating Congo red adsorption of the modified diatomite is exothermal reaction.
2) Through data fitting of the adsorption process, it has been found that Congo red adsorption of the modified diatomite more conforms to the pseudo-second-order kinetics model. And the adsorption rate control is realized through intra-particle diffusion, which is not the only way to control the rate.

## Reference


Aksu Z., Tezer S., 2000, Equilibrium and kinetic modeling of biosorption of Remazol Black B by Rhizopus arrhizus in a batch system: effect of temperature, Process Biochemistry, 36, 431-439.

Attallah M.F., Ahmed I.M., Hamed M.M., 2013, Treatment of industrial wastewater containing Congo Red and Naphthol Green B using low-cost adsorbent, Environ Sci Pollut Res. 20, 1106-1116.

Bhatnagar A., Jain A.K., Mukul M.K., 2005, Removal of congo red dye from water using carbon slurry waste, Environ Chem Lett. 2, 199-202.

Chakrabarti S., Dutta B. K., Apak R., 2009, Active manganese oxide: a novel adsorbent for treatment of wastewater containing azo dye, Water Science & Technology WST, 60, 3017-3024.

Chen H., Zhao J., 2009, Adsorption study for removal of Congo red anionic dye using organo-attapulgite, Adsorption. 15, 381–389.

Majeda A.M., Khraisheh R., 2004, Emediation of wastewater containing heavy metals using raw and modified diatomite, Chemical Engineering Journal. 99, 177-184

Mazeau K., Wyszomirski M., 2012, Modelling of Congo red adsorption on the hydrophobic surface of cellulose using molecular dynamics, Cellulose. 19, 1495-1506.

Omahony T, Guibal E, Tobin J.M. 2002, Reactive dye biosorption by Rhizopus arrhizus biomass, Enzyme and Microbial Technology. 31, 456-463.

Samiey B., Dargahi M.R., 2010, Kinetics and thermodynamics of adsorption of Congo red on cellulose, Cent. Eur. J. Chem. 8, 906-912.

Senthil Kumar P., 2010, Removal of Congo Red from Aqueous Solutions by Neem Saw Dust Carbon, Colloid Journal. 7,703–709.

Tian W., Cui Z., Qin H., Li L., 2017, Conceptual design of the Eastman organic wastewater treatment process, Chemical Engineering Transactions, 61, 109-114, DOI: 10.3303/CET1761016

Wu S.F., Fan J.H., 2017, Study on the environmental effects of electronic information industry in Anhui province based on metering model of industrial waste gas, wastewater and waste, Chemical Engineering Transactions, 59, 1159-1164, DOI: 10.3303/CET1759194

Yang Z.M., 2017, Pharmaceutical wastewater treatment based on mathematical model, Chemical Engineering Transactions, 59, 925-930, DOI: 10.3303/CET1759155

Yermiyahu Z., Lapides I., Yariv S., 2002, Thermo-XRD analysis of the adsorption of Congo-red by montmorillonite saturated with different cations, Journal of Thermal Analysis and Calorimetry. 69, 317–332.