SEQUESTERING ATTRIBUTES OF TYPHA LATIFOLIA AS A LOW COST BIOSORBENT FOR THE REMOVAL OF REACTIVE DYE (DB-K₂RL) FROM AQUEOUS MEDIA

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ABSTRACT: Typha latifolia leaves have been exploited as low cost biosorbent for remediation of aqueous media contaminated with the reactive dye Drimarene Blue K₂RL (DB-K₂RL) discharged from textile effluents. The effect of parameters such as initial concentration of dye, amount of bio-sorbent, initial pH, shaking time and speed were investigated to evaluate its sorption capacity. The maximum sorption was observed on adding 0.03 to 0.05 g mL⁻¹ sorbent at pH 2 at 200 rpm for 2 hr shaking time. The sorption efficiency of acid treated sorbent was also determined and its kinetic data was analyzed using Freundlich and Langmuir models. The uptake capacity of both native sorbent and pretreated biosorbent was compared and it was found that pretreated biosorbent exhibited better sorption ability (q_{max}= 3.5 mg/g) as compared to the native biosorbent (q_{max}= 2.5 mg/g).

Key words: Bio-sorption, Reactive dyes, Textiles effluents, Typha latifolia and Drimarene Blue K₂RL.

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INTRODUCTION

Synthetic organic dyes are broadly are involved in different fields such as food industries, paper industries, fabric industries, cosmetics industries, photography and pharmaceutical industries (Rafi et al., 2009). These dyes usually contain aromatic moieties like benzene, toluene, naphthalene and xylene which confer stability to their structures and render them non-biodegradable (Hu et al., 2006). The dyes and suspended solids in contaminated water of textile industries are serious threats to public health. Such type of materials not only alters the physicochemical properties of clean water but also reduces the penetration of light and potentially stops the photosynthesis (Aksu 2001). The removal of these impurities from fresh water resources is desirable because these are toxic, carcinogenic, and mutagenic (Mohan et al., 2002).

Drimarene Blue K₂RL(4-((2,5-dichloro-6-fluoropyrimidin-4-y1)amino)-9,10dioxo8a,9,10,10a-tetrahydroanthracecine-1-aminium)is reactive anthraquinone dye which is freely soluble, discharged in wastewater of dying industry (Siddiqui et al., 2010).

Several water treatment methods have been developed in order to process the waste water effectively to render it harmless such as activated carbon adsorption, oxidation, coagulation, flocculation, biodegradation, precipitation, osmosis, ultra-filtration and ion exchange (Mostafa and Mohd 2014). Removal of dyes by applying conventional biological treatment methods is ineffective due to non-degradability of synthetic dyes. However, adsorption is considered to be most operative, efficient, economical method for water purification (George et al., 2013).

The agricultural waste has been widely employed due to being an economical and efficient sorbent and now a days, a variety of new agricultural wastes including sago waste, rice husk, peanut skins, sugarcane waste, cassava waste, chaff, banana pith, wheat straw, pomace, coir pith, waste from yellow passion fruit and coconut husk are utilized. The chemically and physically modified sorbents have also been investigated for their enhanced bio-sorption efficiency (Pandima and Muthukumaran 2013). Different bio-sorbents have been investigated for remediation of aqueous media contaminated with dyes.

The accessibility, low cost and effective sorption efficiency are the main factors to be considered for selection of sorbent for water treatment. The roots and leaves of T. Latifolia have been utilized as biosorbent for the removal of heavy metal ions from aqueous media, due to its granular structure and stability. Morphology and FTIR studies have shown that its functional groups such as –OH, =C–H, C=O are responsible for adsorption of dyes (Bukharie et al.; 2013). Therefore, in present study, T. latifolia, a perennial herbaceous plant found in Pakistan and all over the world (Fig.1) as reported by (James and Janet, 1986)was chosen as bio-sorbent for effective removal of Drimarene Blue K₂RL dye which is largely used in textile industry of Pakistan (Siddiqui et

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Therefore efficiency of native and pretreated sorbent was tested and compared using different factors such as initial concentration of dye and sorbent, particle size of sorbent, agitation speed, contact time and pH.

**MATERIAL AND METHODS**

Chemicals and Biosorbent: All chemicals and solvents were of A.R grade (Sigma-Aldrich) Pakistan and were used without further refinement. Drimarene Blue K₂RL was obtained from local market. *T. latifolia* plants were collected from Chak No.92 NB on Jhang road about 17 Km from Sargodha city. The pH of solution was measured by using. The buffer solutions of different pH ranging from1-8 were prepared according to standard procedure reported by (Mohan *et al.*, 2002) and their pH was noted using Ino-lab digital level pH meter was used for swirling the solution. The concentration of the dye was measured by using UV-Vis Spectrophotometer (Schimadzu UV-1700 Japan) at $\lambda_{\text{max}}$ 616 nm and shaking was done using Orbital Shaker OS-752 Optima.

Preparation of bio-sorbent: The samples of bio-sorbents were prepared according to the method reported by (Sararikova 2005). The leaves of *T. latifolia* were washed with distilled water, dried and ground to fine powder, sieved through sieves of 200 mesh size and placed in oven for 12 hr at 383K. The dried samples of sorbents were weighed and preserved for further experiments.

Chemical treatment of the sorbent: Powdered *T. latifolia* leaves were soaked in 0.01M solution of H₂SO₄ (5g adsorbent/100mL of the acid solution) for 1 hr. The sorbent was filtered through 50 mesh sieve, washed, dried at 60°C for 24 hrs and used for adsorption of DB-K₂RL dye under optimum conditions following the procedure of (Jaikumar and Ramamurthi 2009).

Preparation of dye solution: The Drimine Blue K₂RL dye solution of concentration 1g/1000 mL was prepared as standard solution and then solution of different concentration (10-100µg mL⁻¹) were prepared by dilution method (Aksu 2003).

Adsorption Experiments: The adsorption ability of adsorbent was studied under different conditions of pH, agitation speed, temperature etc. The effect of agitation speed on bio-sorption of dye was studied by taking five Erlenmeyer flasks each containing20 mL dye solution (50 µg mL⁻¹). The adsorbent (0.5g) was added to each flask and swirled for 1h at 150-350 rpm on an Orbital Shaker and centrifuged at 4000 rpm. The residual concentration of dye from supernatant was analyzed by Spectrophotometer at $\lambda_{\text{max}}$ 616 nm.

The sorbent doses ranging from 0.2g to 1g/20mL were prepared and their absorbent effect for the dye solution was determined at optimum agitation speed and concentration of the unabsorbed dye in the filtrate was determined.

The solutions of the dye ranging from 10 to 100µg mL⁻¹ were taken in separate flasks to find the effect of dye concentration on sorption. The optimized sorbent dose was added and flasks were agitated at same speed for same interval of time. All sample flasks were agitated at different time intervals with a difference of half an hrs, keeping all other factors constant to find the effect of contact on sorption capacity. The sorption efficiency of the sorbent at different pH (1-10) was determined by keeping other factors constant. The effect of acid treatment on adsorption efficiency was determined at optimum conditions following the procedure reported by (Stephen and Sulochana2002).

Equilibrium models: The best adsorption method was investigated by applying the Freundlich and Langmuir equilibrium models to equilibrium data. The percentage of adsorbate on surface of biomass and in the solution was determined by reading the equilibrium conditions and then constructing the suitable isotherm model (Arca
and Bayramoglu 2007). Similarly, the effect of change in initial concentration of dye was noted while keeping the amount of bio-sorbent for all samples constant. Due to high value of correlation coefficients, the Langmuir isotherm was well fitted than Freundlich is other model according to reported procedure (Jayarajan et al., 2011).

**Statistical Analyses:** Regression analysis was used to carry out analysis of experimental data for estimating the relationships among different parameters using SPSS 16.0 software.

**RESULTS AND DISCUSSION**

For removal of carcinogenic chromium Cr (VI) from aqueous waste, the roots of *T. latifolia* roots were used as adsorbent and its adsorption efficiency was found to be 45% with roots and 60% with pyrolytic ash (Barrera et al., 2004), therefore, this plant was selected for adsorption study of Drimarene Blue K$_2$RL.

**i) Optimization of Shaking Speed:** The adsorption of Drimarene Blue K$_2$RL dye was studied onto sorbent under different shaking speeds in 150rpm-350rpm range. The removal efficiency of the sorbent increased from 150rpm to 200rpm and then decreased slightly with increasing shaking speed. The Fig. 2 showed that 200rpm agitation speed was optimum where removal efficiency reached 72.68%. The decline in adsorption rate was due to desorption that occurred at higher speed and rise in percentage removal of dye at optimum agitation speed lowered the monolayer film covering area around particles, which increased the coefficient for the transfer of outer film. This behavior is exactly similar to the finding of (Orfaco et al., 2006). Batzias and Sidiras found that the mixing at higher agitation rate transferred additional energy and thus greater force which resulted in breaking the bonds between the adsorbent and the dye (Batzias and Sidiras 2007).

**ii) Effect of adsorbent dosage:** The removal efficiency of dye was increased from 54.69 to 73.39% by increasing the sorbent dose from 0.2g to 0.6g and then it became constant or slightly decreased (Fig. 3). The increase in percentage removal of dye was assigned to rise in the surface area of sorbent by enhancing its dose and number of sites available for the adsorption were also increased as reported earlier by Anwar and others (Anwar et al., 2011, Asadullah et al., 2010 and Mane et al., 2007). On increasing the biosorbent dose (>0.6 g), an equilibrium was established between surface dye concentration and solution dye concentration (Jaikumar and Ramamurthi 2009 and Azbar et al., 2004). The decline in the adsorption capability was observed at sorbent dose >0.6 g because some surface area of sorbent remained unsaturated (Gode and Pehlivan 2005) and some adsorption sites were aggregated. As the result the decrease in entire surface area of adsorbent and restriction in diffusion path was observed. On addition of extra amount of adsorbent to the movement of dye molecules to active sites might occur (Araujo and Teixeira 1997).

![Figure 2: Relation between agitation speed and sorption potential of DB-K$_2$RL on the leaves of raw *T. latifolia*.](image)

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![Figure 3: Effect of amount of biosorbent on the sorption of DB-K$_2$RL on *T. latifolia* leaves.](image)

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**ii) Effect of dye concentration:** The adsorption of DB-K$_2$RL was increased from 58.36% to 78.62% (Fig. 4) with an increase in initial concentration of dye up to 50 ppm, after that it decreased even by increasing the initial concentration of dye (Safa and Bhatti 2011). Initially at lower concentration of dye number of sites on sorbent were greater, therefore percentage removal of dye was increased (Aksu and Kabasakal 2004). At higher concentration, active adsorption sites were insufficient and adsorption rate decreased (Orfaco et al., 2006). The results reported by (Paola et al., 2004) revealed that the adsorption of 2,4-dichlorophenoxyacetic acid was fast at the initial stages of contact time and was slowed down near equilibrium due to high affinity of the interacting groups on the surface of the activated carbon, similar results were obtained in our study. The high
adsorption rate at the beginning of adsorption was due to the adsorption of the dye by the exterior surface of the adsorbent. Later on the adsorption was decreased due to decrease of adsorbing sites.

iv) Effect of pH: Adsorption ability and solubility of some dyes was found to be affected by pH of the medium (Fu and Viraraghavan 2001 and Waranusantigul et al., 2003). The maximum sorption for selected dye (87.89%) was achieved at pH 2 followed by decrease in adsorption with an increase in pH (Fig.6). Due to removal of –OH groups from the cellulosic structure of adsorbent at low pH, vacant sites were developed which result in greater adsorption on the sites of adsorbent and negatively charged dye surface. With an increase in pH of the dye solution, removal of –OH decreased along with increase in negatively charge sites (Jaikumar and Ramamurthi, 2009) that resulted in an increase in repulsions within the anions of the dye molecules. At lower pH, the surface of the sorbent acquired positive charge, that resulted in greater electrostatic force for negatively charged anions on the surface of the dye molecules (Tan et al., 2010). The negatively charged adsorbent surface was not favorable for adsorption of dye anions at high pH due to repulsion as reported by (Chiou and Li, 2002, Namasivayam and Kavitha, 2002). Penka and others revealed that the hybrid material consisted of diatomite and activated carbon was also suitable for adsorption of phenol (Penka et al., 2016). The hybrid material exerted a strong influence on its adsorbent texture. The pore size distribution indicated that the sample was nearly mesoporous with non-uniform pore size distribution. The optimal pH value for phenol removal was found to be equal to 5.0 which were also very close to optimum pH (6) of our study. So this works also supported our ideas.

iii) Effect of contact time: The maximum adsorption, 72% for DB-K2RL dye was observed at time interval of 2hr (Fig.5). Initially the adsorptions occurred rapidly but declined slowly after attaining equilibrium. The rapid movement on the outer surface of adsorbent caused quick diffusions in the pores to achieve equilibrium as mentioned by (Abd El-Latif and Amal 2010 and Ho et al., 2005). By increasing contact time, the adsorption increased due to accessibility on further active sites. At equilibrium, binding of dye to sorbent surface became difficult due to repulsive forces. Therefore no considerable rise in efficiency of adsorbent was noted as reported by (Jaikumar and Ramamurthi 2009).

v) Comparison between adsorption capacity of native and pretreated Bio-sorbent: The adsorption capacity of pre-treated sample (TS) for given dye was greater than native sample(Table1). Due to addition of acid, its surface became positively charged due to protonation and an electrostatic force with negatively charge dye was developed. This interaction resulted in enhancement in
the amount of adsorbed dye (Yazici et al., 2008 and Aksu 2005).

Table-1: Effect of NS and TS on removal of Dye

<table>
<thead>
<tr>
<th>Conc. dye (µg mL⁻¹)</th>
<th>Removal % by NS</th>
<th>Removal % by TS</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>63.3</td>
<td>67.31</td>
</tr>
<tr>
<td>20</td>
<td>68.49</td>
<td>70.24</td>
</tr>
<tr>
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<td>40</td>
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<tr>
<td>50</td>
<td>90.95</td>
<td>95.83</td>
</tr>
<tr>
<td>60</td>
<td>84.43</td>
<td>90.78</td>
</tr>
<tr>
<td>70</td>
<td>81.14</td>
<td>87.44</td>
</tr>
<tr>
<td>80</td>
<td>79.21</td>
<td>84.31</td>
</tr>
</tbody>
</table>

*NS, TS=Native and Treated sorbent respectively

vi) **Langmuir and Freundlich isotherm for native Biosorbent:** The equilibrium data was used to develop an equation to correctly characterize the results. The equilibrium data of adsorption by native sorbent was applied to Langmuir equation and plotted a graph between equilibrium concentration Ce (mg/L) and Ce/qₑ (g/L) for selected dye (Fig.7). Freundlich Isotherm model was also tested by plotting graph between log Ce and log qₑ. The Freundlich isotherm was the sign of the surface heterogeneity of the sorbent, while the Langmuir isotherm only indicated the surface homogeneity of the adsorbent (Ahmad et al.; 2009). Results obtained by applying equilibrium models are shown in Fig.7. It indicated that the value of correlation coefficient (0.977) of Langmuir model for DB-K₂RL was higher than Freundlich model. This revealed that the adsorption of DB-K₂RL dye could be better explained by Langmuir model with adsorption capacity (2.4691mg/g) having monolayer adsorption. The correlation coefficient (0.930) from Freundlich plot showed the slope of 1/n less than 1, representing a nonlinear adsorption of DB-K₂RL. The experimental value of Kᵢ(1.0232) and 1/n value less than 1 indicated best adsorption between the biosorbent DB-K₂RL (Febrianto et al., 2009).

![Figure 7: Freundlich model (Left) and Langmuir model (Right) for removal of DB-K₂RL dye by native T. latifolia leaves (200 mesh size) at equilibrium conditions.](image)

vii) **Langmuir isotherm and Freundlich isotherm for pretreated Bio-sorbent:** The Langmuir and Freundlich isotherms were applied for pre-treated adsorbent (Fig. 8 L, R). The value of the correlation coefficient ‘R²’ for Langmuir model was noted as 0.990 which was greater than Freundlich model (0.965) (Table 2). It was indicated that for selected dye, the Langmuir model was best fitted for describing the adsorption mechanism. It also provided the validity of this model over a range of concentration (Ahmad et al., 2009 and Febrianto et al., 2009) and has highest R² value and hence fitted best.

![Figure 8: Freundlich model (Left) and Langmuir model (Right) for removal of DB-K₂RL by treated T. latifolia leaves (mesh size 200) at equilibrium conditions.](image)
Table- 2: Coefficient of Langmuir and Freundlich Isotherm for DB-K2RL.

<table>
<thead>
<tr>
<th>Bio-sorbents</th>
<th>L. Isotherm Coefficients</th>
<th>F. Isotherm Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K (L/mg)</td>
<td>qmax (mg/ g)</td>
</tr>
<tr>
<td>T.L. Leaves</td>
<td>Native</td>
<td>0.2874</td>
</tr>
<tr>
<td></td>
<td>Pretreated</td>
<td>0.6537</td>
</tr>
</tbody>
</table>

Conclusion: From the present study, it may be inferred that partition of dye between the bulk solution and biosorption was indicated from Langmuir isotherms. T. latifolia biomass was found to be most effective minimum cost agro-waste material exhibiting pronounced activity for the removal of reactive dyes from aquatic medium in acidic environments.

REFERENCES


