

## Kinetic studies of Congo Red adsorption onto modified Bentonite

\*Mohan Rao. T<sup>1</sup>, Prof. V VBasava Rao<sup>2</sup>

1\* Associate Prof, Dept. of Chemical Engg, Bapatla Engineering College, Bapatla, Andhrapradesh, India

2 Faculty Dean, Osmania University college of Technology, Hyderabad, India

\*Corresponding author: Email: mohanrtam@gmail.com

### ABSTRACT

Congo Red (CR) dye is a major pollutant and an Eco toxic hazard. It has an adverse effect on aquatic flora and fauna. Clay materials are cost effective & efficient adsorbents to remove pollutants from waste water. Surface modification leads to better performance of adsorbent with improved characteristics. The surface can be modified with various treatments to perform better compared with improved characteristics. In this study it was treated with acid and is called as modified bentonite (MB). This MB is used to remove CR from waste effluent and its kinetics were examined. The experimental data was tested for pseudo first order, Pseudo second order, Elovich, intra particle & film diffusion models. Pseudo second order kinetics better represented the model with highest regression coefficient and the results simulated by this model matched well with that of the experimental values. The mass transfer mechanism was controlled by both film and intraparticle diffusions.

**Keywords:** Congo red, Bentonite, adsorption, kinetics.

### INTRODUCTION

Clay materials are highly significant as adsorbents to remove variety of pollutants from waste water. They have the advantages of high specific surface area and high chemical and mechanical stability with low cost and abundant in availability (Emrah Bulut, 2008). Among these, bentonite is considered to be superior with highest specific surface area & cation exchange capacity (Ari Rahman T U, 2013). The physicochemical properties of bentonite can be altered by various physical & chemical treatments. Acid activated bentonite have many advantages and diverse applications. Enhanced pore structure, surface area, surface acidity and decolorizing power make it the best adsorbent to remove pollutants from waste effluent (Samira Bendou, 2014).

Textile is one of the major industry where reactive dyes are extensively used in dyeing process due to their high reactivity and good resilience (Samira Bendou, 2014). A large amount of water is used in textile industries both for processing & cleaning. Dye residues, usually contain azo-groups which are carcinogenic, enter into waste water causing environmental damage. Anionic dyes are most problematic and usually less adsorptive compared to others (Vipasiri Vimonses et al., 2009). Congo red is the first azo dye produced and is used in many industries like textile, paper, plastic etc. It forms carcinogenic amines in water bodies and also disturbs aqueous eco system. Due to these harmful effects, CR is to be treated before it enters into water bodies (A. Safazcan, 2004).

In this work raw bentonite was modified by interacting with Acid solution to synthesize a new adsorbent (Modified Bentonite) to remove Congo red dye from aqueous solution. The objective of the present study was to investigate kinetics of the adsorption process and mechanism of Congo red removal onto modified Bentonite.

### MATERIALS AND METHODS

Congo red (CR) dye, analytical grade ( $C_{32}H_{22}N_6O_6S_2Na_2$ ; molecular weight 696.68) was obtained Merck (Mumbai, India) and used without further purification. All solutions were prepared in double distilled water.

The Bentonite was activated by adding concentrated  $H_2SO_4$  (1:1 w/v) with constant stirring. The material was kept in a hot air oven at  $110^\circ C$  for 12 hours. This material was washed with distilled water and was soaked in 2%  $NaHCO_3$  solution overnight to remove the residual acid. Then the material was washed with distilled-water, until the pH of the adsorbent reached slightly above 7. Finally, it was dried in a hot air oven at  $110^\circ C$  for 4 hours. The particle size was determined by sieving the dried material and it is  $125\mu m$ . The sieved adsorbent was stored in an airtight container for further experiment.

Batch studies were carried out by preparing a stock solution of the dye with a concentration of  $1000\text{ mg L}^{-1}$  with Millipore water and is diluted to a concentration of  $100\text{ mg/L}$ . 0.1g of Adsorbent was measured accurately with an analytical balance (SHIMADZU –AX200) and added to 50ml of feed solution and agitated with Remi make Temperature Controlled Orbital Shaker (REMI – CIS 24 BL). At the end, the samples were collected and centrifuged to remove the suspended

solid particles using REMI C 24 centrifuge. The clear liquid was collected and analyzed with UV – Visible Spectrophotometer (SYSTRONICS-117) at a wavelength of 498nm.

## RESULTS AND DISCUSSION

**Adsorption Kinetics:** Kinetic analysis is important to determine solute uptake rate which determines the residence time required for the completion of the process. The rate of removal and its efficiency depends on the kinetic characteristics of the process (Y.S. Ho, 2000). Several mathematical models have been proposed in the literature to describe adsorption data. They are classified as adsorption reaction models and adsorption diffusion models which are quite different in nature. Both models are applied to describe the kinetics of adsorption Process. (Qiu et al.2009).

### Adsorption Reaction Models:

**Pseudo First Order Rate equation:** The Lagergren pseudo-first-order rate expression is the foremost model used to describe the kinetics of adsorption process based on solid capacity is generally expressed as (S. Lagergren et al., 1898):

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \quad (1)$$

Where,  $q_e$  and  $q_t$  are the amounts of solute adsorbed at equilibrium and at time  $t$  (min), respectively.  $k_1$  is the rate constant ( $\text{min}^{-1}$ ).

After integration and applying boundary conditions at  $q_t=0$  at  $t=0$   $q_t=q_t$  at  $t=t$ , eq. 1 yields the linear form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

The values of  $k_1$  &  $q_e$  are determined from the slope and intercept of the plot  $\ln(q_e - q_t)$  versus  $t$ . These values along with the correlation coefficients,  $R^2$  are given in Table 1. Significant difference is observed between calculated and experimental equilibrium uptake values and relatively small values of correlation coefficients (Table 1), at different temperatures conclude adsorption of CR on to modified bentonite is not a first-order process.

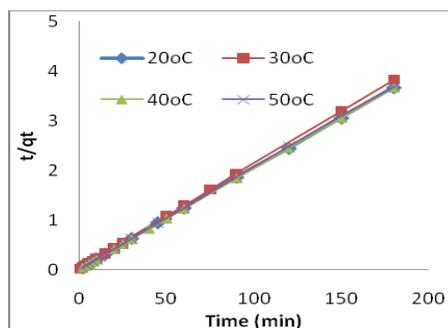
**Pseudo Second Order Rate equation:** Pseudo-second-order kinetic model is widely used to describe the adsorption kinetics which is proposed by Ho and McKay (Y.S. Ho et al., 1999) has the following form:

$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \quad (3)$$

where,  $k_2$  is the rate constant for pseudo-second-order reaction ( $\text{g min}^{-1}$ ). Integrated form of the above equation under the same boundary conditions applied similar to that of first order kinetics is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_{2e}} \quad (4)$$

Experimental data was fitted to the above form (Fig. 1) and the rate constant, equilibrium uptake and correlation coefficients were calculated and presented in the table 1. The calculated uptake values are in correspondence with experimental values and correlation coefficients are almost equal to 1 implies that the adsorption system obeys the pseudo-second-order kinetic model perfectly.



**Fig.1, Pseudo-second-order kinetic model for the adsorption of Congo red on modified Bentonite.**

**Elovich's Equation:** The Elovich kinetic equation is mainly applicable to chemisorptions kinetics. The equation is often valid for heterogeneous surface of adsorption. It is generally expressed as:

$$dq/dt = \alpha e^{-\beta q_t} \tag{5}$$

Integrating the equation for the same boundary condition gives,

$$q_t = 1/\beta(\ln(\alpha \beta)) + 1/\beta \ln t \tag{6}$$

where,  $\alpha$ : the initial adsorption rate (mg/g min),  $\beta$  related with extent of the surface coverage and the activation energy of the chemisorptions(g/mg) where the model is applicable. A plot of  $q_t$  vs  $\ln t$  should give a linear relationship with the slope of  $1/\beta$  and an intercept as  $(1/\beta \ln(\alpha \beta))$ .

The Elovich plots were generated with experimental data (Fig. 2) and the results were presented in table 1. The model is considered to be adequate and satisfactory with regression coefficient values (0.918-0.947) to explain adsorption phenomenon.

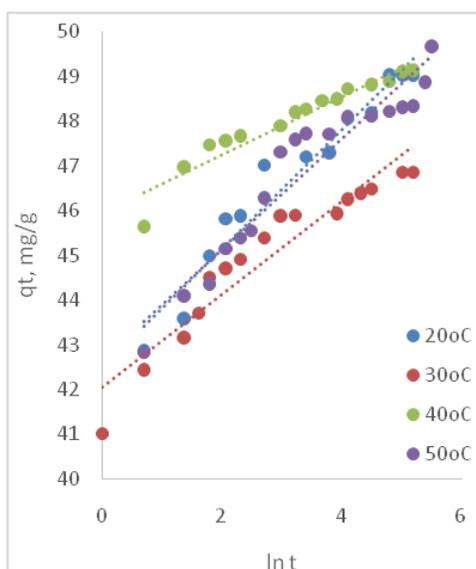


Fig.2.Elovich model for the adsorption of Congo red using modified Bentonite

Table.1.Comparison of reaction kinetic model parameters

Temp. °C	Pseudo First order kinetics			Pseudo Second order kinetics			Elovich Kinetics			q <sub>e</sub> , exp mg/g
	k <sub>1</sub> min <sup>-1</sup>	q <sub>e</sub> , mg/g	R <sup>2</sup>	k <sub>2</sub> g min <sup>-1</sup>	mg/g	R <sup>2</sup>	β g/mg	α mg/g min	R <sup>2</sup>	
20	0.021	4.2844	0.840	0.0240	49.015	0.999	0.748839	8.69348E+13	0.947	49.015
30	0.049	5.9536	0.690	0.0412	47.015	0.999	0.962094	3.83802E+17	0.912	47.015
40	0.048	4.2930	0.713	0.0500	49.120	1.000	1.540832	3.69421E+30	0.917	49.120
50	0.007	3.7848	0.747	0.0190	49.656	0.999	0.810045	1.24846E+15	0.918	49.656

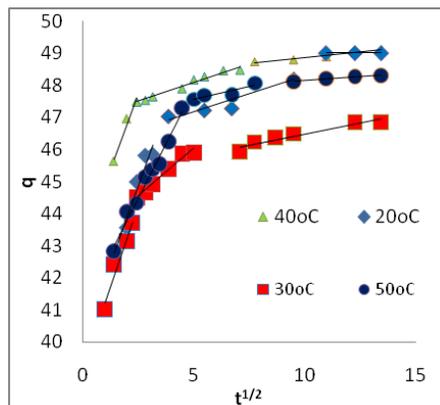
**Adsorption Diffusion Models:**

**Intra particle Diffusion Model:** The structure of the adsorbent and its interaction with the diffusing adsorbate influence the rate of transport, where the solute movement is a function of concentration gradient, and the rate constant (ki) can be determined by intra-particle diffusion model. Weber Morris found that, in many adsorption cases, solute uptake varies almost proportionally with t<sup>1/2</sup> rather than with the contact time t.

$$q_t = k_i \sqrt{t} + C \tag{7}$$

where, q<sub>t</sub> refers to the amount of dye adsorbed in mg/g at time, t; intercept C, indicating the boundary layer effect and k<sub>i</sub>, the intra-particle diffusion rate constant (mg/g.min<sup>1/2</sup>). A plot between amount of dye adsorbed and square root of time should be a straight line passing through the origin, if the intra particle diffusion is the sole rate limiting step. Otherwise adsorption kinetics can be controlled by film and intra particle diffusion simultaneously (Kumar, A. et al., 2007).

Experiments were conducted at different temperatures, intra particle diffusion rate constants can be obtained from the amount of dye adsorbed versus  $t^{1/2}$  plots as shown Fig. 3.



**Fig.3. Intra-particle diffusion for the adsorption of Congo red using modified Bentonite**

The values of the constants,  $k_i$ ,  $C$  and  $R^2$  for intra particle diffusion kinetics have been given in Table 2. The correlation coefficients ( $R^2$ ) are between 0.9055 and 0.9429. The plots do not pass through the origin, indicating the intra-particle diffusion is not the only rate controlling step.

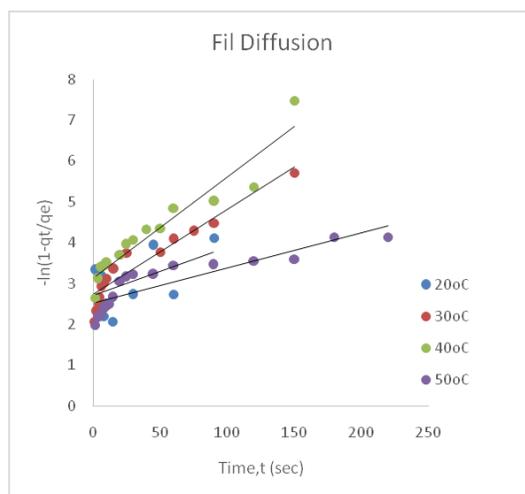
**Liquid film Diffusion Mode:** The film diffusion mass transfer rate equation is presented as :

$$-\ln(1-q_t/q_e) = R' t \quad (8)$$

$$R' = 3D_e' / (\Delta r_0 r_0 k')$$

where  $R'$  (1/min) is the liquid film diffusion constant,  $D_e'$  ( $\text{cm}^2/\text{min}$ ) is the effective liquid film diffusion coefficient,  $r_0$  (cm) is the radius of the adsorbent beads,  $\Delta r_0$  (cm) is the thickness of the liquid film, and  $k'$  is equilibrium constant of adsorption. A plot of  $-\ln(1-q_t/q_e)$  vs.  $t$  should be a straight line with a slope  $R'$  if the liquid film diffusion is the rate limiting step. The liquid film mass transfer equation has been successfully applied to model several liquid solid adsorption systems (Qiu et al.2009).

Experimental data is tested for film diffusion kinetics, and represented in fig. 4. Results indicate nonlinear trend in the beginning period of time and linear later on. Straight lines doesn't pass through origin confirm liquid diffusion is not only the limiting step and there is a chance of mixed kinetics.



**Fig.4. Film diffusion model kinetics for the adsorption of Congo red using modified Bentonite**

Table.2.Comparison of diffusion kinetic parameters

Temp, °C	Intra particle diffusion			Film Diffusion	
	ki mg/g. min <sup>1/2</sup>	C mg/g	R <sup>2</sup>	R'	R <sup>2</sup>
20	0.36	45.000	0.905	0.011	0.254
30	0.13	45.103	0.921	0.021	0.878
40	0.07	48.118	0.934	0.024	0.915
50	0.05	47.668	0.942	0.008	0.773

## CONCLUSIONS

In this study Bentonite was modified with acid treatment and is used for removal of Congo red from waste water. The experimental data was tested for pseudo first order, Pseudo second order and Elovich models. Pseudo second order kinetic models better represented the data with highest regression coefficients of 0.99-1.0. The results simulated by this model matched well with that of the experimental values. Good agreement with Elovich model was an indication for chemical sorption process. Film and intra particle diffusion models were tested to determine diffusion controlling steps. From the results it can be concluded that mass transfer mechanism is controlled by both film & intraparticle diffusion simultaneously.

## REFERENCES

- A. Safa O'zcan, Bilge Erdem, Adnan O'zcan, Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite, *Journal of Colloid and Interface Science*, 280, 2004, 44-54.
- Ari Rahman Takeo Urabeb, Naoyuki Kishimoto, Color removal of reactive procion dyes by clay adsorbents, *Procedia Environmental Sciences*, 17, 2013, 270-278.
- Emrah Bulut, Mahmut O zacar, I. Ayhan S, engil, Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite *Journal of Hazardous Materials*, 154, 2008, 613-622.
- Hui QIU, Lu LV, Bing-cai PAN, Qing-jian ZHANG, Wei-ming ZHANG, Quan-xing ZHANG, Critical review in adsorption kinetic models, *J Zhejiang Univ Sci A*, 10(5), 2009, 716-724.
- Kumar, A., Kumar, S., Kumar, S., & Gupta, D.V, Adsorption of phenol and 4-nitrophenol on granular activated carbon in basal salt medium: Equilibrium and kinetics. *Journal of Hazardous Materials*, 147, 2007, 155-166.
- S. Lagergren, Zurtheorie der sogenannten adsorption geloster Stoffe, *Handlingar*, 24(4), 1898, 1-39.
- Vipasiri Vimonses, Shaomin Lei, Bo Jin, Chris W.K. Chow, Chris Saint, Adsorption of congo red by three Australian kaolins, *Applied Clay Science*, 43, 2009, 465-472.
- Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem*, 34 (5), 1999, 451-465.
- Y.S. Ho, J.C.Y. Ng, and G. McKay, Kinetics of pollutant Sorption by Biosorbents: Review, Separation and Purification methods, 29(2), 2000, 189-232