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Adsorption of Reactive Blue 4 (RB4) onto Rice Husk in Aqueous Solution

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Abstract— Now is the era of development in science and technology and along with those developments environment pollution is one of the major problem we have to face especially in textile and dying sectors, where huge amount of various dye stuff is used. Untreated disposal of such dye contaminated water creates environmental problem in nature. Rice husk can be used as a natural adsorbent to remove those harmful dye stuff from aqueous solution. This study showed that Reactive Blue 4 (RB4) which is widely used in dying industry as blue color can be removed remarkably by Rice Husk. Adsorption method which is very cost effective was used in the process. The adsorption process was endothermic in nature and it was spontaneous. The experimental results showed that the whole process was favorable and Rice Husk is really a useful natural low cost adsorebent.

Index Terms— Adsorption, Dyes, Endothermic, Isotherm, Langmuir, Reactive Blue, Rice Husk, Spontaneous.

1 INTRODUCTION

Textile and dyeing industries are most water consuming industry and they pollute environment by discharging effluent without proper treatment. These waste water contain huge chemicals which are mutagenic/carcinogenic and gentoxic **[1]**. Dyes varies in nature such as anionic and cationic. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate (SO_3^-) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups. Many treatment methods are available to remove dyes from wastewater, which can be divided into
physical, chemical, and biological methods **[2]**. Although chemical and biological methods are effective for removing dyes, they require specialized equipment and are usually quite energy intensive; in addition, large amounts of byproducts are often generated. Generally, physical methods which include adsorption, ion exchange, and membrane filtration are effective for removing reactive dyes without producing unwanted by-products **[3]**.. These include physicochemical methods such as filtration, coagulation, use of activated carbon and chemical flocculation **[4, 5]**. These methods are effective but they are not cheap and involve the formation of a concentrated sludge that creates a secondary disposal problem which requires safe disposal. Among all these methods adsorption has able to receive attention for decolorization of waste waters. It is most economical and effective treatment methods **[6-8]**. Many substances like activated carbon, diatomite, silica, dolomite, Fuller's earth, bentonite, zeolite, peat, lignite, and dyeing industries are most water consuming industry and they pollute environment by discharging effluent without proper treatment. These waste water contain huge chemicals which are mutagenic/carcinogenic and gentoxic [1]. Dyes varies in nature such as anionic and cationic. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate (SO3-) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups. Many treatment methods are available to remove dyes from wastewater, which can be divided into physical, chemical, and biological methods [2]. Although chemical and biological methods are effective for removing dyes, they require specialized equipment fly ash, clay, mud, coal etc. have received considerable interest because of their local availability and effectiveness. Use of biosorbent like baggase **[9],** banana pith **[10]**, sawdust **[11],** leaf powder **[12]**, chitin **[13]** and chitosan [**14]** etc. have been found to be highly effective, cheap and eco-friendly for adsorption of organic pollutants from wastewater. Recently scientists are able to find more and more materials **[15-22]** to adsorb colour from aqueous solution.

In this study untreated rice husk was used as a low-cost adsorbent to adsorb reactive blue 4 (RB4) from aqueous solution. The influence of pHs, solution temperature, concentration, ionic strength, desorption and reuse were studied in batch mode. Various models were tested to investigate the adsorption kinetics and equilibrium adsorption behavior.

2 Experimental

2.1 Materials

Rice husk was collected from local market and crushed them to make. The Reactive Blue 4 (RB4) was obtained from Sigma-Aldrich Germany and was used without purification. The chemical structure of RB4 is shown in Fig: 1.

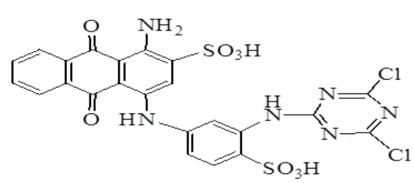

Figure: 1 Chemical structure of Reactive Blue 4 (RB4)

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All other reagents and solvents were commercially available and highest grade of purity; hence they were used without purification. Deionized water was prepared by passing distilled water through a deionizing column (Branstead, Syboron Corporation, boston. USA).

2.2 Batch adsorption experiments

Batch adsorption experiments were carried out to determine the extent of adsorption at various pH, concentrations, ionic strengths and temperatures.

2.3 pH effect

The effect of pH on the adsorption kinetics of RB4 on to rice husk was examined by mixing 0.1 g of rice husk powder with 25 mL of RB4 (100.13 μmole/L) solution with the pH ranging from 2 to 10. A thermostated shaker was used at a speed of 120r/min for equilibrium time. The samples were withdrawn at desired inter intervals. The pH of the samples was adjusted either by adding micro liter quantities of 1 mol/L M HCl or 1 mole/L NaOH and studied by batch adsorption experiment.

2.4 Initial concentration effect

The effects of initial dye concentration on the adsorption were observed under various concentration of RB4 solution (123.13 - 2137.50 μ mole/L) and other fixed operating conditions (30°C, and at pH-2). 0.1 g of rice husk powder with 25 mL of that each RB4 solution. The samples were withdrawn at desired inter intervals from the shaker. The sorbent was separated by centrifugation and the supernatants were analyzed using spectrophotometer

2.5 Ionic strength effect

The effects of ionic strength were observed under various ionic strength (0.01M, 0.05M, 0.10M, 0.15M and 0.20M) of KCl solution and other fixed operating conditions (30°C, initial concentration 98μ mole/L, and at pH-2) of the dye solution).

2.6 Temperature effect

Temperature effect on the adsorption of RB4 onto rice husk were performed at 30, 35, 40 and 45^{o}C at the initial concentration of 100μmole/L (30°C, pH2). Batch adsorption method was followed.

2.7 Isotherm experiments

Equilibrium adsorption of RB4 was investigated at 30°C with 0.1g of rice huskin contact with 25ml of RB4 solution of concentration ranging from 102-2512.50 μmol/L at pH2. Agitation time was 150 min. The dye solution was separated from the adsorbent by centrifuging. The equilibrium concentration of the remaining dye was determined by spectrophotometrically.

2.8 Desorption experiments

For desorption study 0.1g of that complex was taken in to a shaking bottle with 25ml of 0.1M NaOH solution for 180 min and batch adsorption method was followed.

2.9 Reuse experiments

For reuse study 0.1g of that residue was taken in to a shaking bottle with 25ml of 1087.50μmol/L concentration of dye solution for 180 min, also maintained pH2 and batch adsorption process was followed.

2.10 Calculation

The amount of RB4 adsorbed onto rice huskq_t (μmole/g) at any time t and q_e (μmole/g) at equilibrium were determined from the following relationships:

$$q_t = V(C_0 - C_t)/m \quad (1)$$

and

$$q_e = V(C_0 - C_e)/m \quad (2)$$

where C_0 (μ mole/L), C_t (μ mole/L), C_e (μ mole/L), are the liquid-phase concentrations of RB4at initial, at any time t, and equilibrium, respectively; V (L) is the volume of RB4solution and m (g) is the amount of dry rice husk power used.

3 Results and discussion

3.1 Determination of point zero charge (pH_{pzc})

Point zero charge of rice husk was detrmined and it was 5.85. This information helps us to understand the behavior of the surface of rice husk at certain pH such as pH < 5.85 the surface of the rice husk will be positively charged whereas pH > 5.85 the surface of the rice husk will be negatively charged.

3.2 FTIR Analysis

In the spectrum of the FTIR spectrum of RB4 (Figure is not given) the broad region around 3450.68 cm^{-1} can be assigned to overlapping of -OH stretch and -NH functional groups. The peak at 2924.89 and 1654 cm^{-1} (not marked) which corresponds with C-H and C=O stretch, respectively. The band at 1290,89, 1224.13 and 1188.84 cm^{-1} correspond to the S=O stretching, peaks at 796.46 cm^{-1}, 765.20 cm^{-1} for –C-H stretching, 617.94 cm^{-1} –C-Cl stretching.

The FTIR spectra of Rice husk (before adsorption) (Figure is

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not given) the adsorption peaks at 3414.67 cm^{-1} for surface –OH stretching, peak at 2923.37 cm^{-1} for aliphatic C-H stretching, peak at 2852.62 cm^{-1} for aldehyde C-H stretching, peak at 1653.98 cm^{-1} for unsaturated group like alkene, peak at 1560.17 cm^{-1} for aromatic C-NO_2 cm^{-1} stretching, peak at 1077.57 cm^{-1} for Si-O stretching **[23]**.

In the FTIR spectra (Figure is not given) of the rice husk after adsorption of reactive blue 4 (RB4) Band at 3414.89 cm^{-1} attributed to O-H stretching and The band at 1290.89, 1224.13 and 1188.84 cm^{-1} correspond to the S=O stretching in the RB4 FTIR spectrum were absent in FTIR spectrum of rice husk after adsorption of RB4. Peak at 1077.57 cm^{-1} for Si-O stretching in the spectrum of rice husk shifted to 1042.86 cm^{-1} after adsorption of RB4.

This analysis concluded that the adsorption due to the interaction of Si-O groups of rice husk with $–SO3^{-}$ groups of RB4.

3.3 Effect of pH on the adsorption process

The pH is an important parameter for adsorption studies that affects not only the adsorption capacity but also the color and solubility of the adsorbate solutions. The effect of pH on the adsorption of RB4 by rice husk was studied in aqueous solution within pH range 2-10 as shown in Fig-2.

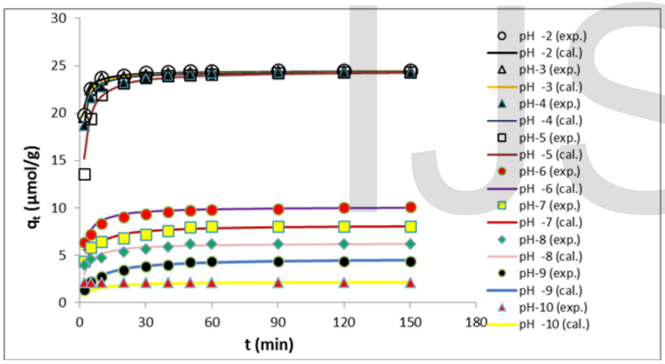

Figure: 2 pH effect on adsorption

The rate of uptake of RB4 on rice husk indicated that about 90-120 min was taken to reach the equilibrium time for all pHs. However, the data was taken for 150 min. to make sure that full equilibrium was established. Before the equilibrium time, it was observed that the initial rate of adsorption (***h***) of RB4 increases significantly with decreasing solution pH. Lower initial rate of adsorption observed at basic pH values is due to competition between the excess hydroxyl ions and the negatively charged RB4 ions for the sorption sites.

Figure: 2 Effect of pH

The experimental results suggest that the initial rate of adsorption (***h***) as well as the equilibrium adsorption capacity of rice husk is suitable at pH- 2 among the observed pH ranging from 2-10 and the initial concentration of RB4 solution was 100.13µmol/L. Similar type of result observe in the adsorption of fluoride using rice husk **[24]**. Results showed the percentage of adsorption increases with the decrease in pH (Table-1).

3.4 Effect of initial dye concentration on adsorption process

It was found that as the initial dye concentration was increased relative to a fixed sorbent dosage, the extent of adsorption increased (Table-1,**).** It indicated that the initial dye concentration was increased, the amount absorbed (q_t) increased for RB4 dye up to respective equilibrium contact time.

One of the possible reasons for such phenomenon is at lower dye concentration, solute concentrations to adsorbent sites ratio is higher, which cause an increase in color adsorption and at higher dye concentrations, solute concentrations to adsorbent sites ratio is lower due to the saturation of adsorption sites, which also results slower rate of color adsorption **[25].**The experimental data were listed in Table-1.The rapid uptake of dye particles at the beginning is due to the occurrence of solute transfer only due to sorbate and sorbent interactions with negligible interference due to solute–solute interactions. The percentage of adsorption increases with the decrease in concentration of the dye solution (Table-1).

3.5 Effect of ionic strength on dye adsorption

The result of the effect of ionic strength is shown in Table-1; it indicates that the higher the KCl concentration is, the lower the adsorption capacity (Figure is not given). Since the addition of KCl reduces the electrostatic interaction between rice husk and dye. This agrees with the prediction of the mechanism of electrostatic interactions.

The addition of salts allows the neutralization of the negative sites of dye molecules which help to lower the attraction force between surface of rice husk and dye molecule results decrease the adsorption. The percentage of adsorption decreases with the increase in ionic strength of the dye solution (Table 1).

3.6 Effect of temperature on adsorption process

Temperature is an important parameter that can influence the equilibrium and rates of sorption processes. This effect helps us to predict about the nature of the adsorption process. Fig: 7 shows the temperature change and the equilibrium capacity (q_e) of RB4 at 30, 35, 40 and 45°C at the initial concentration of 100 µmole/L. A larger amount of RB4 dye was removed by rice husk within 30 min of contact time. When the temperature is raised from 30°C to 45°C, the adsorption RB4 dye by adsorption onto Rice husk increased from 24.18 to 24.58 µmole/g indicating that the process is endothermic (Table-1). The increase in temperature of the system affects the solubility and particularly the chemical potential of the adsorbate dye which is

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known to be a controlling factor in the process of adsorption **[26-27].** Experimental value showed the percentage of adsorption increases with the increase in temperature (Table-1).

TABLE 1

% of Adsorption of reactive blue 4 (RB4) by 0.1g rice husk at various pH, concentrations, ionic strength and temperature of RB4 aqueous solution

At various pH, Initial concentration of RB4 solution 100.13 µmol/L	
pH	**% of Adsorption of Dye**
2	97.63
3	97.38
4	97.25
5	97.13
6	40.32
7	32.08
8	24.59
9	17.35
10	8.49
At various concentrations (µmol/L)	
123.13	96.55
559.38	33.85
1015.63	21.23
1603.13	16.41
2137.50	12.40
At various ionic strength (M), Initial concentration of RB4 solution 98 µmol/L	
0.01	97.57
0.05	97.07
0.10	96.68
0.15	96.43
0.20	94.01
At various temperature (°C), Initial concentration of RB4 solution 101.63 µmol/L	
30	95.45
35	96.19
40	96.43
45	97.05

3.7 Adsorption Kinetics

The study of adsorption kinetics gives the information about the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Three models were used to analyze the data those are pseudo first order Lagergren, pseudo second order kinetic models and Elovich model. Experimental data showed that pseudo second order kinetic model successfully describes the kinetics of dye adsorption because of relatively high R^2 value (0.999) (Figures are not given). Similar results for adsorption kinetics have also been observed in the cases of adsorption of RB5 onto chitosan and biosorption of reactive dyes such as reactive blue 2 (RB2), reactive yellow and ramazol black B on biomass.

3.8 Adsorption mechanism

It is known that a typical liquid/solid adsorption involves film diffusion, intraparticle diffusion and mass action. For physical adsorption mass action is a very rapid process and can be negligible for kinetic study. To determine the rate limiting step and corresponding rate constants, the kinetic data were further processed by the two diffusion models (intraparticle diffusion, Film diffusion). It was seen none of the linear plots at any concentration pass through the origin (Figures are not shown) which means both intraparticle diffusion and film diffusion may involve in the rate limiting steps of the adsorption of RB4 onto rice husk. The above conclusion suggests that all three mechanisms: intrinsic surface reaction, film mass transfer and intraparticle diffusion are rate-limiting steps**.**

3.9 Activation Parameters of the adsorption process

The activation energy (E_a) for the sorption RB4 dye on rice husk can be estimated by using Arhenius equation. In this work, activation energy of sorption process has been calculated using the values of rate constant (k_2) from a pseudo-second-order kinetic equation and using the appropriate solution temperatures (Table-1)**.** When $\ln k_2$ is plotted versus $1/T$ (Fig: 3), a straight line with slope ($-E_a/R$ is obtained).

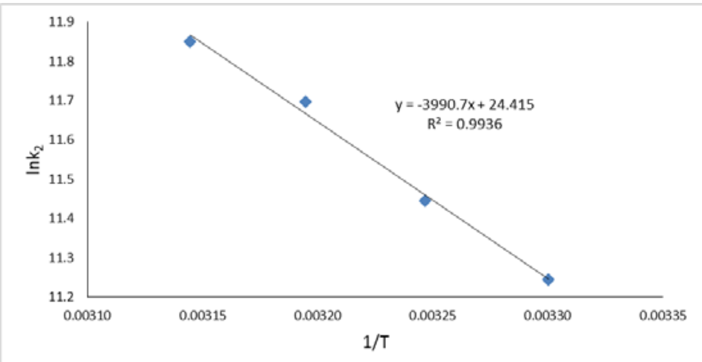

Figure: 3 Activation Parameters

Low activation energies (5–40 kJ/mole) are characteristics for physisorption, while higher activation energies (40–800 kJ/mole) suggest chemisorption. The value of E_a from the slopes of the plots is 33.18 kJ/mole for RB4 dye. Which indicated the adsorption process was physical type.

3.10 Adsorption isotherms

Adsorption isotherm of RB4 dye on rice husk at different temperatures was made by plotting equilibrium adsorp-

Isotherms	Parameters			
Tempkin				
Temperature (°C)	30	35	40	45
K_T (µmole/L)	2.59	3.61	8.09	7.66
b_T (J/mole)	0.003	0.003	0.003	0.003
R^2	0.769	0.842	0.906	0.900
Freundlich				
K_F ((µmol/g)(µmol/L)$^{-1/n}$)	1.41	1.55	1.82	1.82
b_F (J/mole)	0.56	0.55	0.57	0.57
n	1.77	1.77	1.81	1.79
R^2	0.906	0.886	0.843	0.842
Langmuir				
K_L (L/g)	8.10	9.28	11.60	12.58
a_L (µmole/L)	0.123	0.128	0.147	0.155
q_m (µmole/g)	65.79	72.46	78.74	81.30
R_L	0.00003	0.00003	0.00004	0.00005
R^2	0.999	0.999	0.999	0.999
Thermodynamic Parameters				
Temperature (K)	303	308	313	318
ΔG (kJ/mole)	-29.53	-30.11	-30.97	-31.59
ΔH (kJ/mole)	13.24			
Δ S(J/mole/K)	141.03			

tion capacity (q_e) of rice husk versus equilibrium concentration of dye in aqueous phase (C_e) (Fig: 12). It shows adsorption capacity increases with increasing temperature. This observation agrees with the temperature effect. The rise in adsorption capacity is due to the increase in collision frequency between adsorbent and adsorbate, which results in the enhanced adsorption onto the surface of the adsorbent. This enhancement may be due to the creation of new reaction sites or increased rate of inparticle diffusion of adsorbate molecules into the pores of the adsorbent at higher tempeture. Various isotherm equations such as Tempkin, Freundlich and Langmuir were used to describe the equilibrium characteristic of adsorption.

Experimental $\mathbf{R_L}$ values are listed in Table 2 which shows type of adsorption is favorable. K_T (µmol/L) is the Tempkin isotherm constant, b (J/mol) is a constant related to heat of adsorption. R (8.314 J/mol K) is an ideal gas constant and T is a absolute temperature (**K**). K_F ((µmol/g) (µmol/L)$^{1/n}$) and n are Freundlich isotherm constant indicating the capacity and intensity of the adsorption respectively. The values of K_L and a_L were computed from the slopes and y-intercepts of differentlinerarized plots of (C_e/q_e) versus C_e representing temperature (Figure is not shown). Examination of the data shows that the Langmuir adsorption isotherm provides a good description of data for RB4 dye over the whole temperature range studied in single systems since R^2 values from Langmuir isotherms (Table-2) are always greater than that of Freundlich isotherms (Table-2) and Tempkin isotherm (Table-2). Thus, it can be concluded that monolayer adsorption is occurred in this study. This also suggests that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. Thus, the equilibrium constants or binding constants (a_L) obtained from Langmuir isotherms are used to calculate the thermodynamic parameters for the adsorption process.

TABLE 2

Freundlich, Tempkin and Langmuir isotherm constants at different temperatures and thermodynamic parameters for the adsorption of RB4 onto rice husk from aqueous solution at pH 2

3.11 Thermodynamic parameters

The values of **ΔG, ΔH, ΔS** were calculated using Van't Hoff equation, from the slope and y-intercept of Van't Hoff plot of $\boldsymbol{ln a_L}$ *vs.* $\boldsymbol{1/T}$ (Fig: 4).

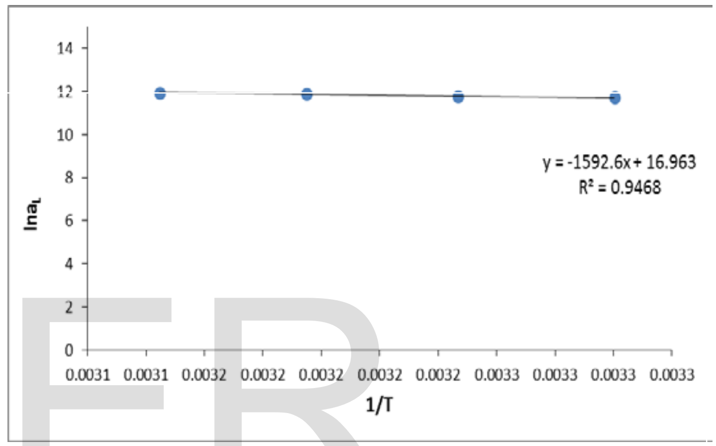

Figure: 4 Thermodynamic Parameters

Generally, a value of ΔH in between 5-40 kJ/mol is consistent with electrostatic interaction between adsorption sites and adsorbing ion (physical adsorption) while a value ranging from 40-800 kJ/mol suggests chemisorption **[28].**

The values of ΔH and ΔS are presented in Table-2. The results show that the changes in enthalpy, ΔH for the adsorption of RB4 by rice husk were 13.24 kJ/mol. ΔH suggests that the interaction of dye adsorbed by rice husk is endothermic which is supported by the increasing adsorption of the dye with the increasing temperature while a negative adsorption standard free energy change (ΔG) and a positive standard entropy change (ΔS) indicate that the adsorption reaction is a spontaneous process. These behaviors seem to be explained by the ionic nature of the dye-rice husk interaction. The positive value of ΔS indicates that the randomness increases at the solid--solution interface during the adsorption of dye onto the rice husk.

3.12 Desorption studies

Desorption studies help to understand the nature of adsorption and recycling of the spent adsorbent and the dye. RB4 desorbs in alkaline solution which suggests the ion exchange mechanism involved in the adsorption **[29].** Figures are not shown.

3.13 Reuse

This step was performed to study the probability and feasibility of rice husk as a reusable adsorbent. It is found that rice husk is as a reusable absorbent.

4 Conclusion

Present study shows that the rice husk can be used as an adsorbent for the adsorption of reactive blue 4(RB4) from its aqueous solution. The amount of dye sorbed was found to vary with pH, initial dye concentration, ionic strength and temperature. The amount of dye uptake (μmol/g) was found to increase with increase in initial dye concentration and solution temperature and decrease with increasing ionic strength. The results demonstrate the adsorption system studied belongs to the second-order kinetic model, Thermodynamic activation parameter shows that the process is endothermic. The negative value of the Gibbs energy change of the adsorption indicates that the adsorption is spontaneous. The positive value of the enthalpy change of the adsorption shows that the adsorption is an endothermic process. Thus, raising the temperature leads to increase adsorption at equilibrium. R_L (Table-2) values show the adsorption process is favorable. The kinetic data may be useful for environmental technologist in designing treatment plants for color adsorption from waste waters enriched with reactive blue 4(RB4). Rice husk has a high potential to adsorb RB4 from aqueous solutions. Therefore, it can be effectively used as an adsorbent for the adsorption of reactive blue4 (RB4) from waste waters.

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REFERENCES

[1] Olsen, *Water Res*.,**1987**, *21*, 517-522.
[2] S.A Muyibi, and A.M.S. Alfugara*Int. J. Environ. Studies*, **2003**, *60*(6), 617-626.
[3] T. Okuda, A.U. Baes, W. Nishijima, and Okada, *Water Res*., **1999**, *33*(15), 3373-3378.
[4] G.K. Folkard, J.P. Sutherland, and W.D. Grant, Natural coagulants as pilot scale. 18th WEDC Conf. Proceedings, 55-58.
[5] A. Ndabigengesere, S. Narasiah, *Water Res*. **1998**, *32* (3) 781-791.*Water Res*. *35*, 405-410.
[6] S.J. Allen and B. Koumanova, *J. Univ. Chem.Technol. Metallurgy*, **2005**, *40*(3), 175-192.
[7] A. Bousher, X. D. Shen and R. G. J. Edyvean, *Water Res*., **1997**, 31, 2084-2092.
[8] S. S. Nawar and H. S. Doma, *Sci. Total Environ*. **1989**, *79*, 271.
[9] S. P. Raghuvanshi, R. Singh and C. P. Kaushik, *Applied Ecol. Environ. Res*., **2004**, *2*, 35-43.
[10] Namasivayam and N. Kanchana, *Chemospere*, **1992**, *25*, 1691-1705.
[11] V.K. Grag, R. Gupta, A. B. Vadar and R. Kumar, *Bioresour. Technol*., **2003**.*89*, 121-124.
[12] K.G. Bhattacharya, and A. Sharma, *Dyes and Pigments*, **2005**, *65*, 51-59.
[13] E. Longhinotti, F. Pozza, L. Furlan, M. Sanchez, M. Klug, M. C. M. Laranjeira, and V. T. Fávere, *J. Braz. Chem. Soc*., **1998**. *9*(5), 435-440.
[14] B. Smith, T. Koonce and S. Hudson, *Am. Dyestuff Reporter*, **1993**, *82*(10), 18-36.
[15] D.B. Jirekar, Arif Ali Pathan, Mazhar Farooqui, *Oriental J. Chem*. **2014**, *30*(3),1263-1269.
[16] N. Abdus-Salam and M. Buhari, *The Pacific J. Sci. Tecnol*. **2014**,*15*(1),232-244.
[17] T. Teka and S. Enyew, *Int. J. Innovation and Scientific Res.* **2014**,*8*(1), 106-111.
[18] H. Kumar and R. Kaur, *J. Mater Environ. Sci*. **2014**,*5*(6), 1830-1838.
[19] Z. Derakhshan, M. Ali Baghapour, M. Ranjbir, M. Framarzian, *Health Scope*, **2013**,*2*(3),136-144.
[20] VK. Gupta, R. Kumar, A. Nayak, TA Saleh and MA Barakat, *Adv. Colloid Interface Sci*, **2013**,193-194,24-34.
[21] M. Ghaedi, B. Sadeghain, AA. Pebdain, R. Sahraei, A. Daneshfar and C. Duran, *J. Chem. Eng.***2012**,*187*, 133-141
[22] K.Y. Foo, B.H. Hameed, *J. Chem. Eng*. **2012**,*184*, 57-65.
[23] Tarun Kumar Naiya, Biswajit Singha and Sunil Kumar Das, *International Conference on Chemistry and chemical process*, **2011**, *IPCBEE* 10.
[24] C.M. Vivek Vardhan, J. Karthikeyan, *Fifteenth International Water Technology Conference, IWTC-15*, **2011**, Alexandria, Egypt.
[25] N.C.G. Tan, Integrated and sequential anaerobic/aerobic biodegradation of azo dyes. PhD thesis, Wageningen University, Wageningen, The Netherlands, **2001.**
[26] M. P. Elizalde-Gonzalez, A A Pelaez-Cid, *Environ. Technol*, **2003**, 24, 821-829.
[27] G. Annadurai & M.R.V Krishanan *Indian j. Chem Technol*, **1997**, *(4)*, 217-222.
[28] M. Dogan, Alkan, O. Demirbas, Y. Ozdemir, C. Ozmetin, *Chem. Eng. J.* **2006**, 12489-101
[29] P.S. Shabudeen Syeed, *Res. J. Chem*.**2011**, ***1***(1).