



## Activated Red Mud as an Adsorbent in the Removal of Anionic Dye, Brilliant Yellow Dye, From Polluted Waters

G.V. Krishna Mohan, A. NagaBabu, K. Kalpana and K. Ravindhranath\*

Dept of Chemistry, K L University, Green Fields, Vaddeswaram-522 502, Guntur Dt., A.P., India

**Abstract :** The sorption nature of acid activated red mud towards anionic dye, Brilliant yellow dye, has been investigated with respect to various physicochemical parameters like pH, sorbent concentration, agitation time, temperature and initial concentration of the dye using simulated waters and the conditions have been optimized for the maximum removal of the dye. The interference of co-ions on the adsorption of the dye has been investigated. The adsorption data is analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. Correlation coefficient ( $R^2$ ) and dimensionless separation factor ( $R_L$ ) values have confirmed that adsorption obeys Langmuir adsorption ( $R^2$ : 0.9914;  $R_L$ : 0.0290) indicating monolayer formation while Temkin isotherm and Dubinin-Radushkevich isotherms indicate that the adsorption is 'physisorption' in nature. Pseudo-first-order, pseudo-second-order, Bangham's pore diffusion and Elovich equations have been applied to identify the kinetics of adsorption process and found that adsorption follows pseudo-second-order kinetics. The thermodynamic study revealed that adsorption of the dye is an endothermic process and the adsorption increases with increase in temperature. The procedures developed in this investigation have been applied to the samples collected from the effluents of textile industries and found to be successful.

**Key Words:** Anionic Dye, Brilliant yellow dye, Pollution and Control, Activated Red mud, adsorption, applications.

### 1: Introduction

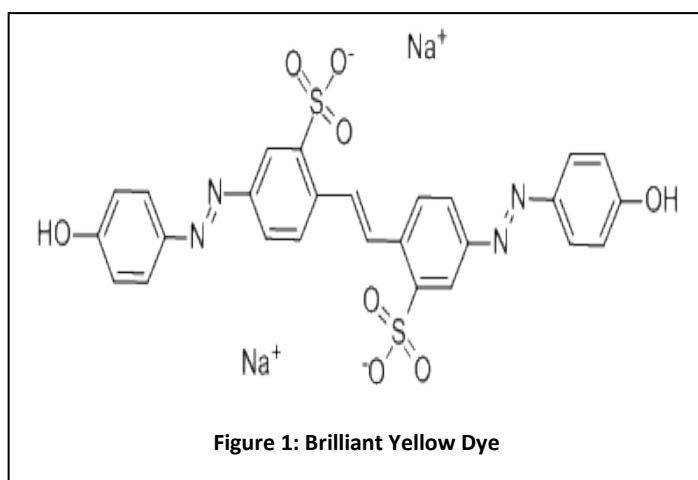
The removal of pollutants from waste waters using un-conventional methods based on adsorption is being widely investigated throughout the Globe to find simple, effective, economical and eco-friendly methodologies. Our research group has been probing these unconventional methods and developed procedures for the removal of Chromium (VI)<sup>1-4</sup>, Zinc<sup>5,6</sup>, Aluminum (III)<sup>7-10</sup>, Fluoride<sup>11-17</sup>, Nitrite<sup>18,19</sup>, Nitrates<sup>20</sup>, Ammonia<sup>21-23</sup>, Phosphate<sup>24, 25</sup> and some Dyes<sup>26-31</sup> and also bio-remediation methods for the removal of some heavy metal ions using oxidation ponds<sup>32</sup>.

In the recent past, red mud, a waste produced in Aluminum manufacturing industries, has attracted the attention of researchers. The adsorption nature of red mud either in its native or activated form, is being investigated in the removal of various pollutants such as As (III,V)<sup>33,34</sup>, Pb (II)<sup>35,36</sup>, Cr(VI)<sup>37</sup>, Co(II)<sup>38</sup>, Zn(II)<sup>39,40</sup>, Phosphate<sup>41-43</sup>, Nitrate<sup>44</sup>, Dyes<sup>45-47</sup> from waste waters and thereby making a waste and potential pollutant material, red mud, for better use.

In the present work, acid activated red mud is investigated for its adsorption nature towards anionic dye, Brilliant Yellow. The presence of even traces of synthetic dyes in waste waters is a potential environmental

threat as the dyes or their degradation products are toxic owing to their complex aromatic nature to aquatic life and human beings. Further, the color of water in water bodies curtails the light and interferes with the photosynthesis and thereby affecting the biota and depending aquatic life. The contamination of water bodies with residues of synthetic dyes coming from the effluents of textile industries is endangering the biota and aquatic life prevailing in the water bodies due to the toxic nature of some of the dyes or their degradation products. Further, the color in water bodies due to the residues of dyes obstruct the sun-light to reach to the biota or aquatic life and thereby retarding or effecting the natural phenomenon such as photosynthesis, metabolisms etc<sup>48</sup>

It is reported that every year nearly 10% of dye used in Textile industry is lost through the sewage and if proper extraction and disposal methods are not envisaged by the industries, they enter into the water bodies causing grave threat to aquatic life<sup>49, 50</sup>.



Brilliant yellow dye is used in industries pertaining to textile, inks and tinting. It is widely used for dyeing the protein fibers like wool, angora, cashmere and silk. The effluents from these industries have to be treated for the complete removal of the dye. If the effluents contain even traces of dyes, they cause polluting the water bodies as it is not bio-degradable and it is hazardous. Hence, treating the wastewaters for the complete removal of this potential hazardous dye is essential.

In this present work methodologies for the removal Brilliant Yellow Dye from waster waters using activated red mud as adsorbent have been investigated with respect to various physicochemical parameters and conditions for the maximum removal of the dyes have been optimized.

## 2: Materials and Methods

**Table No:1 Chemical properties of red mud**

Parameter	Result (%)
Alumina as Al <sub>2</sub> O <sub>3</sub>	15.47
Iron as Fe <sub>2</sub> O <sub>3</sub>	58.78
Silica as SiO <sub>2</sub>	6.58
Titanium as TiO <sub>2</sub>	4.39
Soda as Na <sub>2</sub> O	3.63
Calcium as CaO	1.49
Phosphorus as P <sub>2</sub> O <sub>5</sub>	0.159
Vanadium as V <sub>2</sub> O <sub>5</sub>	0.110
LOI (105-1000 <sup>0</sup> C)	7.22

### 2.1. Adsorbent

The red mud was obtained from Utkal Alumina, Rayagada, Orissa. Red mud samples was washed with distilled water a number times until the pH of the filtrate is almost neutral. Then the red mud was dried at 105<sup>0</sup>C for two hours. Then the sample was grinded to a fine powder and then it was meshed to 150 μ. The meshed sample was stored. From it, a suitable amount of red mud was taken and to it, 1.0 N HCl was added in the ratio: 1:2 (by volume), stirred well and was digested for 12 hrs at 50<sup>0</sup>temperature. Thus treated sample was filtered

and the red mud was washed with distilled water repeatedly until, the pH of the filtrate was neutral. Then the sample was dried at 105°C for two hours. Thus obtained sample was used in this work. The composition of the active red mud is presented in Table 1.

## 2.2. Adsorbate:

An anionic dye, Brilliant Yellow (400 nm) purchased from S.D. fine chemical was used. Stock solution of 1000 ppm was prepared with distilled water and it was suitably diluted as per the need.

## 2.3 Reagents and Chemicals:

All the chemicals used were of Analytical Reagent Grade purchased from Merck. India Pvt. Ltd and Sd. Fine Chemicals and all the solutions were prepared using double distilled water throughout this study. Stock solution of 100 ppm of Brilliant yellow Dye was prepared and was suitably diluted as per need.

## 2.4: Method:

Batch modes of extraction were adopted<sup>51-53</sup>. 100 ml of Brilliant Yellow Dye solution (100 ppm) was taken into 250ml conical flask and to it definite quantity the activated red was added. pH was adjusted to a desired value. Then the solution was shaken in horizontal shaker at 250rpm. After a definite contact time, the conical flask was removed from shaker and the solution was filtered through Whatman No.1 filter paper and the filtrate was analyzed for the residual dye concentration using Spectrophotometric method.

## Estimation of the Dye:

The dye has  $\lambda_{max}$  at 400 nm below pH: 6.5 and obeys Beers-Lamberts law even at low concentrations. The O.D. measurements were made at the said  $\lambda_{max}$  using UV-Visible Spectrophotometer(Elico) against blank. The obtained O.D value for un-known solution was referred to standard graphs (drawn between O.D and concentration) prepared with known concentrations of the dye by adopting method of Least Squares to know the concentration of the dye.

The influence of pH, sorbent dosage, equilibration time, initial concentration of the dye and temperature on the % removal of the dye with the Activated red mud was studied and conditions were optimized.

The dye uptake capacity was calculated using Amount adsorbed  $q_e = \frac{(C_0 - C_e)}{m} \times V$ ,  $q_e$  is the amount of dye adsorbed,  $m$  is the mass of adsorbent (g),  $V$  is the volume of the solution (L),  $C_0$  is the initial Concentration of dye (mg/ L),  $C_e$  is the equilibrium dye concentration (mg/ L) and  $q_e$  is the amount of dye quantity adsorbed at equilibrium (mg/g). The percent removal of dye from the solution was calculated by the following equation: % removal =  $\frac{(C_0 - C_e)}{C_0} \times 100$

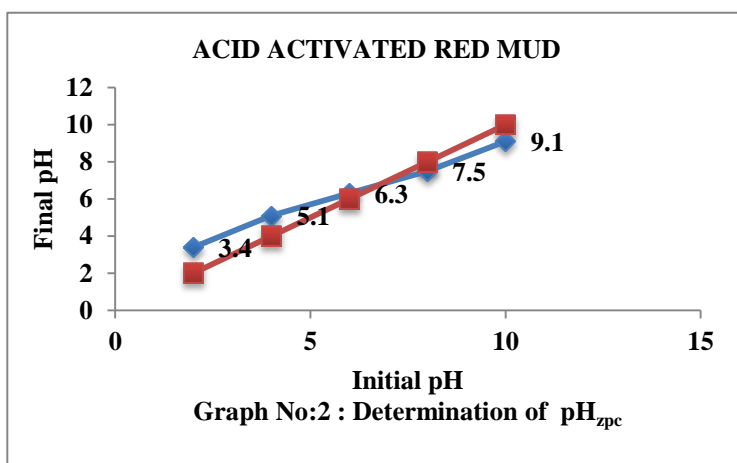
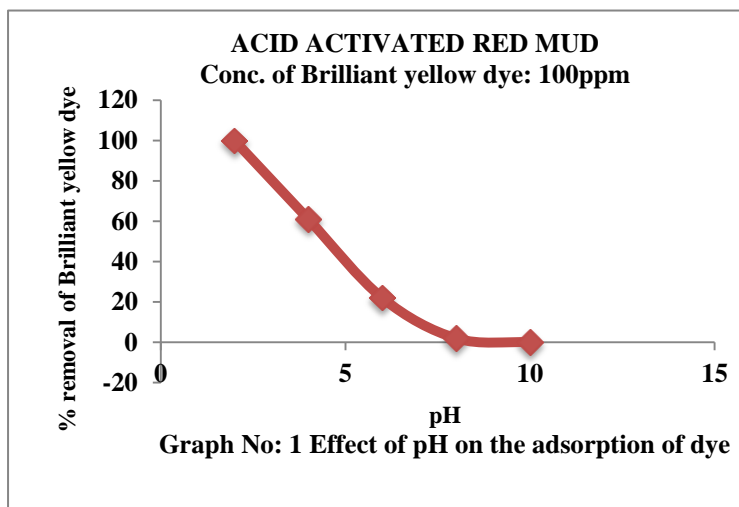
where  $C_0$  (mg/L) and  $C_e$  (mg/L) are the initial and final dye concentrations.

The obtained results were presented in the Graph No. 1-9 Table No.2 and 3.

## 3: Results and Discussions

The sorption of characteristics of the activated Red mud towards the Brilliant yellow dye by varying pH, adsorbent dosage, temperature, initial concentration of dye and interfering ions has been investigated and the finding are presented comprehensively hereunder:

### 3.1: Effect of pH:

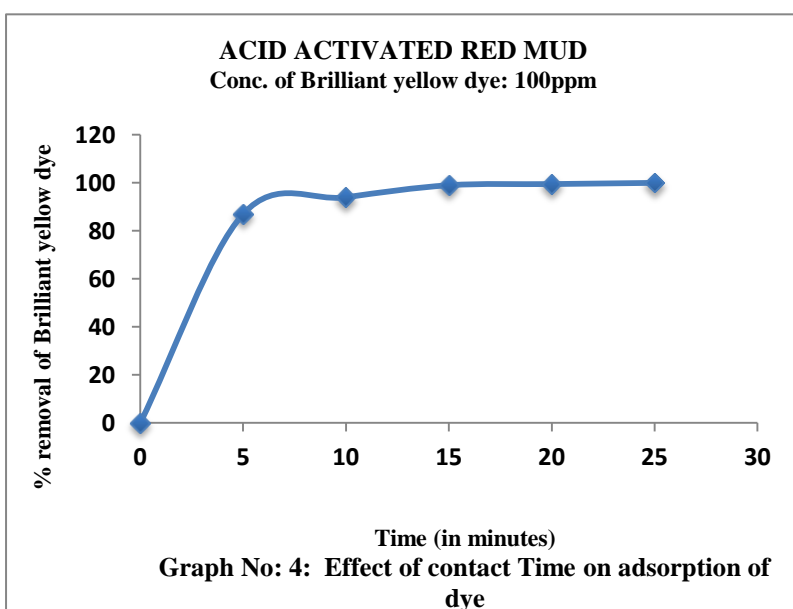
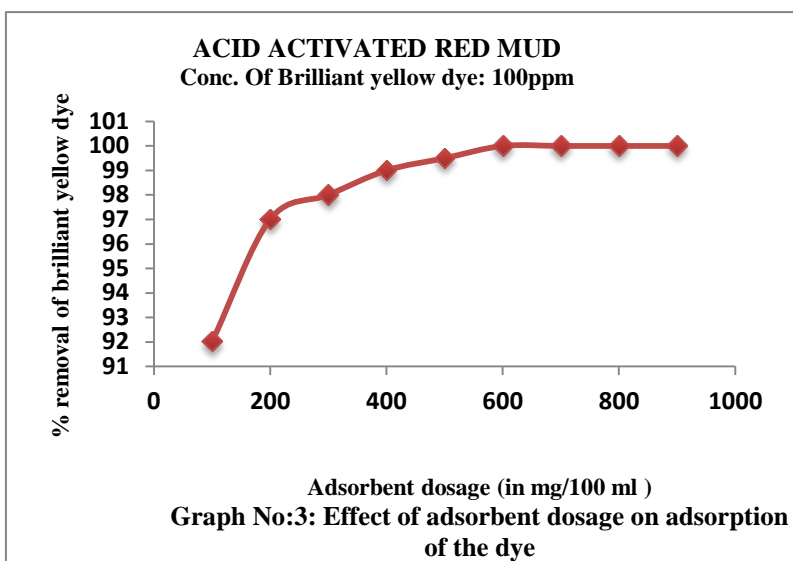


The pH of the dye solution plays an important role in the whole adsorption process. The effect of pH has been studied by varying the pH from 2 to 10 under other optimum parameters: initial conc. of dye: 100ppm; adsorbent dosage: 0.6gm/100ml, contact time:25 minutes; rpm:250 temperatures: 30<sup>0</sup> C. The results are presented in Graph No.1. It is observed from the Graph that 100% removal is possible at pH 2; and% of extraction is progressively decreased as Ph is increased from 2 to 10. So it is inferred that acidic conditions favour the adsorption of dye.

This can be attributed to the function groups present on the surface of the adsorbent and anionic nature of the dye. The  $pH_{zpc}$  is found to be 6.5 (vide Graph No. 2) and below this pH, the surface acquires+ positive charge and a thrust for anions. This is reflected in the adsorption nature of the dye. As the dye is anionic in nature, the % removal is progressively increased with the decrease in the pH because, the surface acquires +ve charge at low pH values and the dye being anion is held to the surface due to electrostatic interactions. If the pH is more than 7, adsorption of the dye is marginal because, above pH: 6.5, the surface acquires negative charge and thus causes repulsion of the negatively charged anion

### 3.2: Effect of adsorbent dosage:

The effect of adsorbent dosage was studied by varying the sorbent dosage from 100mg to 1000mg/ 100ml at other optimum extraction conditions namely: pH: 2, time of equilibration: 25 min, rpm: 250; initial conc. of dye: 100 ppm; temp.:30<sup>0</sup>C. The results are depicted in the Graph No. 3.

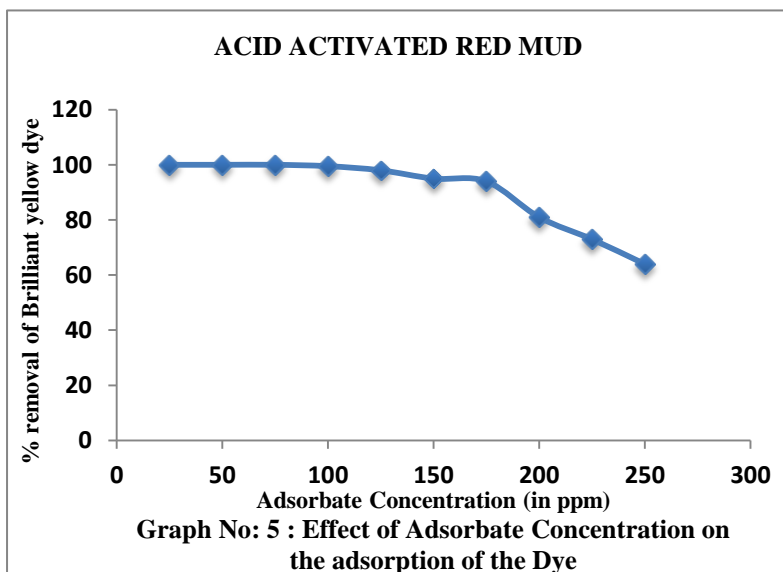


From the graph it is inferred that with increasing the sorbent dosage, the % removal of the dye also increased but after certain dosage, it remains constant. It is observed from the Graph that the % removal of the dye is increased from 92.0% to 100% as the sorbent dosage is increased from 100 mg to 600mg /100 ml. As the concentration of the sorbent is increased, the availability of active sites increases and hence, the increase in the % removal of the dye. But at high concentrations of the adsorbent, some of the active sites may be blocked resulting a steady state at optimum dosages of the adsorbent concentrations.

### 3.3: Effect of Contact time:

To determine the optimum equilibrium time, the time is varied from 0 to 30 minutes at optimum conditions of pH: 2, dosage: 600 mg/100ml, rpm: 250 and temp. 30<sup>0</sup>C. It is observed from the Graph No: 4, that the % removal of the dye is 87.0% within 5 minutes of equilibration and the adsorption process is slowed down and 100% removal is observed only after 25 minutes of agitation. The rapid adsorption at the initial contact time can be attributed to the large number of vacant adsorbent sites and the high gradient of solute concentration, whereas the slower rate with the increasing time may be ascribed to the saturation of the available adsorbing sites.

### 3.4: Effect of initial concentration:

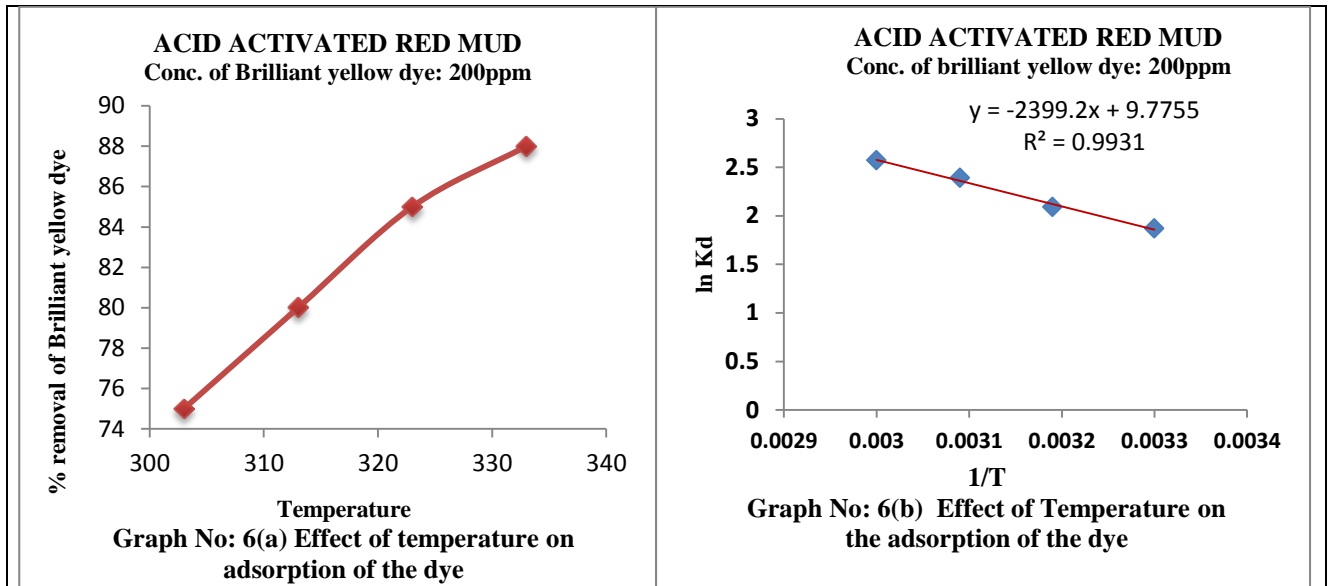


In the Graph No. 5, the effect of initial concentration of the dye on the % of extraction when all the other conditions are constant is depicted. % of extraction of the dye decreases from 100 to 64% with the increase in the initial concentration from 25 to 250 mg/L for a fixed concentration of the adsorbent, 600 mg/100ml. This is expected because at low concentrations of the dye, many active sites are available on the adsorbent. At high concentrations of the dye, the demand of active sites is more but the available active sites are limited as the concentration of the adsorbent is constant and hence, % removal is less.

### 3.5: Effect of temperature:

The effect of temperature on the extraction of the dye of concentration 200 ppm has been studied in the temperature range: 303 to 333 K at optimum extraction conditions: pH: 2, agitation time: 25 minutes, rpm: 250 and dosage: 600mg/100 ml and the results have been depicted in the Graph No. 6a & 6b.

Free energy change ( $\Delta G$ ) (KJ/mole), enthalpy change ( $\Delta H$ ) (KJ/mole) and entropy change ( $\Delta S$ ) (KJ/mole) were determined using the equations;  $\Delta G = -RT \ln K_d$ ;  $\ln K_d = \Delta S / R - \Delta H / RT$ ;  $K_d = q_e / C_e$ ;  $\Delta G = \Delta H - T\Delta S$ , where  $K_d$ : distribution co-efficient of the adsorption,  $q_e$ : the amount of dye adsorbed,  $C_e$ : equilibrium conc. of dye,  $T$ : the absolute temperature in Kelvin,  $R$ : the gas constant. The values of  $\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of the plot between  $\ln K_d$  and  $1/T$ .<sup>54-58</sup>. The values are presented in the Table No: 2. % of extraction increases from 75% to 88% with the increase in temperature from 303 to 333 K for dye solution of 200 ppm concentration.



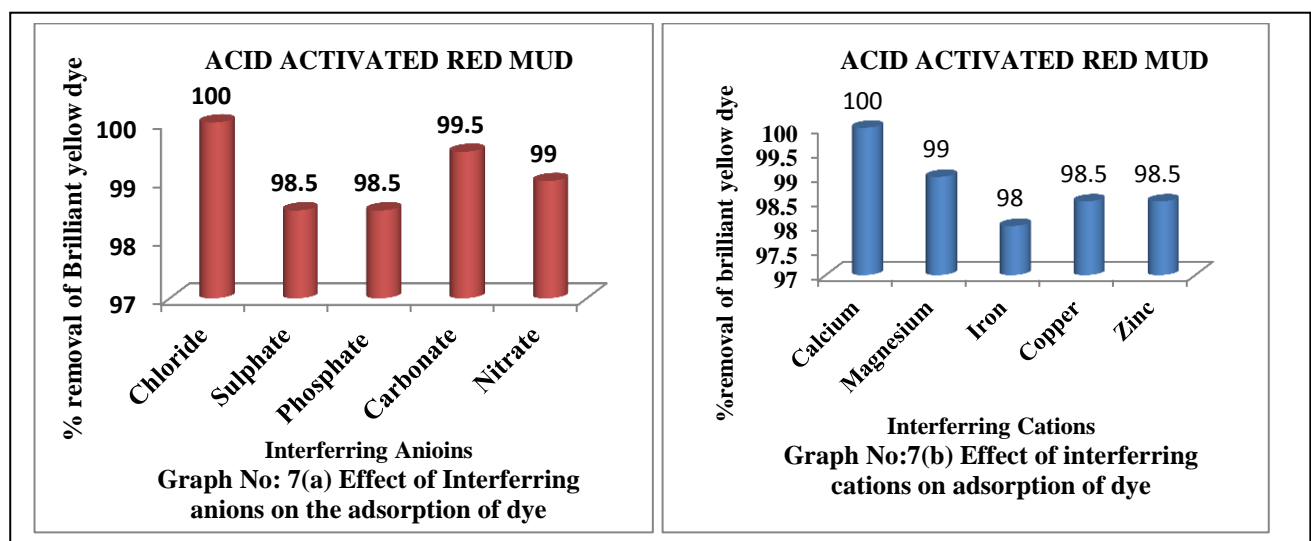
**Table No: 2 Thermodynamic Parameters of Adsorption of dye on acid activated red mud**

$\Delta H$ (KJ/mole)	$\Delta S$ (KJ/mole)	$\Delta G$ (KJ/mole)				R2
19.94	81.27	-4.677 (303k)	-5.490 (313k)	-6.303 (323k)	-7.115 (333k)	0.993

The negative values of  $\Delta G$  indicate that the adsorption of the dye is feasible and spontaneous in nature. The positive value of  $\Delta H$  (19.94 kJ/mol) reflect the endothermic nature of the adsorption process. The positive  $\Delta S$  value reflects an increase in randomness at the solid/solution interface with the increasing of temperature, which implies the more possible arrangement during the adsorption of the dye.

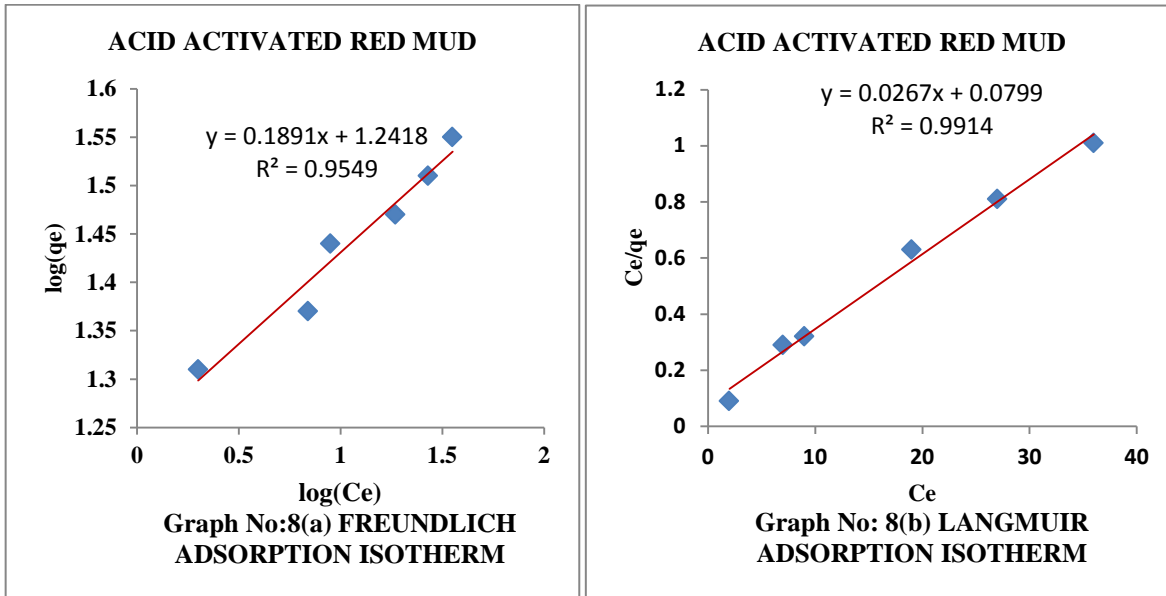
**3.6: Effect of Co-ions:**

The interference of co-ions (fivefold excess) on the % of extraction of the dye has been

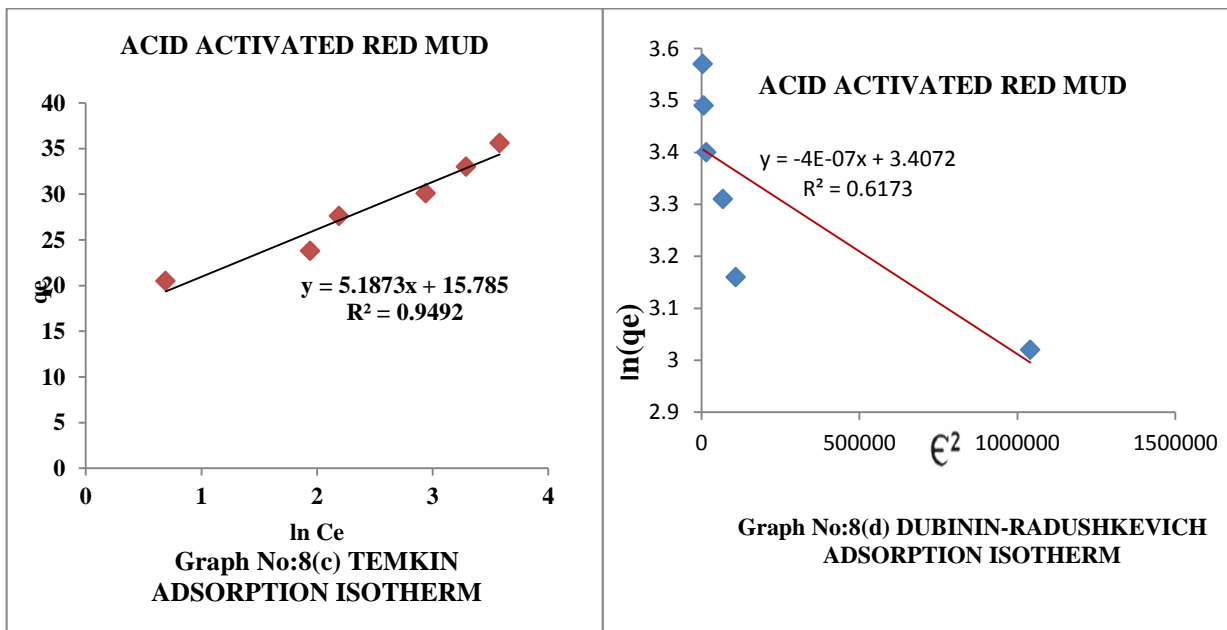


Presented in Graph No. 7a & b. It can be inferred from the data that the studied co-ions have either not interfered or marginally effected the % of extraction and at any condition, the % of extraction has not come down below 98.0%.

**3.7:Adsorption Isothems:**



Four well known adsorption isotherm models, Freundlich<sup>59</sup>, Langmuir<sup>60</sup>, Temkin<sup>61</sup> and Dubinin-Radushkevich<sup>62</sup> isotherms have been selected to evaluate nature of adsorption. Linear form of Freundlich equation is  $\log(q_e) = \log k_f + (\frac{1}{n}) \log C_e$ ; Linear form of Langmuir equation is  $C_e/q_e = (a_L/k_L)C_e + 1/k_L$ . According to Hall et al<sup>63</sup>, the nature of the adsorption process is unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) and irreversible ( $R_L = 0$ ) and the significant feature of the Langmuir isotherm model can be defined by the dimensionless separation factor,  $R_L = 1 / (1 + a_L C_i)$ . The linear plots of these two adsorption isotherms were as shown in Graph Nos :8a & b and isothermal constants along with the correlation coefficient values were presented in Table 3.





Freundlich isotherm  $\{\log (q_e) \text{ vs } \log (c_e)\}$  and Langmuir isotherm  $(C_e/q_e \text{ vs } C_e)$  have been presented in the Graph No. 8a and 8b respectively. The slope  $(a_L/k_L)$ , intercept  $(1/k_L)$ , and  $R^2$  and  $R_L$  values have been calculated and presented in the Table No. 3

$R^2$  values are: 0.9914 for Langmuir isotherm model and 0.9549 for Freundlich model indicating that the Langmuir isotherms are more suitable for describing the adsorption process. Further,  $R_L = 0.0290$  indicates that the adsorption of the dye is onto the surface of the adsorbent. Thus, the adsorption of the dye on the surface of the adsorbent is monolayer and homogeneous.

Further, the adsorption process is modeled with Linear form of Temkin equation:  $q_e = B \ln C_e + B \ln A$  where  $RT/b = B$  and Linear form of Dubinin-Radushkevich equation:  $\ln q_e = -\beta \varepsilon^2 + \ln q_m$ , where  $\varepsilon = RT \ln(1 + 1/C_e)$ . The linear plots of these two adsorption isotherms are depicted in Graph.No: 8c & d and isothermal constants along with the correlation coefficient values are presented in Table 2. The mean free energy (E) and heat of sorption (B) are characteristics of adsorption and as E value is less than 8 kJ/mol and B is less than 20 kJ/mol, the adsorption is "physisorption" in nature i.e. non-specific adsorption due long range weak Vander Waals forces.

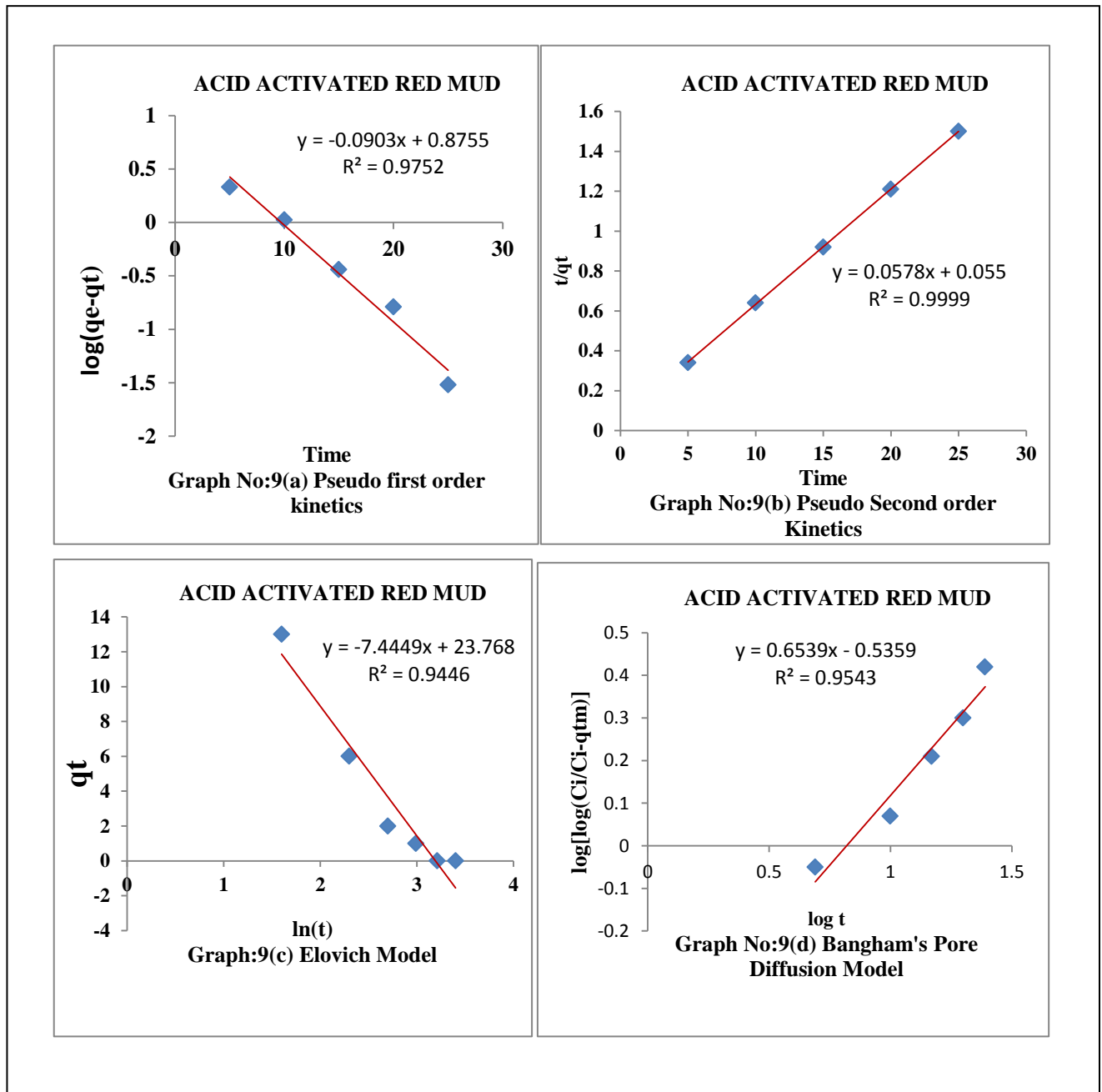
### 3.8: Adsorption kinetics:

**Table 3: Adsorption and Kinetic parameters**

S.No.	Adsorption and Kinetic parameters		Slope	Intercept	$R^2$
1.	Freundlich Isotherm		0.1891	1.2418	0.9549
2.	Langmuir Isotherm	$R_L = 0.0290$	0.0267	0.0799	0.9914
3.	Temkin Isotherm	$B = 5.1873$	5.1873	15.785	0.9492
4.	Dubinin-Radushkevich Isotherm	$E = 1.118$	-4E-07	3.4072	0.6173
5.	Pseudo- first-order model		-0.0903	0.8755	0.9752
6.	Pseudo-Second-order model		0.0578	0.055	0.9999
7.	Elovich Model		-7.4449	23.768	0.9446
8.	Bangham's pore diffusion model		0.6539	0.5359	0.9543

Kinetics of adsorption is studied using pseudo first-order model<sup>64,65</sup>, pseudo second-order model<sup>66,67</sup>, Bangham's pore diffusion model<sup>68,69</sup> and Elovich equations<sup>70,71</sup>. The pseudo first-order equation is  $\log (q_e - q_t) = \log q_e - k_1 t / 2.303$ ; the pseudo second-order equation is  $t/q_t = 1/k_2 q_e^2 - (1/q_e) t$ ; Bangham's pore diffusion equation is  $\log [\log (C_i/C_i - q_t/m)] = \log (k_0 / 2.303 V) + \alpha \log (t)$ ; Elovich equation is  $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$

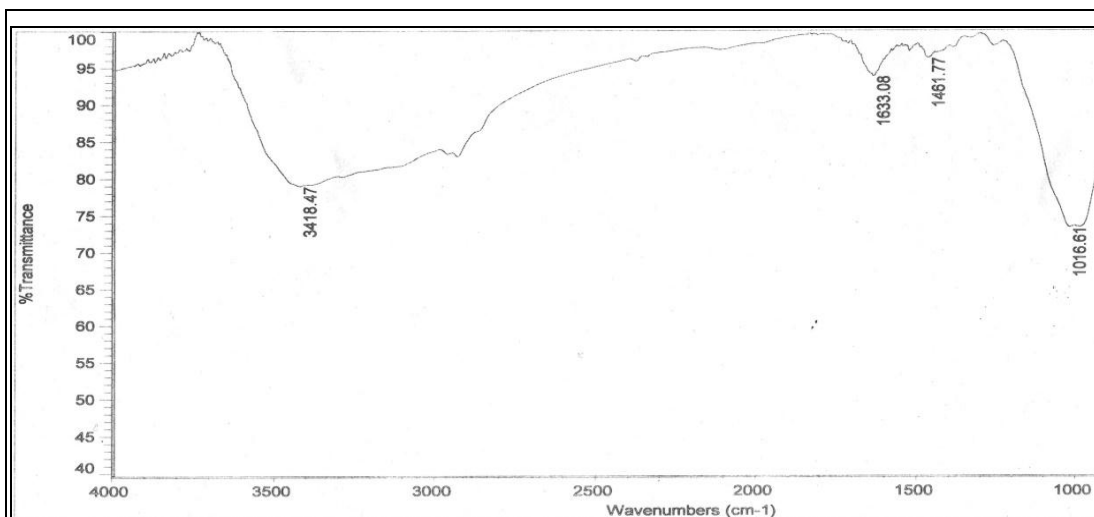
The data of these four kinetic models are presented in Graph Nos: 9-a to d, and rate constants along with the correlation coefficient values are presented in Table 3.



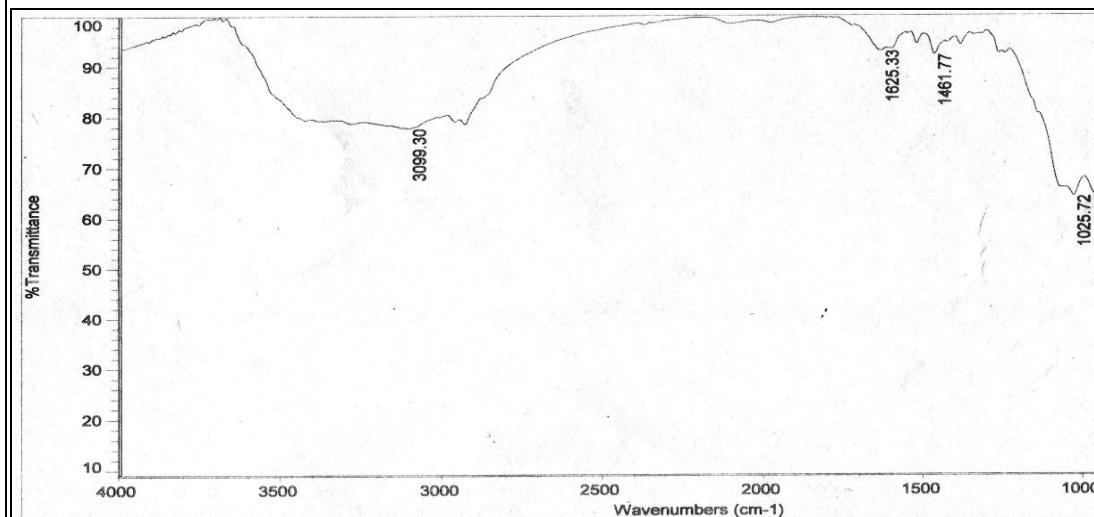
On perusal of the correlation coefficient ( $R^2$ ) values, it may be inferred that the kinetics of adsorption follows the order: pseudo second-order > pseudo first-order > Bangham's pore diffusion >> Elovich model. Hence, the adsorption kinetics can be well defined by pseudo second-order and least by Elovich model.

### 3.9: I R Spectral Data:

FTIR data before and after adsorption of the dye are presented in the Fig No. 2a&b. It is revealed from the data that the broad band around  $3418\text{ cm}^{-1}$  and the narrow band around  $1638\text{ cm}^{-1}$  assigned to the \OH stretching vibration and bending vibrations of adsorbed water are shifted to  $3099.30$  and  $1625.33\text{ cm}^{-1}$  respectively with decrease of intensity. This indicates the involvements of the -OH functional groups in the adsorption process. Further, the appearance of new bands in the range  $1380$  to  $1510\text{ cm}^{-1}$  (characteristics of aromatic nature) in the spectrum of dye adsorbed red mud indicate the presence of dye on the red mud. The shifting of band at  $1016.61\text{ cm}^{-1}$  pertaining to Si-O-Si, to  $1025.72$  and appearance of bands at  $960.46$  and  $800\text{ cm}^{-1}$  also indicated the sorption of the dye on the surface of the red mud.



**Figure 2a: FT-IR Analysis Report of Red mud Before adsorption**



**Figure 2b: FT-IR Analysis Report of Red mud After adsorption**

**4: Applications**

The procedures developed in this investigation were applied to the samples collected from effluents of textile industries at Mangalagiri and Machilipatnam of Andhra Pradesh. The samples were analyzed for the actual amounts of the said dye and then the samples were fed with known amounts of the dye.

**Table No:4 Removal of color in swages of dyeing industries**

S. No.	Water samples	C <sub>i</sub> (mg/lit) (initial concentration of dye)	C <sub>f</sub> (mg/lit) (concentration of dye after removal)	% Removal
1	Sample 1	50	0	100
2	Sample 2	62	5	91.9
3	Sample 3	75	9	88
4	Sample 4	100	21	79

Then these samples were subjected to extraction adopting the methodologies developed in this work. The obtained results were presented in the Table No. 4. It can be seen from the table that the procedure developed in this work successfully remove the said anionic dye.

## 5: Conclusions

- The adsorption nature of Activated red mud towards anionic dye, Brilliant Yellow Dye, has been investigated by varying various physicochemical parameters such as pH, sorbent concentration, agitation time, temperature and initial concentration of the dye. Batch methods of extractions have been adopted using simulated water. The extraction conditions are optimized for the maximum removal of the dye.
- Complete removal of the dye is observed pH:2; extraction time: 25 minutes; 250 rpm, temp: 30<sup>0</sup>C, initial conc. of the dye: 100 ppm and sorbent dosage: 0.6 g/100ml.
- Fivefold excess of co-ions normally exists in sewages viz., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup> and Cu<sup>2+</sup> have shown marginal interference.
- The adsorption data is analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. Correlation coefficient (R<sup>2</sup>) and dimensionless separation factor (R<sub>L</sub>) values have confirmed that adsorption obeys Langmuir adsorption (R<sup>2</sup>: 0.9914; R<sub>L</sub>: 0.0290) indicating monolayer formation while Temkin isotherm and Dubinin-Radushkevich isotherms indicate that the adsorption is 'physisorption' in nature.
- Pseudo-first-order, pseudo-second-order, Bangham's pore diffusion and Elovich equations have been applied to identify the kinetics of adsorption process and found that adsorption follows pseudo-second-order kinetics.
- The thermodynamic study revealed that adsorption of the dye is an endothermic process and the adsorption increases with increase in temperature.
- The procedures developed in this investigation have been applied to the samples collected from the effluents of textile industries and found to be successful.

## Acknowledgement:

The authors thank the Ministry of Environment & Forests (MOEF), New Delhi, for granting the project entitled "Red mud as an adsorbent for the removal of pollutants" (File No: 19/16/2014-RE) and under whose financial aid, this work has been carried out.

## 6: References

1. O. Sree Devi, K. Ravindhranath, Control of Chromate in Polluted Waters: A Biological Approach, *Indian Journal of Environment Protection*, 2012, 32(11), 943-951.
2. A. Naga Babu, G.V. Krishna Mohan, K Ravindhranath, Removal of Chromium (VI) from Polluted waters Using Adsorbents Derived from Chenopodium Album and Eclipta Prostrate Plant Materials, *International Journal of ChemTech Research*, 2016, 9 (3): 506-516.
3. Y. HanumanthaRao, K. Ravindhranath, New bio-sorbents in the extraction of Chromium (VI) from polluted waters, *Der PharmaChemica*, 2015, 7(12):286-298.
4. K.P.C. Sekhar, R. V. Vishnu Babu, D. Srividhya, K. Ravindhranath, Removal of Chromium (VI) from Waste Waters Using Leaves Powders of Justicia adhatoda, Cissus quadrangularis, Soapnut Acacia, *Der PharmaChemica*, 2012, 4 (2):664-673.
5. K. Papodu, Y HanumanthaRao, K. Ravindhranath, Removal of Zinc from waste waters using new biosorbents derived from Terminalia arjuna, Atlantia monophylla(L) correa and Madhuca Indica plants, *Der PharmaChemica.*, 2014, 6(6):19-34
6. Y. HanumanthaRao, G. V. Krishna Mohan, K. Ravindhranath, Extraction of zinc from polluted waters using bio-sorbents derived from Prosopis cineraria, Tephrosia purpurea and Justicia adhatoda plants, *Journal of Chemical and Pharmaceutical Research.*, 2015, 7(9), 794-808.
7. Anna Aruna Kumari, K. Ravindhranath, Extraction of Aluminum (III) Ions from Polluted Waters Using Bio-Sorbents Derived from *Acacia Melanoxylon* and *Eichhornia Crassipes* Plants, *Journal of Chemical and Pharmaceutical Research.*, 2012, 4 (5), 2836-2849.
8. Anna Aruna Kumari, K. Ravindhranath, Extraction of Aluminum (III) Ions from Polluted Waters Using New Bio-Sorbents, *Asian Journal of Research in Chemistry.*, 2012, 5(7), 882-892.

9. Anna ArunaKumari, K. Ravindhranath, Removal Of Aluminum (III) Ions From Polluted Waters Using Bio-Sorbents Derived From *MoryngeaMillingtonia* And *CygiumArjunum* Plants, *International Journal of ChemTech Research.*, 2012,4(4), 1733-1745.
10. Anna ArunaKumari, K. Ravindhranath , *Removal Of Aluminium (III) From Polluted Waters Using Biosorbents Derived From Achiranthusaspera And Cassia Occidentalis* , *International Journal of Water Resources and Environmental Sciences.*, 2012, 1(1): 08-19
11. M. Suneetha, B. SyamaSundar, K. Ravindhranath, Removal Of Fluoride From Polluted Waters Using Active Carbon Derived From Barks Of VitexNegundo Plant, *Journal of Analytical Science and Technology.*, 2015, 6:15.
12. M. Suneetha, B. SyamaSundar, K. Ravindhranath, Studies on fluoride removal from polluted waters using active carbon derived from stems of abutilon indicum plant, *J of Chemical and Pharmaceutical Research.*, 2014, 6(10), 574-592.
13. M. Suneetha, B. SyamaSundar, K. Ravindhranath, Ground Water Quality Status with Respect to Fluoride Contamination in VinukondaMandal, Guntur District, Andhra Pradesh, India and Defluoridation with Activated Carbons, *International Journal of ChemTech Research.*, 2014-15, 07(01), 93-107
14. M. Suneetha, B. SyamaSundar, K. Ravindhranath, Extraction Of Fluoride From Polluted Waters Using Low-Cost Active Carbon Derived From Stems Of AcalyphaIndica Plant, *Asian Journal of Water, Environment and Pollution.*, 2015, 12(3), 33-49.
15. M. Suneetha, B. SyamaSundar, K. Ravindhranath, Defluoridation Of Waters Using Low-Cost HnO<sub>3</sub> Activated Carbon Derived From Stems Of SennaOccidentalis Plant, *International Journal of Environmental Technology and Management.*, 2015, 18 (3), 420-447.
16. Hanumantharao, Medikondur Kishore, K. Ravindhranath, Characterization and Adsorption Studies Of "LagenariaSiceraria" Shell Carbon for the Removal of Fluoride, *International Journal of ChemTech Research.*, 2012, 4(4), 1686-1700.
17. V. Hanumantharao, Medikondur Kishore, K. Ravindhranath, Characterization And Defluoridation Studies Using Activated *Acacia Farnesiana* Carbon As Adsorbent, *Electronic Journal of Environmental, Agricultural and Food Chemistry.*, 2012, 11(5), 442-458.
18. M. Suneetha, K. Ravindhranath, Extractability of nitrites from polluted waters using bio-sorbents derived from leaves, barks or stems of some herbal plants, *J of Chemical and Pharmaceutical Research.*, 2014, 6(8), 408-420.
19. M. Suneetha, K. Ravindhranath, Removal of Nitrite from Polluted Waters using Bio-sorbents derived from Powders of Leaves, Barks or Stems of Some Herbal Plants, *International Journal of Chemical, Environmental and Pharmaceutical Research.*, 2012, 3(1), 24-34.
20. M. Suneetha, K. Ravindhranath, Ashes Of Leaves of Some Plants As Bio-Adsorbents in the Control of Nitrate Pollution in Waste Waters, *Journal of Pharmaceutical And Biomedical Sciences.*, 2012, 25(25), 322-329.
21. K. Pameela Rani, K. Ravindhranath, The Use of Bio-Adsorbents Derived From Cassia Auriculata, CelastrusPaniculata And Carmona Retusa In The Removal Of Ammonia From Polluted Waters, *Der PharmaChemica.*, 2014, 6(3), 56-63.
22. M. Suneetha, K. Ravindhranath, Removal of ammonia from polluted waters using biosorbents derived from powders of leaves, stems or barks of some plants, *Der PharmaChemica.*, 2012, 4 (1), 214-227.
23. K. Pameela Rani, K. Ravindhranath, Removal Of Ammonia From Polluted Waters Using New Bio-Sorbents, *Journal of Chemical and Pharmaceutical Research.*, 2014, 6(5), 889-900.
24. Y. HanumanthaRao, K. Ravindhranath, New methodologies in phosphate pollution control: using biosorbents derived from *Terminaliaarjuna* and *Madhucaindica* plants, *International Journal of ChemTech Research*, 2015, 8(12), 784-796.
25. M. DivyaJyothi, K. RohiniKiran, K. Ravindhranath, New Bio-Sorbents in the Control of Phosphate Pollution in Waste Waters, *International Journal of Applied Environmental Sciences.*, 2012, 7 (2), 127-140.
26. B. Srinivasa Reddy, K. Ravindhranath, Leaves and barks of some plants as bio-adsorbents in the control of methylene blue dye from waste waters, *International J of Chem. Tech Research.*, 2014, 6(14), 5612-5624.
27. ShaikKarimullaY. HanumanthaRao, and k. Ravindhranath , Removal of Methyl Orange Dye from Polluted Waters Using Bio-Adsorbents Derived from *Aeschynomeneaspera* and *Ficusreligiosa* Plants, *International Journal of Research in Chemistry and Environment*, 2014, 4(4), 124-136.

28. B. Srinivasa Reddy, B. Krishna Veni, K. Ravindhranath, Removal Of Methylene Blue Dye From Waste Waters Using New Bio-Sorbents Derived From Annona Squamosa And Azadiracta Indica Plants, *Journal of Chemical and Pharmaceutical Research.*, 2012 , 4 ( 11), 4682.
29. Shaik Karimulla, K. Ravindhranath, Extraction of Methyl Orange Dye from Polluted Waters using Bio-Sorbents Derived From Thespesia Populnea and Pongamia Pinnata Plants, *Der PharmaChemica.*, 2014, 6(4), 333-334.
30. K. G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of Methylene Blue adsorption on Neem (Azadiracta indica) leaf powder, *Dyes Pigment.*, 2005, 65, 51-59.
31. B. Srinivasa Reddy, K. Ravindhranath, New bio-sorbents in the extraction of methylene blue dye from waste waters, *Der Pharmacia Lettre.*, 2015, 7 (1), 159-171.
32. Y. Hanumantha Rao, K. Rohini Kiran, K. Ravindhranath, Extraction of Some Pollutive Ions Using Different Biomasses in Oxidation Ponds, *J of Chemical and Pharmaceutical Research.*, 2014, 6(9), 48-54.
33. H. Soner Altundog˘an, Sema Altundog˘an, Fikret Tu˘men, Memnune Bildik, Arsenic removal from aqueous solutions by adsorption on red mud, *Waste Management*, 2000, 20, 761±767.
34. Shuwu Zhang, Changjun Liu, Zhaokun Luana, Xianjia Peng, Haijing Rena, Jun Wang, Arsenate removal from aqueous solutions using modified red mud, *Journal of Hazardous Materials*, 2008, 152, 486–492.
35. Ghorbani, M. Nazarfakhari, Y. Pourasad and S. Mesgari Abbasi, Removal of Pb ion from water samples using red mud (bauxite ore processing waste), *EDP Sciences*, 2014
36. Vinod K. Gupta, Monika Gupta and Saurabh Sharma, Process development for the removal of Lead and Chromium from aqueous solutions using red mud-An aluminium industry waste, *Water Research*, 2001, Vol. 35, No. 5, 1125–1134.
37. Min Ma, Yifeng Lu, Rongzhi Chen, Lan Ma, Ying Wang, Hexavalent Chromium Removal from Water Using Heat-Acid Activated Red Mud, *Open Journal of Applied Sciences*, 2014, 4, 275-284.
38. Hayrunnisa Nadaroglu and Ekrem Kalkan, Removal of cobalt (II) ions from aqueous solution by using alternative adsorbent industrial red mud waste material, *International Journal of Physical Sciences*, 2012, 7(9), 1386 – 1394.
39. Ramesh Chandra Sahu, Rajkishore Patel, Bankim Chandra Ray, Adsorption of Zn(II) on activated red mud: Neutralized by CO<sub>2</sub>, *Desalination*, 2011, 266, 93–97.
40. Sujata Kumar, Dhanesh Singh, Saroj Kumar, Red Mud as Low Cost Adsorbent for Zn(II) ion – Kinetic, Thermodynamic and Equilibrium Study, *American International Journal of Research in Formal, Applied & Natural Sciences*, 2014, 2328-3793.
41. Sukru DURSUN, Dunyamin GUCLU, Mehmet BAS, Phosphate removal by using activated red mud from Seydisehir Aluminium Factory in Turkey, *J. Int. Environmental Application & Science*, 2006, vol-1 (3&4), 98-106.
42. A.M. Baraka, Marwa M. EL-Tayieb, Maha El Shafai, Nouran Yussri Mohamed, Sorptive Removal of Phosphate From Wastewater Using Activated Red Mud, *Australian Journal of Basic and Applied Sciences*, 2012, 6(10): 500-510.
43. Weiwei Huang, Shaobin Wang, Zhonghua Zhua, Li Li, Xiangdong Yao, Victor Rudolph, Fouad Haghseresht, Phosphate removal from wastewater using red mud, *Journal of Hazardous Materials*, 2008, 158, 35–42.
44. Hamidreza Gharibia, Abolghasem Alighardashib, Shahram Rayganc, Abbas Akbarzadehd, Use of Alumina Producing Waste (Red Mud) As an Adsorbent to Remove Nitrate from Water, *Hydrometallurgical Processes*, 2014.
45. G.M. Ratnamala, K. Vidya Shetty, G. Srinikethan, Optimization studies for removal of Remazol Brilliant Blue dye from aqueous solution using acid treated red mud, *International Journal of Current Engineering and Technology*, 2013.
46. Luyi Zhang, Huayong Zhang, Wei Guo, Yonglan Tian, Removal of malachite green and crystal violet cationic dyes from aqueous solution using activated sintering process red mud, *Applied Clay Science*, 2014, 93-94, 85–93.
47. Shaobin Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, *Water Research*, 2005, 39, 129–138.
48. B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, *Journal of Hazardous Materials.*, 2009, 164, 870–875.

49. S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design, *Water Research.*, 2012, 46, 1933–1946.
50. L.G. Devi, K.E. Rajashekhar, K.S.A. Raju, S.G. Kumar, Kinetic modeling based on the non-linear regression analysis for the degradation of Alizarin Red S by advanced photo Fenton process using zero valent metallic iron as the catalyst, *Journal of Molecular Catalysis A Chemistry.*, 2009, 314, 88–94.
51. A R K Trivedy, *Pollution Management in Industries*, Environmental Publications, 2<sup>nd</sup> Ed. (1995), Karad, India.
52. Gerard Kiely., *Environmental Engineering*, McGraw-hall International Editions 1998.
53. Metcalf and Eddy. *Wastewater Engineering: Treatment of Reuse*. 4th. Ed McGraw Hill Co., New York, 2003.
54. G. Alagumuthu, M. Rajan, Kinetic and equilibrium studies on fluoride removal by zirconium (IV)-impregnated ground nutshell carbon, *Hem. Ind.*, 2010, 64(4), 295-304.
55. G. Karthikeyan, S. Siva Elango, Fluoride sorption using MoringaIndica-based activated carbon, *Iran J. Environ. Health. Sci. Eng.*, 2007, 4(1), 21-28.
56. M. Sekar, V. Sakthi, S. Rengaraj, Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell, *J. Colloid Interface Sci.*, 2004, 279, 307-313.
57. M. Horsfall, A. Spiff, Effects of temperature on the sorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solution by *Caladium bicolor* (Wild Cocoyam) biomass, *J. Biotechnol.*, 2005, 8, 162-169.
58. N. Viswanathan, S. Meenakshi, Enriched fluoride sorption using alumina/chitosan composite, *J. Hazard. Mater.*, 2010, 178, 226-232
59. H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.*, 1906, 57, 385-471.
60. Langmuir, The adsorption of gases on plane surfaces of glass, mica, and platinum, *J. Am. Chem. Soc.*, 1918, 40, 1361-1368.
61. Maryam Fayazi, Masoud Ghanei Motlagh, Mohammad Ali Taher, The adsorption of basic dye (Alizarin red S) from aqueous solution on to activated carbon/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nano-composite: Kinetic and equilibrium studies, *Materials Science in Semiconductor Processing.*, 2015, 40, 35–43
62. Lulu Fana, Ying Zhang, Xiangjun Li, Chuannan Luo, Fuguang Lua, Huamin Qiu, Removal of alizarin red from water environment using magnetic chitosan with Alizarin Red as imprinted molecules, *Colloids and Surfaces B: Biointerfaces.*, 2012, 91, 250–257
63. Hall, K.R., Eagleton, L.C. Acrivos, A. and Vermevlem, T. (1966), Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Ind. Eng. Chem. Fundam.*, 5, 212-219.
64. G. Ravindra Kumar, Ackmez Mudhoo, Ch. Mahesh Chandra, Kinetic, equilibrium, thermodynamic studies and spectroscopic analysis of Alizarin Red S removal by mustard husk, *Journal of Environmental Chemical Engineering.*, 2013, 1283–1291.
65. M. Ghaedi, A. Hassanzadeh, S. Nasiri Kokhdan, Multiwalled carbon nanotubes as adsorbents for the kinetic and equilibrium study of the removal of Alizarin Red Sand morin, *Journal of Chemical & Engineering Data.*, 2011, 56, 2511–2520.
66. Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.*, 1999, 34, 451–465.
67. B. Ahmad, Chirangano Mangwandi, *Journal of Environmental Management.*, 2015, 164, 86-93
68. V.E.M. Filho, A.L.B. Marques, J. Zhang, G.O. Chierice, Surface complexation of copper(II) with Alizarin Red S adsorbed on a graphite electrode and its possible application in electroanalysis, *Electroanalysis.*, 1999, 11, 1130–1136.
69. J. Kurepa, T. Paunesku, S. Vogt, H. Arora, B.M. Rabatic, J. Lu, M.B. Wanzer, G.E. Woloschak, J.A. Smalle, Uptake and distribution of ultrasmall anatase TiO<sub>2</sub> Alizarin Red S nanoconjugates in *Arabidopsis thaliana*, *Nano Letters.*, 2010, 10, 2296–2302.
70. S. Lagergren, About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 1898, 24(4), 1-39.
71. Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, *Sep. Purif. Methods*, 2000, 29, 189-232.

\*\*\*\*\*