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Adsorption of Commercial Dye (Red-Cls-Bar) Onto Ash Collected from Brick Kiln

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Abstract: In this paper low cost waste material, the ash collected from brick kiln was used as an adsorbing agent for the removal of reactive dye Red-Cls-Bar. The ash has been collected from brick kiln after coal combustion that is used as a fuel to fire the clay bricks. Adsorption experiments were performed as a function of contact time, pH, initial dye concentration, adsorbent dose and temperature. Removal efficiency was found to increase from 57.81 to 59.50 with decreasing adsorbent dose 1.5g to 0.5g, decreasing temperature 308K to 298K and increasing initial concentration 6ppm to 14ppm. The maximum adsorption of Red-Cls-Bar was obtained at pH=7 and contact time of 60 minutes. Adsorption data were modeled using the Langmuir, Freundlich and Tempkin isotherms. The correlation coefficient R² values of Red-Cls-Bar were calculated for Langmuir, Freundlic and Tempkin adsorption isotherms and these were found to be 0.988, 0.938 and 0.968 for Langmuir, 0.999, 0.885 and 0.771 for Freundlich and 0.788, 0.977 and 0.921 for Tempkin at 298K, 303K and 308K, respectively. Adsorption kinetic was evaluated by pseudo-first-order, pseudo-second-order, Elovich rate equations and intra-particle diffusion models. It was inferred that sorption follows pseudo-second-order kinetic model. The linear correlation coefficients were obtained to be 0.860, 0.874, 0.893, 0.950 and 0.974 for 6-14ppm at 298K, respectively. Thermodynamic parameters for sorption process were also found out. Spontaneous and endothermic nature of sorption was obtained due to negative value of free energy and positive value of enthalpy changes.

Key words: Isotherm • Kinetics • Thermodynamics • Sorption

INTRODUCTION

In Pakistan, the textile industry is the largest manufacturing industry. The textile industry of Faisalabad constitutes more than 65% of the textile export market. Large volumes of synthetic dyes are used by several industries including textile dyeing, paper and plastic matter. In almost all cases, the Pakistani industries (textile, paper, plastic, leather, food, cosmetic, etc) release their untreated or partially treated waste waters into municipal sewers or directly into nearby drains, rivers, stagnant ponds, lagoons, or lakes [1]. Most hazardous waste comes from industrial sources. The (Environmental Protection Agency) EPA specifies four different categories of hazardous wastes that are subject to regulation. A commercial chemical product that may be discarded used in the manufacture of drugs, detergents, lubricants, dyes and pesticides is one of those categories [2-3]. Especially the dyeing industry effluents not only

result in the need of treating the problematic waste water with high chemical and biological oxygen demands, suspended solids and toxic compounds, but also color that is perceived by human eyes at very low concentration [4]. Such waste water disposal may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at large scale [5].

Hence their removal from aquatic environment is important and subject of many scientific researchers. The methods of color removal from industrial effluents include biological treatment [6], coagulation [7], oxidation [8], hyper filtration [9] and adsorption [10]. Among the treatment options, adsorption appears to have considerable potential for the removal of color from industrial effluents [11, 12].

Adsorption can perform many separations that are impossible or impractical by conventional techniques such as distillation, absorption and even a membrane based system [13]. Applications for adsorption have been

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expanded rapidly because of sharply rising environmental or quality requirements and advances in adsorption quality have made it possible to many of those demands [14, 15]. The best known application of adsorption is the purification of municipal water at low cost level [16, 17]. The most important attributes of adsorbent to application of adsorption are capacity, selectivity, regeneratability, kinetics, compatibility and cost [18]. Adsorption is used for water and waste water treatment to remove hazardous organic compounds and those that impart odor or taste [19].

At present, there is a growing interest in using low cost sorbents for dye sorption. If a sorbent is inexpensive and ready for use, the sorption process will be a promising technique. Recently, many lingo-cellulosic materials had been used as low cost sorbent for removal of dyes from water, which included banana pith [20], coir pith [21], eucalyptus bark [22] and wheat straw [23], rice husk [24], pine sawdust [25], peanut hull [26], lemon peel [27], almond shell [28] and neem leaf powder [29]. Generally, dye sorption capacity of natural lingo-cellulosic materials is low and to improve their dye sorption capacity, these materials had been subjected to chemical modification [30, 31].

Activated carbon is the most widely used adsorbent for this purpose because of its extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity [32, 33]. However, commercially available activated carbons are very expensive and the laboratory preparation of activated carbons also accompanied by a number of problems such as combustion at high temperature, pore blocking and hygroscopicity. This has led to search for cheaper and simplest substituents.

In this work ash collected from brick kiln was used as an adsorbent to remove reactive Red-Cls-Bar dye from aqueous solution. The effect of adsorption parameters such as pH, adsorbent concentration, contact time and initial dye concentration adsorbed was studied. The purpose of the present work was to utilize new low cost sorbent for enhancing the treatment of environmental pollution and reducing the cost of pollution treatment.

MATERIALS AND METHODS

Preparation of Sorbent: The ash used as an adsorbent was collected in raw powdered form from brick kiln at Faisalabad. It was sieved to remove impurities, dirt particles and clinkers. The adsorbent was sieved for several times to get it pure and clean form. Moisture content in adsorbent was calculated using method

Velmurugan *et al.* [34] and that was found to be 1%. Bulk density of adsorbent was also measured [35] and it was found to be 0.479g.dm⁻³.

Preparation of Dye Solutions: The Red-Cls-Bar obtained from Arzoo textile mill (Faisalabad) Pakistan was used in commercial purity without further purification. Its colour was dark dull reddish. The stock solution was prepared by dissolving accurately measured 100 mg of dye in distilled water in 1000 ml measuring flask. The stock solution was further diluted to the desired concentrations. For absorbance measurements a UV-VIS spectrophotometer (1100 BMC Range is 300-1100 nm) was employed using silica cells of path length 1 cm. The maximum absorbance of Red-Cls-bar was measured at 540 nm. The concentration of solutions after adsorption was determined using Beer Lamberts law [36].

Adsorption Studies: Batch experiments were conducted by shaking 0.50g-1.50g ash with 50 ml of aqueous solution of each concentration (4ppm, 6ppm, 10ppm, 12ppm,14ppm) for 60 minutes in an electric shaker water bath (Glass - Col Iso 9001) at various temperatures. 0.1 M NaOH and 0.1 M HCl solutions were used to adjust required pH.

The adsorbed amount of dye was calculated using mass balance equation as following [37];

$$qe = \frac{Gi - Ge}{M} \times V \tag{1}$$

Where qe is the amount of dye adsorbed, Ci is the initial concentration of the dye solution, Ce is the equilibrium concentration in mg/L, V is the volume of the adsorbate solution and M is the mass of adsorbent.

RESULTS AND DISCUSSION

Effect of Contact Time: The optimum contact time is very important for determining the maximum possible adsorbate removal. Effect of contact time on the removal of Red-Cls-Bar at pH 7, adsorbent dose 0.50g by varying dye concentration from 6-14 ppm was shown in Fig 1. The percentage removal of Red-Cls-Bar was rapid in the beginning but it gradually decreased with time until it reached at equilibrium [38]. All the patterns were found to be same for all concentrations. The plot revealed that maximum percent removal of the Red-Cls-Bar took place after 60 minutes of shaking. The removal efficiency was higher in the beginning due to availability of larger surface area of adsorbent.

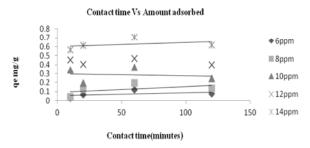


Fig. 1: Effect of contact time on the removal of Red-Cls-Bar (6-14ppm) onto Ash collected from brick kiln (0.50g) at room temperature (298K) and pH=7

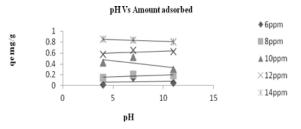


Fig. 2: Effect of pH on the removal of Red-Cls-Bar (6-14ppm) on Ash collected from brick kiln (0.50g) at room temperature (298K)

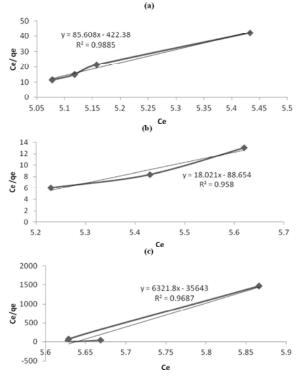


Fig. 3 (a-c): Langmuire isotherm for adsorption of Red-Cls-Bar (6-14ppm) onto Ash collected from brick kiln at pH=7 and at temperature (a) 298K (b) 303K (c) 308K

Effect of pH: Figure 2 shows the effect of the change in pH on the removal of Red-Cls-Bar, dose of adsorbent 0.50g and dye concentration 6-14 ppm at 298K. The percentage removal of Red-Cls-Bar was found to rapid in the beginning but it gradually decreased with increasing pH until it reached equilibrium [39]. The patterns of graphs are same for different dye concentrations. The plots revealed that maximum percent removal of the Red-Cls-Bar is at pH=7.

Adsorption Isotherms: In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations for the equilibrium data for each system. Three isotherm models have been tested in the present study; Langmuir, Freundlich and Tempkin isotherms (Table 1). The applicability of the isotherm equations was compared by judging the correlation coefficient, R².

Langmuir Model: Langmuir theory was based on the assumption that adsorption is a type of chemical combination or process and the adsorbed layer is unimolecular. The theory can be represented by the following linear form uni-molecular [15].

$$\frac{Ge}{qe} = \frac{1}{bQo} + \frac{Ge}{Qo} \tag{2}$$

Where qe is adsorbed amount, Ce is the equilibrium concentration, Q_0 (mg g⁻¹) and b (L mg⁻¹) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively and are obtained from slope $(1/Q_0)$ and intercept $(1/bQ_0)$ of linear plot of Ce/qe versus Ce

Figure 3 (a-c) represent the Langmuir isotherms of Red-Cls-Bar contacted with 0.50g-1.50 g of ash for 60 minutes at three different temperatures 298K, 303K and 308K, respectively and pH 7. The values of Q₀ and b were determined from intercept and slopes of the linear plots of Ce/qe vs. Ce. The applicability of adsorption process was investigated by correlation coefficient R²values.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor RL. According to the value of $R_{\rm L}$ (Table 2) the type of adsorption may be interpreted as follows;

$$RL = \frac{1}{1 + LGo} \tag{3}$$

Where L is the Langmuir constant and C_0 is the highest initial dye concentration (mgL⁻¹). Values were shown in (Table 1). According to the value of R_L (Table 2) the type

Table 1: Langmuire, Freundlich and Tempkin Model Constants and correlation coefficients for adsorption of Red-Cls-Bar onto brick kiln ash

Langmuir isotherm							
Temp(K)	b (L/mol) ⁻¹	Q ₀ (mol/g) x ¹⁰⁻³	\mathbb{R}^2	$R_{\rm L}$			
298	-4.933	-0.11	0.988	-0.034			
303	-4.919	0.055	0.938	-0.035			
308	-5.638	1.58×10^{-4}	0.968	0.030			
Freundlich Isotherm							
Temp (K)	n	K_F	\mathbb{R}^2				
298	0.123	6.74×10^{-07}	0.999				
303	0.065	6.845×10^{-13}	0.885				
308	0.347	1.08×10^{-03}	0.771				
Tempkin isotherm							
Temp (K)	$a_T (Lg^{-1})$	$b_T (mgL^{-1})$	В	\mathbb{R}^2			
298	0.297	1681.99	1.473	0.788			
303	0.204	2126.9	1.184	0.977			
308	0.182	685.37	3.736	0.921			

Table 2: R_L values of Langmuir Isotherm

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Value of R _L	Type of adsorption			
RL > 1.0	Unfavourable			
RL = 1.0	Linear			
0 < RL < 1	Favourable			
RL = 0	Irreversible			

of sorption may be interpreted as follows; values of $R_{\rm L}$ calculated at 288, 298 and 308K were not in range between 0 and 1 which indicated that the adsorption is not favourable at operation conditions studied.

Freundlich Model: The Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed, qe is related to the equilibrium concentration of solute in solution, Ce as following [40];

$$ln qe = ln Kf + \frac{1}{n} ln Ge$$
(4)

Where qe, amount adsorbed, Ce, the equilibrium concentration, K_F , the constant for the system, related to the bonding energy, (defined as the adsorption or distribution coefficient and respects the quantity of dye adsorbed onto carbon adsorbents for a unit equilibrium concentration) and n. The slopes (1/n) ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value get closer to zero. A value for 1/n below one indicates a normal Freundlich isotherm while 1/n above one is an indicative of cooperative adsorption. K_F and n are obtained from slope (1/n) and intercept (Anti $\ln K_F$) of linear plot of $\ln n$ versus $\ln n$.

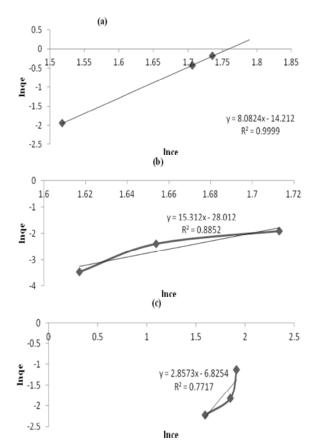


Fig. 4 (a-c): Freundlich isotherm for adsorption of Red-Cls-Bar (6-14ppm) onto 0.50g-1.50g of Ash collected from brick kiln at pH=7 and at temperature (a) 298K (b) 303K (c) 308K

Freundlich isotherms of Red-Cls-Bar contacted for 60 minutes with (0.50-1.50) g of ash at three different temperatures 298K, 303K and 308 K, respectively and pH 7 was shown in Fig. 4 (a-c). The values of $K_{\rm F}$ and n were determined from intercept and slopes of the linear plots of lnqe vs. lnCe. The applicability of adsorption process was investigated by correlation coefficient R^2 values. Based upon the correlation coefficients (R^2) shown in (Table 1), it can be said that the adsorption data can be described by Freundlich isotherm is better than that of Langmuir isotherm.

Tempkin Isotherm: The Tempkin isotherm assumes that the heat of adsorption of all the molecules increases linearly with coverage [41]. The linear form of this isotherm can be given by Eq. (4).

$$qe = \frac{RT}{bT} \ln aT + \frac{RT}{bT} \ln Ge$$
 (5)

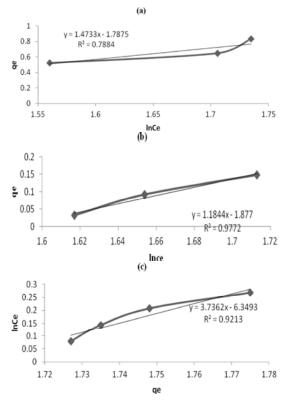


Fig. 5 (a-c): Tempkin isotherm for adsorption of Red-Cls-Bar (6-14ppm) onto 0.50g-1.50g of Ash collected from brick kiln at pH=7 and at temperature (a) 298K (b) 303K (c) 308K

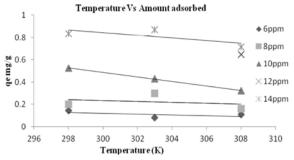


Fig. 6: Effect of temperature on removal efficiency of Red-Cls-Bar onto Ash collected from brick kiln (0.50g-1.50g) contacted for 60 minutes at pH=7

Tempkin isotherms of Red-Cls-Bar contacted for 60 minutes with (0.50-1.50) g of ash at three different temperatures 298K, 303K and 308 K, respectively and pH 7 was shown in Fig. 5 (a-c). qe is the amount adsorbed at equilibrium in mg/g; k1 is the Tempkin isotherm energy constant. The slopes and intercept obtained from the graphical plot qe against lnCe were used to calculate the Tempkin constants (Table 1). Based upon the correlation

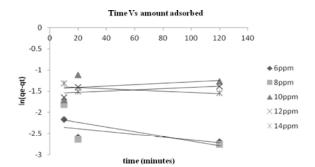


Fig. 7: Legergren plots Red-Cls-Bar (6-14ppm) by adsorption onto 0.50g of Ash collected from brick kiln at room temperature (298K) and pH=7

coefficients (R²) shown in (Table 1), it can be said that the adsorption data can be described by Tempkin isotherm is better than that of Langmuir and Freundlich isotherm.

Effect of Temperature: The effect of temperature on removal efficiency of Red-Cls-Bar onto ash (0.50-1.50) g contacted for 60 minutes at pH=7 was shown in Fig. 6. The effect of change in temperature ranging from (298 - 308) K showed that amount dsorbed and percentage removal efficiency of Red-Cls-Bar decrease with increase in temperature. The maximum adsorption capacity amongst all temperatures was obtained at 298K.

Adsorption Kinetic Studies: In order to evaluate the kinetic mechanism which controls the process, the Lagergren first order [42], pseudo second order [43], Elovich [44] and intra particle diffusion [45-46] models were tested and the validity of the models were verified by linear equation analysis log (q_e. q_t) vs t, (t/q_t) vs t and q_t vs t^{1/2}, respectively. Good correlation with the kinetic data explains the dye adsorption mechanism in the solid phase [47]. Kinetic parameters for the sorption of Red-Cls-Bar onto ash collected from brick kiln were shown in (Table 3).

Pseudo-first-order Model: Lagergren plots for the removal of Red-Cls-Bar by adsorption on 0.50 g of adsorbent at room temperature (298K) and pH=7 was shown in Fig 7.The kinetics of adsorption of Red-Cls-Bar onto ash was studied by applying the Lagergeren first order rate Eq. (5).

$$ln(qe - qt) = inqe - K1t$$
 (6)

Where qt, the amount of dye adsorbed at time t, qe, the amount of dye adsorbed at equilibrium and Kt is the equilibrium rate constant of adsorption. The plot of the

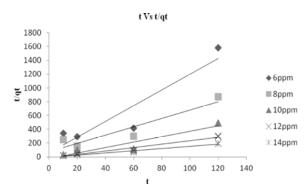


Fig. 8: Pseudo second order plot for the adsorption of Red-Cls-Bar onto ash collected from brick kiln at room temperature (298K) and pH=7

Table 3: Kinetic parameters for the sorption of Red-Cls-Bar onto ash collected from brick kiln.

	6 (mg/L)	8 (mg/L)	10 (mg/L)	12 (mg/L)	14 (mg/L)
qe mgg ⁻¹	0.1434	0.2016	0.5237	0.6489	0.8331
Lagergren-first order					
K1(min ⁻¹)	-0.003	-0.005	0.001	0.001	-0.001
qe (mgg ⁻¹)	0.098	0.119	0.234	0.212	0.249
R2	0.524	0.438	0.113	0.378	0.467
Pseudo second order					
K2 (g mg ⁻¹ min ⁻¹)	0.448	2.030	-1.461	-2.187	-1.506
qe (mgg-1)	0.087	0.165	0.253	0.406	0.634
t ½ (min)	5.14	12.30	-5.773	-5.380	-2.374
ho,2(mgg-1min-1)	3.39x10-3	0.054	-0.093	-0.358	-0.603
\mathbb{R}^2	0.860	0.874	0.893	0.950	0.974
Elovich model					
A	9.80x10-3	0.015	0.180	0.130	0.519
В	15.62	11.49	8.40	8.47	6.49
\mathbb{R}^2	0.997	0.962	0.430	0.687	0.948
Intraparticle diffusion equation					
Kint [mg/(gmin ^{1/2})]	0.024	0.032	0.051	0.048	0.060
\mathbb{R}^2	0.996	0.908	0.543	0.786	0.986

Table 4: Values of thermodynamic parameter of Red-Cls-Bar at three different temperatures (298K, 303K and 308K) onto Ash collected from brick kiln

Temperature (K)	$\Delta G^{\circ}(KJmol^{-1})$	$\Delta H^{\circ}(KJmol^{-1})$	$\Delta S^{\circ}(KJ^{-1}mol^{-1})$
298	-9.8035	+132.69	-487.69
303	-16.8767		
308	-18.6692		

log $(q_e$ - $q_i)$ as a function of t provides the k_i and q_e values. The results of first order kinetics at various temperatures were given in (Table 4). From the linear correlation coefficients (R^2) , it was seen that Lagergren equation does not represent a good fit with the experimental data.

Pseudo-second-order Model: Pseudo second order plots for the removal of Red-Cls-Bar by adsorption on 0.50 g of adsorbent at room temperature (298K) and pH=7 wasshown in Fig 8.The pseudo - second-order equation based on the adsorption capacity at equilibrium may be expressed by the following equation:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{t}{qe} \tag{7}$$

Where k_2 (g mg⁻¹min⁻¹) is the pseudo-second - order adsorption kinetic parameter. From the slope and intercept of the (t/q₁) as a function of t, k_2 and q_e can be obtained. The linear correlation coefficients were obtained to be 0.860, 0.874, 0.893, 0.950 and 0.974 for 6-14ppm at 298K, respectively. The pseudo second order rate constant firstly increased then decreased from 10ppm - 14ppm at 298K. Also, as shown in Table 1, due to fact that the calculated amounts of adsorbed Red-Cls-Bar at equilibrium were close to experimental values, it can be said that sorption of Red-Cls-Bar onto ash collected from brick kiln follows the pseudo-second-order kinetic model.

The initial rate of sorption was estimated from pseudo-second order kinetic model from the below equation;

$$h0,2 = k2 \text{ qe}2$$
 (8)

The half-sorption time, t1/2 known as the time required for the sorption to take up half as much Red-Cls-Bar as its equilibrium value. The time is often used as a measure of the adsorption rate.

$$t1/2 = \frac{1}{K2ae} \tag{9}$$

Elovich Model: The Elovich equation is mainly applicable for chemisorptions kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as;

$$qt = \frac{1}{B}\ln(aB) + \frac{1}{B}\ln t \tag{10}$$

Where α is the initial adsorption rate (mg g⁻¹ min) and β is related to the extent of surface coverage and the activation energy for chemisorptions (g mg⁻¹). Elovich plot for the adsorption of Red-Cls-Bar onto ash collected from brick kiln at room temperature (298K) and pH=7 was shown in Fig. 9. A plot of q_tvs. In t gave a linear trace with a slope of (1/ β) and an intercept of 1/ β ln (α β). The plot was linear with good correlation coefficient (R²= 0.997 to 0.948). The initial adsorption rate, a decreased form 9.8x10⁻³ to 0.519 while increasing the initial dye concentration form 6ppm-14ppm. The results of Elovich plot for the adsorption of Red-Cls-Bar by ash collected from brick kiln at various initial dye concentrations were given in (Table 4).

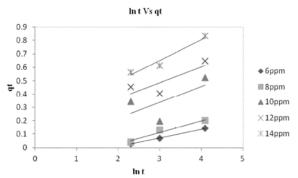


Fig. 9: Elovich plot for the adsorption of Red-Cls-Bar onto ash collected from brick kiln at room temperature (298K) and pH=7

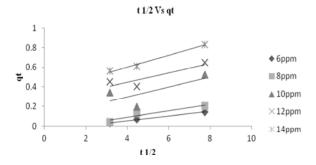


Fig. 10: Intra Particle Diffusion plot for the adsorption of Red-Cls-Bar onto ash collected from brick kiln at room temperature (298K) and pH=7

Intra Particle Diffusion Model: The intra particle diffusion model was applied to describe the competitive adsorption. In a liquid-solid system, the fractional uptake of the solute on particle varies according to a fraction of D the diffusivity within the particle and r is the particle radius. The initial rate of intra particle diffusion are obtained by linearization of the curve q_i = Ki ($t^{1/2}$).

$$qt = ki1/2 \tag{11}$$

Intra Particle Diffusion plot for the adsorption of Red-Cls-Bar onto ash collected from brick kiln at room temperature (298K) and pH=7 was shown in Fig. 10. If the intra particle diffusion is involved in the adsorption processes, then the plot of the square root of time versus the amount of adsorbed (qt) must give a straight line with a slope that equals ki and an intercept equal to zero [48]. Namely, the intra particle diffusion would be a controlling step if this line passed through the origin. As can be seen from Table 3, the intra particle diffusion did not control the adsorption process since the linear correlation coefficient values of model for the plots were in the range

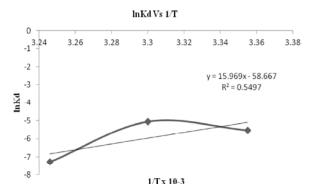


Fig. 11: Plot of ln Kd versus 1/T

0.543-0.996. Moreover, since the plots do not pass through the origin, this indicative of some degree of boundary layer control and this further shows that the intra particle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption. [49-50]

Thermodynamic Studies: Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were estimated for Red-Cls-Bar adsorption onto as collected from brick kiln. ΔG values at different temperatures were calculated from the following equations;

$$\Delta G$$
=-RTlnKd (12)

$$Kd = \frac{qe}{ce} \tag{13}$$

Where qe is the amount of Red-Cls-Bar (mg) adsorbed by ash collected from brick kiln per L of solution at equilibrium, Ce is the equilibrium concentration (mg L⁻¹) of dye in solution, Kd is the distribution coefficient for the adsorption. The average standard enthalpy change (Δ H) is obtained from Van't Hoff equation [14];

$$\ln Kd = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{14}$$

Where T is the absolute temperature, R is gas constant $(8.314 \, \mathrm{Jmol^{-1} \, K^{-1}})$. From the slope and the intercept of the plot of ln Kd versus 1/T, as presented in Fig. 11, $\Delta \mathrm{H}$ and $\Delta \mathrm{S}$ values were calculated. The calculated parameters by using above equations were presented in Table 4. As can be seen in Table 4, $\Delta \mathrm{G}$ values were obtained to be -9.80, -16.87 and -18.66 kJ mol⁻¹ for 298, 2303 and 308 K, respectively. Negative value of Gibbs free energy values shows the spontaneous nature of Red-Cls-Bar adsorption

on ash collected from brick kiln. The positive value of enthalpy change (ΔH) indicates endothermic nature of sorption. The absolute magnitude of ΔG may give an idea about the type of adsorption. Chemisorption has an energy range 80-400 kJ per unit mole, physical sorption has a range 0 to -20 kJ per unit mole [51]. Since ΔG values obtained in this study were in the range 0 to -20 kJ mol⁻¹, sorption of Red-Cls-Bar onto ash collected from brick kiln can be considered as physisorption process.

The results obtained from the present investigation are helpful to develop a new and efficient adsorbent of direct dyes. Low cost waste material [Ash collected from brick kiln] has been used successfully as an adsorbing agent for the removal of reactive dye [Red-Cls-Bar] from industrial waste water. Removal efficiency increased with decreasing temperature. The maximum adsorption of Red-Cls-Bar by Ash collected from brick kiln occurred at pH=7 and contact time of 60 minute. The data were in good agreement with Tempkin isotherm than Langmuir and Freundlich isotherms. It was shown that the adsorption of Red-Cls-Bar onto Ash collected from brick kiln best fitted by Pseudo second order model. The thermodynamic study suggested that the dye adsorptions were spontaneous and endothermic. Since Ash collected from brick kiln, an industrial solid waste used in this study possesses feasible availability and maximum utility for purification of industrial waste water. The adsorption process is expected to be economically viable for wastewater treatment and minimization of water pollution in the environment of Pakistan. This leads to its superiority as a potential adsorbent in removal of some colored dyes from waste waters.

REFERENCES

- McKay, G., J.F. Porter and G.R. Prasad, 1998. The removal of dye colors from aqueous solutions by adsorption on low-cost materials. Journal of Water Air Soil Pollution, 114: 423-438.
- Konduru R. Ramakrishna and T. Viraraghavan, 1997.
 Dye removal using low cost adsorbents. Journal of Water Science and Technology, 36: 189-196
- 3. Al-Qodah, Z. and W. Lafi, 2003. Adsorption of reactive dyes using shale oil ash in fixed beds. Journal of Water SRT-Aqua, 52: 189-198
- McKay, G., M.S. Otterburn and D.A. Aga, 1985. Fullers earth and fired clay as adsorbent for dye stuffs, equilibrium and rate constants. Journal of Water Air Soil Pollution, 24: 307-322.

- Namasivayam, C., 2002. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments, 54: 47-58.
- Sharifi, M.K., Yazdi C. Azimi and M.B. Khalili, 2001. Study of the Biological Treatment of Industrial Waste Water by the Activated Sludge Unit, Journal of Iranian J. Publ. Health, 30: 87-90.
- Justin, K., Maghanga and Fred K. segor, 2009. Lazareetiégni and Johnlusweti, Electrocoagulation method for color removal in tea effluent. Bulletin of the chemistry Society of Ethopia, 23: 371-381.
- Galindo and C. Kalt, 1998. A UV-H₂O₂ oxidation of monoazo dyes in aqueous media: a kinetic study. Dyes Pigments, 40: 27-35.
- Tarley, C.R.T. and M.A.Z. Arruda, 2004. Biosorption of heavy metals using rice milling by-products Characterization and application for removal of metals from aqueous effluents. Chemosphere, 54: 987-995.
- Nagarethinam Kannan and Mariappan Meenakshi, 2001. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons a comparative study. Dyes and Pigments, 51: 25-40.
- Dushenkov, V., P.B.A.N. Kumar, H. Motto and I. Raskin, 1995. Rhizo filtration: the use of plants to remove heavy metals from aqueous streams. Journal of Environmental Science and Technology, 29: 1239-1245
- Mohan, D., K.P. Singh, S. Sinha and D. Gosh, 2004. Removal of pyridine from aqueous solution using low cost activated carbons derived from agricultural waste materials. Carbon, 42: 2409-2421.
- 13. Ngwasiri Pride Ndasi and Mbawala Augustin, 2011. Biodecolourisation of textile dyes by local microbial consortia isolated from dye polluted soils in ngaoundere (Cameroon). International Journal of Environmental Sciences, 1: 1403-1419
- 14. Renmin Gong, 2009. Isothermal, kinetic and thermodynamic studies onbasic dye sorption onto tartaric acid esterified wheat straw. Journal of African Biotechnology, 8: 7138-7147.
- Tebrez A. Khan, Ved Vatisingh and D. Kumar, 2004.
 Removal of some basic dyes from artificial textile wastewater by adsorption on Akash Kinari coal.
 Journal of Scientific and Industrial Research, 63: 355-364.

- Canan Akmil Başar, 2006. Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot. Journal of Hazardous Materials, 135: 232-241.
- 17. Satesh patel and Sameer Renukdas, 2011. Removal of methylene blue, a basic dye from aqueous solutions by adsorption using teak tree (Tectona grandis) bark powder, International Journal of Environmental Science, 1: 69-76.
- Aylin Altinisik and Emel Gur, 2010. A natural sorbent, Luffa cylindrica for the removal of a model basic dye. Journal of Hazardous Materials, 179: 658-664
- Mahjoub, B., 2007. Adsorptive removal of textile reactive dye using Posidoniaoceanica (L.) fibrous biomass. International Journal of Environmental and Science Technology, 12: 433-440.
- Namasivayam, C., N. Kanchana and R.T. Yamuna, 1993. Waste banana pith as adsorbent for the removal of Rhodamine B from aqueous solution1 Water Management, 3: 89-95.
- Namasivayam, C. and K. Kadirvelu, 1994. Coir pith, an agricultural waste byproduct for the treatment of dyeing wastewater. Bioresource Technology, 38: 79-81.
- Morais, L.C., O.M. Freitas, E.P. Goncalves, L.T. Vasconcelos and C.G.G. Beca, 2010. Reactive Dyes Removal from Wastewaters by Adsorption on Eucalyptus Bark. 21: 577-583.
- 23. Robinson, T., B. Chandran and P. Nigam, 2002. Removal of dyes from asynthetic textile dye effluent by biosorption on apple pomace and wheat straw. Journal of Water Res., 36: 2824-2830.
- Vadivelan, V. and K.V. Kumar, 2005. Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. Journal of Colloid and Interface Science, 286: 90-100.
- 25. Ozacar, M. and A. Engil, 2005. Adsorption of metal complex dyes from aqueous solutions by pine sawdust. Bioresource Technology, 96: 791-795.
- Gong, R., M. Li, C. Yang, Y. Sun and J. Chen, 2005. Removal of cationic dyes from aqueous solution by adsorption on peanut hull. Journal of Hazardous Materials, 121: 247-250.
- 27. Kumar, K.V. and A. Kumaran, 2005. Removal of methylene blue by mangoseed kernel powder. Journal of Biochemical Engineering, 27: 83-93.
- Ardejani, F.D., K. Badii, N.Y. Limaee, S.Z. Shafaei and A.R. Mirhabibi, 2008. Adsorption of Direct Red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration and shell type. Journal of Hazardous Materials, 151: 730-737.

- Tahir, H., U. Hammed, Q. Jahanzeb and M. Sultan 2008. Removal of fast green dye (C.I. 42053) from an aqueous solution using Azadirachtaindicaleaf powder as a low cost adsorbent. Journal of African Biotechnology, 7: 3906-3911.
- 30. Low, K.S. and C.K. Lee, 1997. Quaternized rice husk as sorbent for reactive dyes. Bioresource Technology, 61: 121-125.
- 31. Marchetti, V., P. Gérardin and B. Loubinoux, 2011. Preparation and use of saw dusts bearing quaternary ammonium groups for removal of anionic dyes from water. Journal of Chemical Engineering, 70: 115-124.
- 32. Konduru R. Ramakrishna and S.T. Ramesh, 2013. Removal of dyes using agricultural waste as low-cost adsorbents. Journal of Applied Water Science, 3, 773-790.
- 33. Pignon, H.M. and C. Faur, 2007. Pignon Metivier, Adsorption of dyes onto activated carbon cloth: Using QSPRs as tools to approach adsorption mechanisms. Chemosphere, 66: 887-893.
- Velmurugan, Rathinakumar and Dhinakaren, 2011.
 Dye removal from aqueous solution using low cost adsorbent. International Journal Of Environmental Science, 1: 897-912.
- 35. Muhammad A. Rauf, I Shehadeh and Amal Ahmad, 2009. Removal of methylene Blue from aqueous solution by using gypsem as low cost adsorbent. Journal of World Academy of Science, Engineering and Technology, 31: 604-609.
- 36. Xiao and Yan Yang, 2001. Application of branched pore diffusion model in the adsorption of reactive dyes on activated carbon. Journal of Chemical Engineering, 83: 15-23.
- 37. Ola Abdel Wahab, Ahmed El Nemr and Amany El Sikaily, 2005. Use of rice husk for adsorption of direct dyes from aqueous solution: a case study of direct f. Scarlet. Egyptian Journal of Aquatic Research, 31: 1-11
- 38. Tan, I.A.W., 2007. Equilibrium and kinetic studies on basic dye adsorption by oil palm fiber activated carbon. Journal of Chemical Engineering, 127: 111-119.
- Yahya and S. Al-Degs, 2008. Effect of solution pH, ionic strength and temperature on adsorption behavior of reactive dyes on activated carbon. Dyes and Pigments, 77: 16-23.
- 40. Malik, P.K., 2003. Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow. Dyes and Pigments, 56: 239-249.

- Allen S.J. and G. Mckay, 2004. Adsorption isotherm models for basic dyes and adsorption by peat in single and binary component systems Journal of Colloid and Interface Science, 280: 322-333.
- 42. Feng-Chin Wu, Ru-Ling Tseng and Ruey-Shin Juang, 2001. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. Journal of Water Resource, 35: 613-618
- 43. Ho. Y.S. and Mckay, 1999. Pseudo-second order model for sorption process. Process Bichem, 34: 451-465.
- 44. Namasivayam, C. and Kavitha, 2002. Removal of congo red from water b adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments, 54: 47-58.
- 45. Weber, W.J., 1962. Advances in water pollution research: removal of biologically resistant pollutant from waste water by adsorption, International Conference on Water Pollution Symposium, 2, Pergamon Oxford, pp. 231-266.
- 46. Ibrahim, S.C. and M.A.K.M. Hanfiah, 2006. Removal of cadmium form aqueous solution by adsorption onto sugarcane baggase. Journal of American Eurasian Agricultural and Environmental Science, 1: 179-184.

- 47. Wu, F., R. Tseng and Juang, 2001. Kinetic modeling of liquid phase adsorption of reactive dyes and metal ions on chitosan, Water Res., 35: 613-618.
- 48. Bulut, E., M. Ozacar and I.A. Sengil, 2008. Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, Microporous Mesoporous Mater., 115: 234-246.
- Gerente, C., V.K.C. Lee, P. Le Cloirec and G. McKay, 2007. Application of chitosan for the removal of metals from wastewaters by adsorption mechanisms and models review, Crit. Rev. Env. Sci. Technol., 37: 41-127.
- 50. Crini, G., H.N. Peindy, F. Gimbert and C. Robert, 2007. Removal of C.I. Basic Green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin based adsorbent: kinetic and equilibrium studies, Sep. Purif. Technol., 53: 97-110.
- Bekci, Z., Y. Seki and L. Cavas, 2009. Removal of malachite green by using an invasive marine alga Caulerpa racemosa var. Cylindracea, J. Hazard. Mater., 161: 1454-1460.