I.A.U.
Karaj Branch

Journal of Applied Chemical Research, 10, 1, 35-47 (2016)

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

# Removal of Alizarin Red Dye Using Calcium Hydroxide as a Low-cost Adsorbent

**Thimmasandra Narayan Ramesh*, Ashwathaiah Ashwini, Devarahosahally Veeranna Kirana**
*Department of Studies and Research in Chemistry, Tumkur University, Tumkur, India*

*(Received 14 Jun. 2015; Final version received 17 Nov. 2015)*

## Abstract

Calcium ions have very strong affinity and binds effectively to alizarin red dye during staining of biomaterials. This promotes us to choose calcium hydroxide as a low cost adsorbent for the removal of alizarin red dye. Various parameters such as pH, concentration, dose of adsorbent, time, and temperature have been investigated. In addition, enthalpy, entropy, free energy and activation energy have been estimated. Different types of isotherms have been evaluated to understand the nature adsorption and its kinetics. It has been found that the adsorption equilibrium can be obtained after 120 minutes. The adsorption of alizarin red dye on calcium hydroxide is endothermic in nature and occurs spontaneously. It has been found that the adsorption is effective at pH = 12 (60 $^{o}$C) and the kinetic parameters indicate that the adsorption phenomena is of monolayer type and fits well for the pseudo-second order rate equation.

***Keywords***: *Adsorption, Alizarin red, Calcium hydroxide, Isotherms, Dyes.*

## Introduction

There are certain compounds which can either absorb or emit light in the visible region and such materials are called colorants [1]. The colorants comprise of organic and inorganic compounds which can be classified into natural and synthetic in nature. Dyes and pigments are considered as prominent colorants [2]. Dyes are soluble in water or organic solvents while pigments are insoluble in nature and are most widely used in paints. On the other hand, dyes will bind to the fabric and imparts color to it. Therefore the essential criteria for dyes are that they must possess strong affinity for the

---

***Corresponding author: Thimmasandra Narayan Ramesh, Department of Studies and Research in Chemistry, Tumkur University, Tumkur, P.O.Box: 572 103, India. Tel: +91-0816 2260220; Fax: +91-0816-2270719.***

substrate. Dyes are classified as ionic, aromatic dyes with delocalized electron systems in conjugated as well as aryl rings. The presence of double bonds will impart color to the dye and such groups are called chromophores. Depending on the type of the chromophore, dyes will be considered as anthraquinone, pthalocyanine, triarylmethane and azo dyes. The azo dyes comprise of nitrogen groups and are most widely used in textile industries. There are other types of dyes used as food colorants, in hair dyes etc. In addition to the above, there are acidic, reactive, mordants, basic dyes and the list of dyes and their classification has been reported [3].

Paper and pulp industries are the largest consumers of water and at the same time generate highly toxic pollutants. In addition to the above, textile industries use dyes on fabrics and these dyes used are highly toxic and carcinogenic in nature [4, 5]. These dyes have been used in large quantities and even after treating the effluents the above industries release large quantity of water which is highly colored [6-8]. There are several physic-chemical methods are used for the treatment of dyes [9-11]. Of which, chemical methods such as coagulation, floatation, precipitation and oxidation process are effective routes while physical methods such as membrane filtration processes, electrodialysis, electrokinetic coagulation, electrochemical treatment have been adopted [12-16]. In addition to the above, irradiation, photocatalysis, etc have also been employed.17 The biological methods such as treatment of effluents with fungi and other microbes are effective and at the same time not scalable.13 The above methods are expensive, energy intensive and generate large quantities of sludge and its disposal was found to be a problem for the environment. Adsorption was found to be effective. There are different kinds of adsorbents which have been used.9-11 Most commonly used adsorbents are metal oxides, clays, charcoal and activated carbon [18,19]. These adsorbents are expensive, as a alternative to the above, These effluents cannot be treated effectively using conventional methods [20, 21]. As an alternative to this, agrowaste has also been employed for the removal of dyes using adsorption process McKay [22]. Chatterjee et al [23] investigated the capacity of adsorption of carbon nanotubes on the impregnated chitosan hydrogel the adsorption performance of chitosan (CS) hydrogel beads for the removal of Congo-red (CR) as an anionic dye. Unfortunately, the agrowaste are not effective and also large quantity is required. The criteria for choosing the adsorbent are that i) it should have high affinity for the dyes, ii) ecofriendly and safe to handle and iii) preferably regenerative. There are no adsorbents which can fulfill all the requirements and proved to be effective in removing water soluble textile dyes. Among the most commonly used dyes, alizarin red dye has several applications in addition to the dyeing the fabrics such as to stain to detect the calcium content and calcium deficiency related disorders. This motivates us to explore calcium hydroxide for the treatment of alizarin red dye. Several adsorbents such as alumina, calcium oxide and cynodon dactylon have been used as adsorbents for alizarin red dye [24, 25]. We had examined the removal of alizarin red dye onto calcium oxide and magnesium oxide as adsorbents separately and the results reveal that both are effective adsorbents [26, 27]. As an extension of our previous work, in this article, we report on the use of calcium hydroxide as a low cost adsorbent to examine its effectiveness on the removal of alizarin red dye by varying different parameters such as pH, dose, concentration, temperature and analyzed the nature of adsorption process.

## Experimental

### *Materials and methods*

Calcium hydroxide and alizarin red dye were procured from commercial source (SD-Fine Chemicals, India) and used without purification.

### *Preparation of alizarin red dye solution and evaluation of adsorbent efficiency*

Sixty mg of alizarin red dye was dissolved in distilled water and made up to 1000 mL to prepare stock solution. Series of dye concentrations in the range of ($1.6472 \times 10^{-5}$ M to $1.6472 \times 10^{-4}$ M or 0.60 mg to 6.0 mg/100 mL) were prepared by proper dilution of 10 mL, 20 mL, 30 mL, 40 mL, 50 mL and 100 mL of the dye solution to 100 mL using distilled water. The pH of the alizarin red-S dye solution were adjusted using either 1M HCl or 1M NaOH [pH=3, pH=6, pH=9, pH=12] to test the effect of pH on the adsorption of dye on calcium hydroxide. To test the effect of dosage, 0.2g, 0.4g, 0.6g or 0.8g of calcium hydroxide were added to alizarin red dye solutions maintained at different pHs (pH=6, pH=9, pH=12) and concentrations ($1.78455 \times 10^{-5}$ M to $1.784 \times 10^{-4}$ M or 0.60 mg to 6.0 mg/100 mL) separately. The effect of temperature on the adsorption of alizarin red dye solutions (at different pH, dosage – 0.8 g) was measured. The duration at which equilibrium state attained was estimated to determine the effectiveness. The effect of temperature as a function of time (30, 60, 90, 120, 150 min) on the dye removal was examined at predetermined equilibrium conditions i.e pH = 12, dose of calcium hydroxide – 0.8 g. The adsorbent was filtered and for the filtrate, measurements were carried out to estimate the absorbance by using colorimeter fixed at a wavelength $\lambda = 510$ nm/450 nm filters. A blank solution containing no dye solution and other containing dye solution only were used for different batch of samples.

### *Adsorption isotherms*

Different models will be evaluated to

determine the nature of adsorption process.

### *Characterization*

Elico CL-63 colorimeter was used to measure the absorbance of the dye solutions and $\lambda_{max}$ was set to 520 nm at pH 12 and $\lambda_{max}$ at 450 nm for pH<6 solutions respectively. Calcium hydroxide sample was characterized using Bruker D-8 Advanced X-ray powder diffractometer with Cu Kα = 1.5418 Å, scan rate 2° $min^{-1}$ (steps: 0.02°); scan range of 10-55°.

## Results and discussion

The powder X-ray diffraction pattern of calcium hydroxide shows that it crystallizes in hexagonal system with the space group P-3m1. The crystallite size of calcium hydroxide was estimated using Scherrer formula [28]

$$D = 0.9\,\lambda / \beta Cos\theta$$

where

D = average crystallite size in (Å)

λ = wavelength of the X-ray radiation (1.5418 Å),

θ = Bragg's angle and

β = full width at half maximum (FWHM) of the peak in the diffraction pattern.

The crystallite size was found to be in the range of 30-50 nm.

The effect of initial pH of the dye solution, dosage of adsorbent (calcium hydroxide) will be discussed below

### *Effect of pH*

The pH of the system exerts significant effect on the adsorptive uptake of dye molecule due to the ionisation/dissociation of the adsorbate molecule. The effect of pH (6, 9, 12) on the adsorption of alizarin red dye on calcium hydroxide is shown in Figure 1. It can be observed that adsorption is maximum at pH 12. At pH lower than 9, adsorption is low due to higher affinity of calcium hydroxide towards water.

### *Adsorbent dose*

Figure 2 shows the effect of adsorption of alizarin red dye as a function of an increase in the dosage of calcium hydroxide. The data clearly indicates that the adsorption increases with increase in the dose quantity. The equilibrium adsorption was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)\,V}{\text{weight of adsorbent (mg)}}$$

Higher the dosage content, higher the surface area and the number of available adsorption sites will also be large. The adsorption is maximum at higher dosage i.e., when 0.8 g of calcium hydroxide was used at pH-12. Thus the optimum quantity i.e 0.8 g of calcium hydroxide was used for all the future investigations.

### *Dye Concentration*

Dye concentrations i.e., 0.6-6 mg/100 mL were varied as a function of time at pH 12 (298K). The equilibrium adsorption ‘qe’ can be estimated using:

$$q_e = \frac{(C_o - C_e)}{weight\ of\ adsorbent\ (mg)} V$$

where $C_o$ – initial concentration of dye
$C_e$ – concentration at equilibrium
V – volume of the dye solution

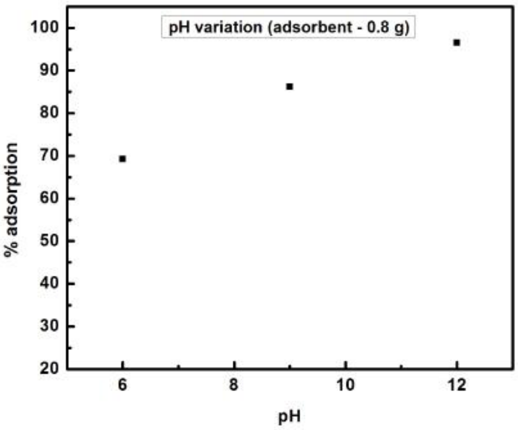

**Figure 1.** Effect of pH variation as a function of adsorption.

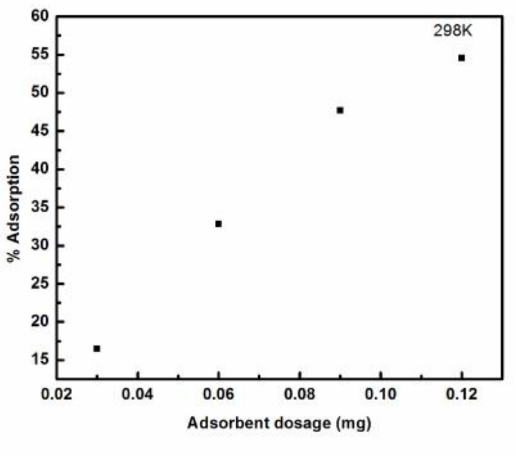

**Figure 2.** Effect of adsorbent dosage.

Figure 3 shows the effect of concentration of adsorption of alizarin red dye solution on calcium hydroxide. The adsorption was maximum when 0.8 g of calcium hydroxide was used as an adsorbent. The effect of various dye concentrations (0.6. to 6.0 mg/100mL), time (180 min) and pH 12 was monitored at 298K. The results are shown in Figure 3. The increase in adsorption with increase in concentration is due to the more number of available sites for the adsorption. Also in Figure 3 are shown the effect of temperature on the adsorption capacity of alizarin red dye at different concentrations. The adsorption is found to be linear increase with increase in temperature.

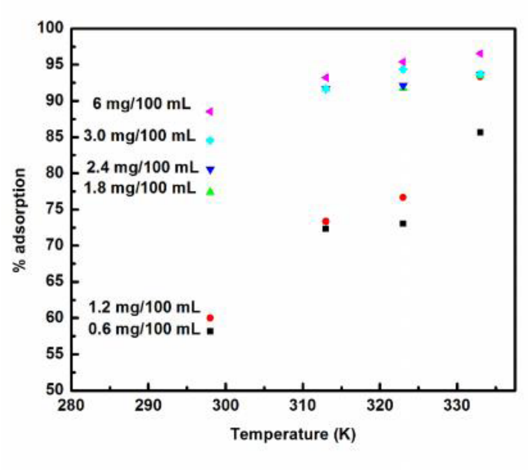

**Figure 3.** Effect of concentration as a function of % of adsorption.

*Effect of duration*

Adsorption of alizarin red on calcium hydroxide at different contact time has been examined by adding 0.2g, 0.4g, 0.6g, 0.8g and 1.0g of adsorbent to alizarin red dye solution (6 mg/100 mL). Figure 3 also shows the effect of duration or contact time on the adsorption of alizarin red on calcium hydroxide. It is found that at 150 minutes, the adsorption is maximum at different temperatures i.e 298K, 313K, 323K and 333K respectively.

*Effect of Temperature*

Temperature can affect the rate of adsorption drastically. Figure 3 shows the percentage of adsorption with increase in temperature (i.e., 298K, 313K, 323K and 333K). It is found that at 333K, the adsorption is maximum (pH = 12). With increase in temperature, adsorption also increases indicating the reaction is endothermic in nature. The variation of change in the initial concentration after equilibrium using calcium hydroxide on alizarin red dye solution has been calculated. The difference between the maximum adsorption capacity ($q_e$) and the equilibrium concentration ($C_e$) was evaluated. The adsorption of alizarin red on calcium hydroxide at different temperatures (pH = 12) (see supplementary data Table ST1-ST4). In Table 1 is shown the summarized data for the parameters obtained for alizarin red dye adsorption on calcium hydroxide at 333 K (pH =12).

While investigating the phenomena of adsorption, we should consider both thermodynamic and kinetic parameters to understand the mechanism and its feat. The kinetic parameters provide about the nature of solute intake, the rate at which adsorption takes place etc.

The equation:

$$k = [2.303/t] \, . \, \log_{10} [C_i/C_e]$$

is used to calculate the rate constant where

$C_i$ = initial concentration (mg/L)

$C_e$ = equilibrium concentration (mg/L)

$T$ = minutes

$k$ = rate constant

The adsorption kinetic constants (K-min$^{-1}$), effect of temperature on the adsorption equilibrium constant have been estimated. The value of $K_R$ (dimensional separation factor) is used to evaluate the nature of absorption and its favorability (see supplementary data-table ST-5). If i) $K_R$ =1, then the adsorption is linear, ii) $K_R$>1, unfavourable adsorption, iii) KR = 0, irreversible adsorption is observed, iv) 0< $K_R$<1, then adsorption process is more favorable. The correlation coefficient ($r/R^2$) and the dimensional separation factor as a function of temperature is determined [see supplementary information- table ST4). It is clearly evident that the values are close to zero at higher temperature indicating that the adsorption is irreversible, whereas at lower temperature, adsorption does not vary linearly but is more favorable (Figure 4).

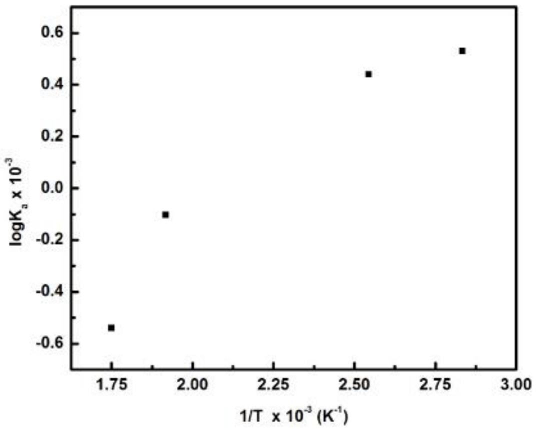

**Figure 4.** Plot of logKa as a function of inverse of temperature

*Different type of adsorption isotherms- data analysis*

Langmuir isotherm, Freudlich isotherm, Temkin isotherm, Harkin-Jura isotherm, Halsey isotherm and Redlich-peterson isotherms have been analyzed for the adsorption data of alizarin red dye on calcium hydroxide (see supplementary information figures S3-S6) [29-32]. Different types of adsorption isotherms and their equations were used to derive information on the nature of interaction of adsorbent and adsorbate. Table 1 provides the correlation coefficients for the different isotherm models and the equations used to calculate the R/r value are given below. The $R^2$ or r values, correlation coefficient and the factors derived for correlation coefficients of Langmuir isotherm, Freundlich isotherm, Temkin isotherm, Harkin-Jura isotherm, Halsey isotherm and Redilch-Peterson isotherms has been tested (for more information see supplementary data- Tables

ST5-ST8). In Figures 5 and 6 shows the plots of Freundlich isotherm and Halsey isotherms respectively. Also Freunclich constant *1/n* = 1.1578 indicates that the adsorption phenomenon is easier occur. Temkin constant or heat of sorption bT < 8 i.e *bT*=0.83 indicates that the interaction between the adsorbent and the adsorbate is not strong while $R^2$ value fits well for Freundlich isotherm and for Harkin-Jura isotherm is < 1 (-0.7860) indicates that the adsorption could be monolayer. Therefore the adsorption isotherm model fits better for Freundlich isotherm and Halsey isotherm models.

**Table 1.** Summary of the data analyzed for different types of isotherms at 333K.

| **Isotherm** | **Parameters** | |
|---|---|---|
| Freundlich | *1/n* | 1.1578 |
| | $K_f$ | -0.4365 |
| | $R^2$ | 0.9083 |
| Temkin | *KT* | 0.2928 |
| | *bT [kJ/mol]* | 0.8344 |
| | $R^2$ | 0.8579 |
| Harkin-Jura | *A* | 0.1136 |
| | *B* | -0.6 |
| | $R^2$ | -0.786 |
| Halsey isotherm | *N* | 1 |
| | *K* | 0.1090 |
| | $R^2$ | 0.9084 |

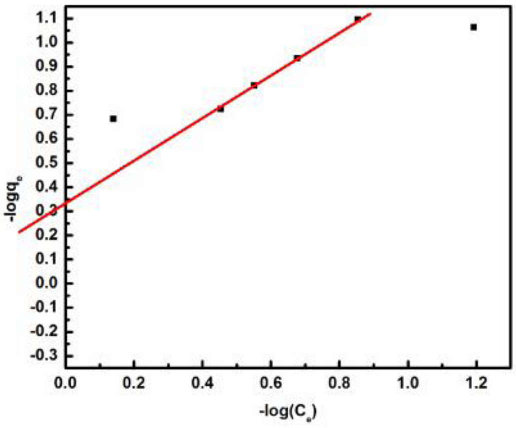

**Figure 5**. Plot of -logCe vs -logqe for Freundlich isotherm.

*Kinetics of adsorption process*

Adsorption reaction and diffusion during adsorption are the two models used to determine the kinetics of the adsorption process. [31].

Diffusion model for adsorption takes into account i) diffusion of adsorbate on to the adsorbent, ii] intra-particle diffusion and iii] nature of desorption and adsorption.

The adsorption models described are of two types i) first order, ii) pseudo-first order, iii) second order, iv) pseudo second order.

Lagergren pseudo first-order model proposes to understand the chemical kinetics of solid-liquid adsorption process. The Larergren model has been effectively used to provide explanation for the adsorption of methylene blue, malachite green and other dyes on biomass waste. Pseudo-first order rate equation is given by:

Where O $$\frac{dq_t}{dt} \quad kp_1(q_e-q_t)$$

$\frac{dq_t}{dt}$ represents the rate of change of adsorption as a function of time kp1 (min-1) indicates the rate of the reaction

$q_e$ (mg/g) equilibrium adsorption capacity

$q_t$ (mg/g) adsorption capacity after certain time ‘t’

t- time in minutes

The above equation can be rearranged and written as:

$$\log(q_e-q_t) = \log(q_e) - \frac{kp_1}{2.303}t$$

by plotting a graph of $\log(q_e-q_t)$ vs time (t), we can calculate kp1 and qe by using slope and intercept values respectively.

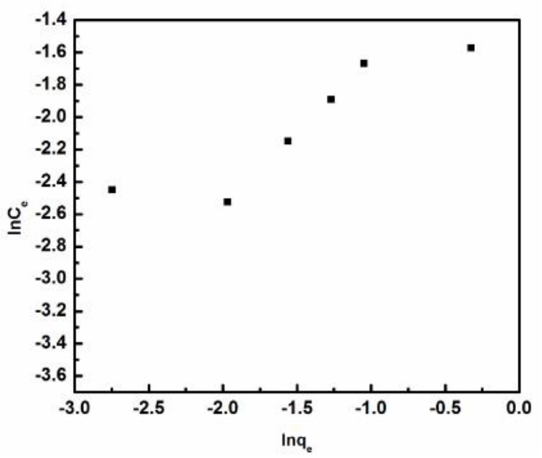

**Figure 6.** lnCe vs lnqe for Halsey isotherm.

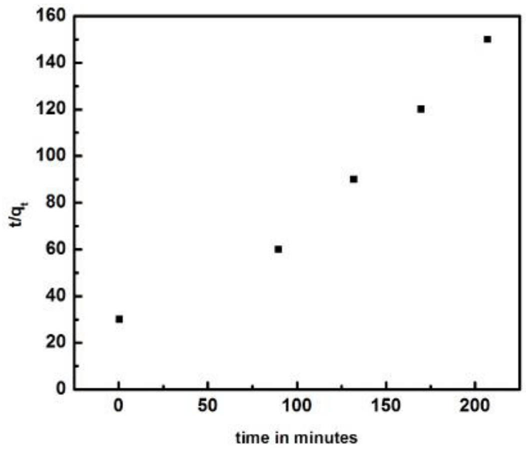

**Figure 7.** pseudo-second order kinetics.

In Table 2 is shown the data obtained for the pseudo-first order rate equation.

*Pseudo-second-order rate equation*

If the adsorption involves chemical interaction/bonding due to charge transfer process between the adsorbent and adsorbate then pseudo-second order rate equation should be considered and the equation is:

$$\frac{t}{q_t} = \frac{1}{v_0} + \frac{1}{q_e}$$

where $V_o = k_p^2 q_e^2$

$V_o$ represents the initial adsorption rate and the rate constant was determined from the experimental data [33].

**Table 2.** List of parameters used to evaluate the pseudo-first order rate equation.

| Kinetic model | Parameters | | | | |
|---|---|---|---|---|---|
| | dye [mg/100 mL] $C_o$ | $q_e$ [experimental] | $K^2$ | $q_e$ [calculated] | $R^2$ |
| Pseudo-first order kinetics | 6.0 | 0.7241 | 0.037 | 0.8912 | -0.9264 |

Tables 3 and 4 provide the parameters used for the evaluation pseudo-second order rate equation for the adsorption of alizarin red on calcium hydroxide. Figure 9 shows the graph which fits reasonable well with a straight line to predict the adsorption process to be pseudo-second order process. The calculated r or $R^2$ value is 0.97 indicates that adsorption follows pseudo-second order. The experimental and calculated '$q_e$' values are closer indicating that the adsorption could be of pseudo-second order in nature (Figure 7).

**Table 3.** List of parameters used to evaluate the pseudo-second order rate equation.

| **Kinetic model** | **Parameters** | | | | |
|---|---|---|---|---|---|
| | **dye [mg/100 mL] $C_o$** | **$q_e$ [experimental]** | **$K^2$** | **$q_e$ [calculated]** | **$R^2$** |
| Pseudo-second order kinetics | 6.0 | 0.7241 | 10.469 | 0.69118 | 0.97 |

**Table 4.** List of parameters used to evaluate the pseudo-second order rate equation.

| **Time [min]** | **$t/q_t$** | **$t^2$** | **$t/q_t{}^2$** | **$t \quad t/q_t$** |
|---|---|---|---|---|
| 30 | 46.403 | 900 | 2153.3 | 1392.111 |
| 60 | 89.847 | 3600 | 8072.51 | 5390.472 |
| 90 | 132.15 | 8100 | 17465.86 | 11894.265 |
| 120 | 169.778 | 14400 | 28824.63 | 20373.384 |
| 150 | 207.153 | 22500 | 42912.65 | 31073.055 |
| $\sum t = 450$ | $\sum t/q_t = -645.3413$ | $\sum t^2 = 36540$ | $\sum t/q_t{}^2 = 99426$ | $\sum t \times t/q_t = 70123.28$ |

### *Thermodynamic parameters*

The free energy, (ΔGº), enthalpy (ΔHº) and entropy (ΔSº) changes for the adsorbents were obtained using equilibrium constant Ka values and the data are given in Table 5.

The negative value of free energy shows that the adsorption process is spontaneous at higher temperatures while it is not favorable at lower temperature.

**Table 5.** Thermodynamic parameters for adsorption of alizarin red.

| **Adsorbent** | **Temperature [K]** | ***G*° [kJ mol$^{-1}$]** | ***H*° [kJ mol$^{-1}$]** | ***S*° [kJ mol$^{-1}$K$^{-1}$]** |
|---|---|---|---|---|
| Alizarin red | 298 | 3.0726 | 5.4 | 0.1818 |
| | 313 | 0.612 | | |
| | 323 | -2.722 | | |
| | 333 | -3.383 | | |

The effect of temperature on the free energy change was derived and the data shows that, lower the negative free energy with increase in temperature indicates that the adsorption process is more favorable. The estimated activation energy (Ea) for the adsorption of alizarin red dye on calcium hydroxide is -3.3837 kJ mol$^{-1}$.

## Conclusion

Adsorption isotherms of alizarin red dye on calcium hydroxide have been reported.

The thermodynamic parameters such as free energy, entropy, enthalpy and activation energy were calculated during the adsorption of alizarin red dye on calcium hydroxide. The results demonstrate that the process of adsorption is endothermic, spontaneous, monolayer in nature and fits to pseudo-second order rate equation. Calcium hydroxide can be used as an effective low cost adsorbent for the removal of alizarin red dye.

## Acknowledgements

Authors gratefully thank Tumkur University for its support and facilities. TNR express his deepest gratitude to Prof. P Vishnu Kamath for extending unconditional support throughout his academic career and for providing lab facilities.

## References

[1] H. Zollinger, *Color Chemistry – Synthesis, Properties of Organic Dyes and Pigments*, VCH Publishers, New York (1987).

[2] K. Hunger., Industrial Dyes: *Chemistry, Properties, Applications*, Wiley-VCH, Weinheim, Cambridge (2003).

[3] G. Barman, Master of Technology (Research) In Chemical Engineering, National Institute of Technology, Rourkela (2011).

[4] C. O. Neill, F. R.Hawkes, D. L. Hawkes, N. D. Lourenço, H. M. Pinheiro, W. Delée, *J. Chem. Tech. Biotech.*, 74, 1009 (1999).

[5] P. C. Vandevivere, R. Bianchi, W. Verstraete, *J. Chem. Tech. Biotech.*,72, 289 (1998).

[6] T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresource Tech.*, 77, 247 (2001).

[7] I. M. Banat, P. Nigam, D. Singh, R. Marchant, *Bioresource Tech.*, 58, 217 (1996).

[8] F. Banat, Sameer Al-Asheh, Leema Al-Makhadmeh, *Process Biochem.*, 39, 193 (2003).

[9] A.K. Jain, V. K. Gupta, A. Bhatnagar, Suhas, *J. Hazard. Mater., B*101, 31 (2003).

[10] Y. S. Ho, G. McKay, *Process Biochem.*, 38, 1047 (2003).

[11] F. Derbyshire, M. Jagtoyen, R. Andrews, *Carbon materials in environmental applications*. In: Radovic L R (Ed), Chemistry and Physics of Carbon, Marcel Dekker, New York, 27, 1 (2001).

[12] M. Alkan, O. Demirba, M. Doˇgan, *Fres. Environ. Bull.*, 13, 1112 (2004).

[13] C.G. Namboodri, W.S. Perkins, W.K. Walsh, Am. Dyestuff Republic, 83, 7 (1994).

[14] León, C. A., Radovic, L. R., *Interfacial chemistry and electrochemistry of carbon surfaces.* In: P.A. Thrower, Editor, Chemistry and physics of carbon, Dekker, New York, 24, 213 (1994).

[15] Z. Song, L. Chen, J.Hu, R. *Richards*, Nanotech, 20, 275707 (2009).

[16] A. K. Golder, A. N. Samanta, S. Ray, *Chem. Eng. J.,* 122, 107 (2006).

[17] T.K. Ghorai, D. Dhak, S.K. Biswas, S. Dalai, P. Pramanik, *J. Mol. Cat. A: Chem.*,

273, 224 (2007).

[18] Babel, S., Kurniawan, T. A., *J. Hazard. Mater., B*97, 219 (2003).

[19] Keith, K.H. Choy, G. McKay, J. F. Porter, *Res. Conserv. Recycling*., 27, 57 (1999).

[20] M. F. R. Pereira, S. F. Soares, J. J.M Órfão, J. L. Figueiredo, *Carbon*., 41, 811 (2003).

[21] A. Marco, S. Esplugas, G. Saum, P. Dell, R. Donald and J. McIntosh, *Water Sci. Tech*., 35, 321 (1997).

[22] S.M. Ghoreishi, R. Haghighi, *Chem. Eng. J*., 95, 163 (2003).

[23] S. Chatterjee, M. W. Lee, S.H. Woo, *Bioresource Tech*., 101, 1800 (2010).

[24] R. Rehman, T. Mahmud, J. Anwar, M. Salman, *J. Chem. Soc. Pak*., 33, 228 (2011).

[25] J. Samusolomon and P. M. Devaprasath, *J. Chem. Pharm. Res*., 3, 478 (2011).

[26] T. N. Ramesh, T. N. Mohana Kumari, D. V. Kirana, A. Ashwini, *Conference Proceedings*, pp. 100 (2013).

[27] T. N. Ramesh, J. M. Prathiba, D. V. Kirana, T. N. Mohana Kumari, A. Ashwini, *Conference Proceedings*, pp. 113 (2013).

[28] A. L. Patterson, *Phys. Rev*., 56, 978 (1939).

[29] C. H. Giles, D. Smith, A. Huitson, *J. Colloid Inter. Sci.,* 47, 755 (1974).

[30] J, M.Van Bemmelen, *Die Landwristschaftliechen Versuchs Stationen*., 35, 69 (1988).

[31] I. M. Aghri, F. A. Grissi, M. Elukoali, A. Kenz, O. Tanane, M. Talbi, S, M. Alouhi, *Global J. Sci. Frontier Res*.,12, 7 (2012).

[32] H.M. F. Freundlich, *Z. Phy.Chem*., 57A, 385 (1906).

[33] M. Li, H. Wang, S. Wu, F. Li, P. Zhi, *RSC Advances*, 2, 900 (2012).