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Use of *Opuntia dillenii* Seeds for Sorptive Removal of Acidic Textile Dyes from Water in Benign Way

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In this study, the use of *Opuntia dillenii* seeds (O.D.S) has been investigated as an adsorbent for removing two textile dyes *i.e.*, drimarene blue K_2RL and eosin B, from aqueous medium. Adsorption related factors, like adsorbent dose, contact time, pH of dye solution and temperature were optimized in batch mode by adopting one variable methodology for optimizing conditions. Then isothermal, thermodynamical and kinetic studies were carried out at optimized conditions of adsorption and it is found that maximum adsorption capacity of *Opuntia dillenii* seeds for removing drimarene blue K_2RL and eosin B were 100 and 7.96 mg g^{-1}, respectively, following pseudo-second order kinetic model. Ethanol and NaOH were found suitable for regenerating used *Opuntia dillenii* seeds as compared to HCl or water. So, *Opuntia dillenii* seeds can be effectively employed for waste water treatment in economical way, using indigenous sources.

Key Words: *Opuntia dillenii* seeds, Eosin B, Drimarene blue K_2RL, Adsorption.

INTRODUCTION

Wastewater treatment by adsorption is gaining importance now-a-days. Researchers all over the world are trying to explore new adsorbents for replacing activated charcoal from their indigenous sources. These adsorbents are mostly originated from agrowaste, like peels of banana, orange or pea; corncobs or barley husks, rice husk, wheat husks, plant leaves, seeds of melon or guava, *etc*. or industrial waste like municipal waste sludge, deoiled soya[1-12]. Main advantage of using them is low cost of raw materials. Others are: recycling of waste, less import cost due to the use of simple machinery and indigenous adsorbents and last but not the least, it is environmental friendly process. Other water treatment methodologies, like chemical precipitation, photochemical oxidation, ozonation or microbial degradation processes are not environmental friendly, nor very cost effective. Expensive machinery and specialists are required for them[13-16].

Wastewater containing synthetic dyes is difficult to treat because of stability of dye molecules and other by products produced either by their excess reactivity, like metal complexes or by photochemical degradation processes. In textile industry, mostly synthetic dyes are employed. They belong to various classes, like cationic, anionic, neutral, anthraquinone, metal complexes, *etc*. In following study, drimarene blue K_2RL (D.R) and Eosin B (E.B) have been investigated. Drimarene blue K_2RL is an example of anthraquinone dye (Fig. 1), which

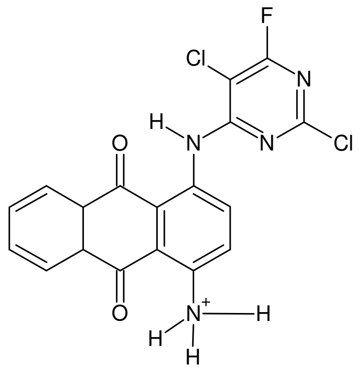

Fig. 1. Drimarene blue K_2RL dye

represents the second largest class of textile dyes (reactive dyes) and are used extensively due to their wide array of colour shades, ease of application and minimal energy consumption. They are resistant to biodegradation due to their complex aromatic structure[17]. Eosin B ($C_{20}H_6Br_2N_2Na_2O_9$) is a dibromo dinitro derivate of fluorescein (dibromodinitrofluorescein sodium, Fig. 2) having molecular formula with molecular weight 624.06 amu. Its systematic name is disodium 2-(4,5-dibromo-2,7-dinitro-6-oxido-3-oxo-3*H*-xanthen-9-yl) benzoate. It is widely used as a biological staining to estimate a wide range of proteins because in acidic solution, it binds to proteins. It is harmful in case of swallowing, inhaling or skin contact resulting in gastrointestinal tract infection and skin rashes[18].

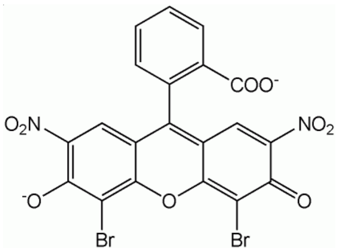

Fig. 2. Eosin B dye

In this case, finally crushed seeds of *Opuntia dillenii* are used for adsorption studies. Its other botanical name is *Cactus indicus* Roxb. and local names are Vidhara, Vishwa, Saraka, Nagphani. It belongs to Cactaceae family of plant. It is a succulent, perennial, xerophytic shrub, growing up to 1 m high. They grow from rounded cushion like tubercles, having yellow flower and purple fruit with curved thrones. Fruits fleshy contain compressed stony hard seeds. Its various parts are used in ayurvedic medicines for treatment of burning sensations, asthma, whooping cough, hepatitis, poison, fever, constipation, conjunctivitis, boils, ulcers, edema and leucorrhea *etc*. The chemical characteristics of *Opuntia dillenii* seeds are given in Table-1[19,20].

TABLE-1
CHARACTERIZATION OF *Opuntia dillenii* SEEDS

Parameters	Contents values
Moisture (%)	81.68
Fibre (%)	9.49
Ash (%)	0.437
pH	3.34
Acidity (g/100 g)	1.23
Phenolics (mg/100 g)	117

EXPERIMENTAL

Preparation of adsorbent: The adsorbent, *Opuntia dillenii* seeds (O.D.S.) were collected from Quaid-e-Azam campus of Punjab University Lahore. They were washed and dried in sunlight for 5 days and then in an oven at 80 ºC. Dry biomass was crushed into granules, sieved through 50 mesh and preserved in sample bottles for use.

Preparation of adsorbate: Drimarene blue K_2RL (Clariant Sandoz, C.I: Reactive blue 209) and eosin B ($C_{20}H_6Br_2N_2Na_2O_9$, acid red-91, C.I: 45400, MW 624.1, xanthene dye example) were obtained from Clariant Pakistan limited and used without any further purification. Stock solution of 1000 ppm concentration of these dyes were prepared using 0.1 g dye powder/100 mL double distilled water. Further standards and working solutions were prepared by diluting respective dye stock solution.

Batch adsorption experiments: Adsorption experiments were performed by taking 50 mL dye solution of dye (50 mg L^{-1}) and treated with 0.1 g of adsorbent dose. The variables studied were: solution pH (2-10), temperature (20-70 ºC), adsorbent dose (0.1-1.0 g) and contact interval between dye and *Opuntia dillenii* seeds (10-60 min). After adsorption, samples were centrifuged to remove *Opuntia dillenii* seeds and progress of adsorption was determined spectrophotometrically by setting λ_{max} at 620 and 530 nm for drimarene blue K_2RL and eosin B, respectively. Optimized conditions of all variables were further employed for isothermal, thermodynamical and kinetic studies. The percentage adsorption of dyes on *Opuntia dillenii* seeds were quantified by eqn. 1.

$$\text{Adsorption}\ (\%) = \left[\frac{(C_o - C_e)}{C_o}\right] \times 100 \quad (1)$$

In eqn. 1, C_o is dye concentration before adsorption and C_e representing concentration in mg L^{-1}. Experiments were performed in duplicate order and average values were used for graphical spinel representation of optimization of adsorption factor and line-to-line trend model is adopted for graphical representation of isothermal and kinetic modeling of equilibrium data[21-24]. For regenerating used *Opuntia dillenii* seeds, its 5.0 g was dipped separately in 100 mL of distilled water, ethanol, 0.01 M HCl and 0.01 M NaOH solutions for 0.5 h, while shaking at 100 rpm on orbital shaker. Then percentage desorption of dyes from *Opuntia dillenii* seeds were quantified by eqn. 2.

$$\text{Desorption}\ (\%) = \frac{q_{des}}{q} \times 100 \quad (2)$$

where q and q_{des} are mg g^{-1} of dye adsorbed and desorbed, respectively[25].

RESULTS AND DISCUSSION

Optimization of adsorption parameters of dye: The optimization of adsorption parameters of drimarene blue K_2RL and eosin B dyes were carried out separately on *Opuntia dillenii* seeds in batch mode and their results are given in Figs. 3-6 in comparative mode.

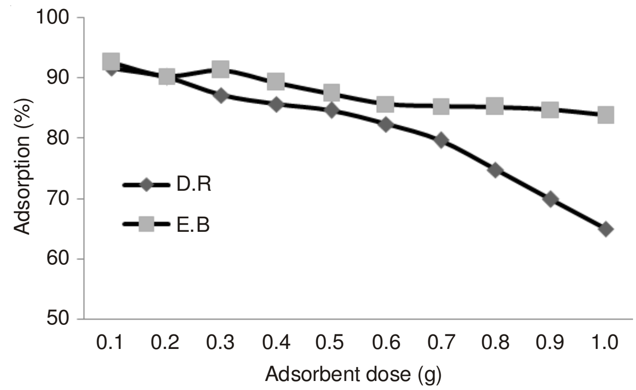

Fig. 3. Effect of adsorbent dose on percentage removal of dyes using *Opuntia dillenii* seeds. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

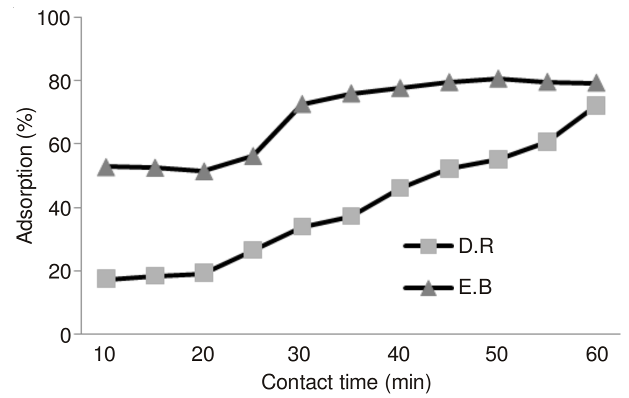

Fig. 4. Effect of contact time percentage removal of dyes using *Opuntia dillenii* seeds. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

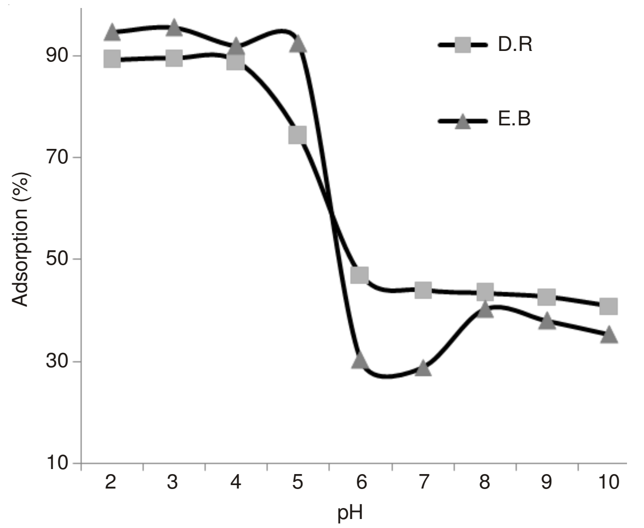

Fig. 5. Effect of pH on percentage removal of dyes using *Opuntia dillenii* seeds. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

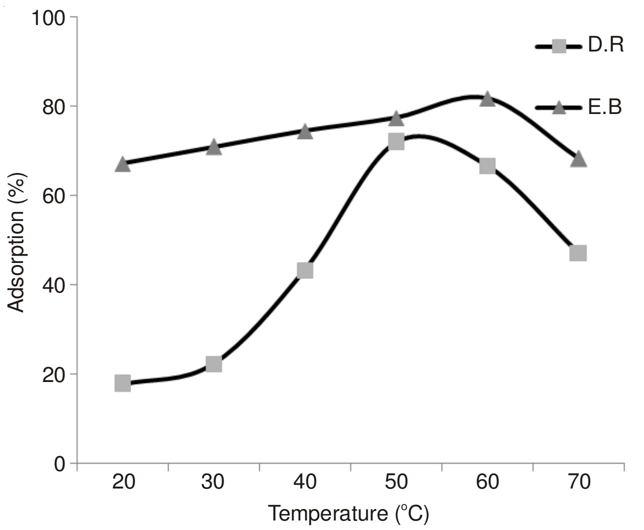

Fig. 6. Effect of temperature on percentage removal of dyes using *Opuntia dillenii* seeds. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

Fig. 3 shows the effect of adsorbent dose on percentage removal of dyes using *Opuntia dillenii* seeds. It can be seen from this figure that maximum adsorption of drimarene blue K_2RL occurred when adsorbent dose was 0.3 g, while for eosin B, it was 0.1 g. Requirement of small quantities of *Opuntia dillenii* seeds for maximum removal of dyes indicated that it has good adsorption tendency due to its mucilaginous, acidic, phenolic and fibrous nature, which was found during its characterization by Medina *et al*.[20]. Further increase in adsorbent dose showed negative impact on adsorption due to agglomeration of *Opuntia dillenii* seeds particles in solution, which reduces exposed surface area of *Opuntia dillenii* seeds

Fig. 4 is representing the effect of contact time on percentage removal of dyes using *Opuntia dillenii* seeds. In both case, maximum removal of dyes occurred at 1 h interval. There is a rapid increase in adsorption rate at the beginning following in gradual consistency till equilibrium. At initial stages, more vacant adsorption sites were available at the surface of *Opuntia dillenii* seeds, but after 30-40 min, adsorption rates become slower due to the penetration of larger dye, molecules in inner binding sites of *Opuntia dillenii* seeds, which were not directly exposed to dye solution.

The pH effect of dye solution on adsorption is shown in Fig. 5. It clearly shows that drimarene blue K_2RL and eosin B adsorbed more in acidic conditions and adsorption decreased to very low level in basic conditions. Maximum adsorption of drimarene blue K_2RL and eosin B on *Opuntia dillenii* seeds occurred at pH 4 and 5, respectively. In acidic conditions dye species exit in ionic form which can interact more with chelating sites of adsorbent. Acidic conditions also help in hydrolysis of ligno-cellulosic material of *Opuntia dillenii* seeds, which results in exposure of more binding sites for chemisorptive removal of dye[26].

Effect of temperature on adsorption of drimarene blue K_2RL and eosin B dyes by *Opuntia dillenii* seeds is shown in Fig. 6. It shows that maximum adsorption of drimarene blue K_2RL and eosin B on *Opuntia dillenii* seeds occurred at 50 and 60 ºC, respectively. At higher temperature, *Opuntia dillenii* seeds cellulosic components are swelled up, exposing more porous sites which help in physiosorptive removal of dye molecules in efficient way. At relatively high temperature, thermal degradation of dye molecules results in smaller fragments, which can be adsorbed better as compared to bigger one. But at high temperature, adsorption is retarded because it is an exothermic process naturally[25,27].

Kinetic modeling of adsorption: Pseudo-second order kinetic model is usually followed in adsorption of dye molecules by agrowaste materials[12-22]. Linear form of Ho and McKay pseudo-second order kinetic model is given in eqn. 3[28].

$$\frac{t}{q} = \frac{1}{k_2 q_e} + \frac{1}{q_e t} \tag{3}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g^{-1}) and k is the rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). A line-to-line trend showing plot is drawn using 1/t at x-axis and t/q at y-axis and presented in Fig. 7. Correlation coefficient 'R^2' values are 0.765 and 0.844 for adsorption of drimarene blue K_2RL and eosin B dyes by *Opuntia dillenii* seeds adsorbent, indicating that this model is applicable on this adsorption system. It means chemisorptive removal of dyes occurred involving intra-particle diffusion and mass transfer mechanisms[28].

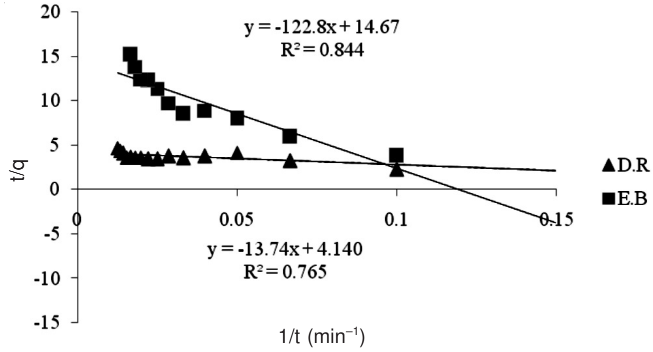

Fig. 7. Psudo-second order modeling of equilibrium data for adsorption of dyes by *Opuntia dillenii* seeds. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

Isothermal and thermodynamical modeling of adsorption: These modeling of equilibrium data are carried out by applying the optimized conditions simultaneously at higher dye concentration solutions and results are graphically represented in Figs. 8 and 9 and related parameters are given in Table-2.

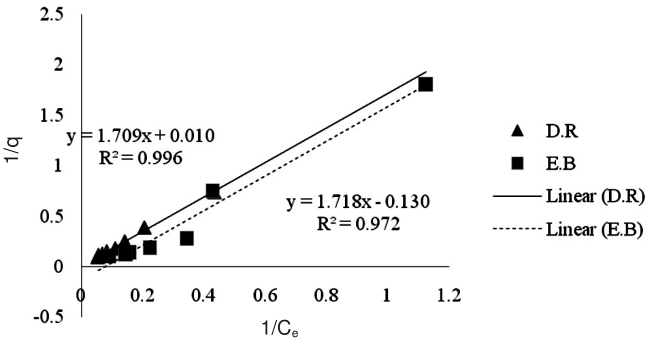

Fig. 8. Langmuir isotherms for dyes using *Opuntia dillenii* seeds as adsorbent. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

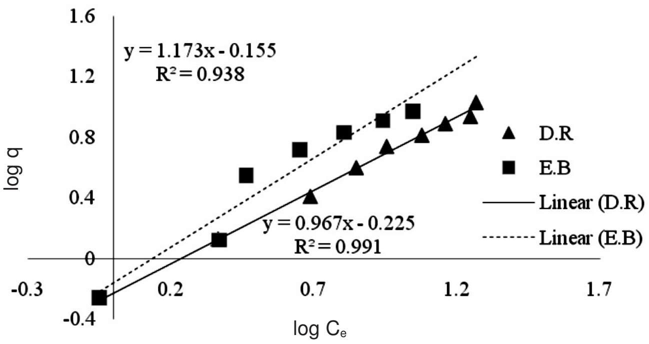

Fig. 9. Freundlich isotherms for dyes using *Opuntia dillenii* seeds as adsorbent. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

Langmuir isotherm: Its linearized form is given in eqn. 4[25]:

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (4)$$

Here 'b' (L g^{-1}) is empirical constant, indicating the affinity of *Opuntia dillenii* seeds towards dyes, used further for thermodynamic calculations and 'q_{max}' is maximum adsorption capacity of *Opuntia dillenii* seeds (mg g^{-1}). Their values are determined from regression analysis of graph showing in Fig. 8. Maximum adsorption capacity of *Opuntia dillenii* seeds for removing drimarene blue K_2RL is 100 mg g^{-1}, while for removing eosin B, it is 7.69 mg g^{-1}. The parameter 'b' is used to calculate separation factor 'R_L' using eqn. 5[25]:

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

'R_L' values between 0-1 depicts favourable adsorption. In this case, 'R_L' for drimarene blue K_2RL is 0.00034 and for eosin B, it is 0.208. It clearly favours the feasibility of this process. Further 'b' is used to determine Gibbs free energy change (ΔG^o) using eqn. 6[25]:

$$\Delta G^o = -RT \ln(K) \quad (6)$$

where ΔG^o in KJ/mol, 'T' is room temperature in Kelvin, 'R' is the universal gas and 'K' is the reciprocal of Langmuir constant 'b'. Negative values indicate the spontaneity of this process.

Freundlich isotherm: The equilibrium data obtained with varying concentration of dye and fixed dose of adsorbent was applied to the Freundlich isotherm (eqn. 7)[25]:

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

'K_F' and 'n' are Freundlich constants, calculated by slope and intercept of the graph between 'log C_e' and 'log q'.

The values of n are lie between 0 and 1 (Table-2), indicated that physiosorptive removal of dyes occurred efficiently.

On the whole, Langmuir model is more applicable to equilibrium data as compared to Freundlich model, as clear from their respective correlation coefficient values, which are greater in case of Langmuir model. It means that chemisorptive removal of dye molecules occurred more on homogenously distributed binding sites on *Opuntia dillenii* seeds in monolayer fashion as compared to physiosorption on heterogeneous binding sites in multilayer fashion.

Regeneration of adsorbent: The used *Opuntia dillenii* seeds was regenerated by using double distilled water, ethanol, NaOH and HCl and results shown in Fig. 10. It is clear from this graph that ethanol is more efficient in desorbing dye from *Opuntia dillenii* seeds as compared to other desorbents used. The relative order is as followed: ethanol > water > NaOH > HCl. Dyes are more soluble in ethanol as compared to water due to their aromatic nature, that's why desorb more with it. While using acid or base for desorption, base is more efficient

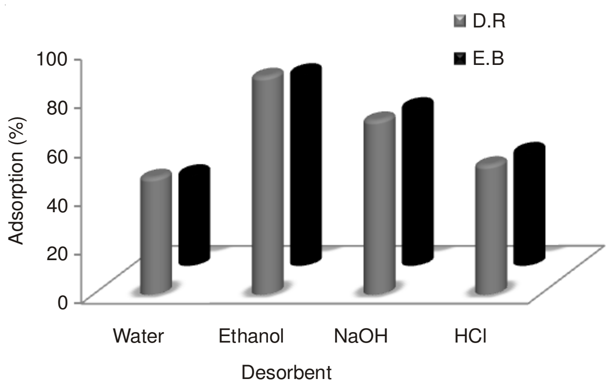

Fig. 10. Regeneration of *Opuntia dillenii* seeds using different eluents. Where D.R = drimarene blue K_2RL dye and E.B = eosin B dye

TABLE-2
ISOTHERMAL AND THERMODYNAMICAL PARAMETERS FOR BIOSORPTION OF DYES ON *Opuntia dillenii* SEEDS

Dyes	Langmuir isotherm parameters				Freundlich isotherm parameters			Thermodynamic parameters
	R^2	q_m (mg g^{-1})	b (L g^{-1})	R_L	R^2	K_F	n	ΔG^o (KJ/mol)
Drimarene blue K_2RL	0.996	100	58.51	0.00034	0.991	0.595	0.852	10.08
Eosin B	0.972	7.69	0.076	0.208	0.938	0.699	1.034	-6.38

in this case, because these dyes are acidic in nature, so more easily neutralized by base and desorbed from adsorbent.

Conclusion

So, it is obvious from results that *Opuntia dillenii* seeds can be efficiently employed for removing acidic synthetic dyes, namely: drimarene blue K_2RL and eosin B, from aqueous medium. Optimized conditions for removal of drimarene blue K_2RL by *Opuntia dillenii* seeds are: pH = 4, contact time = 1 h, temperature = 50 ºC, adsorbent dose = 0.1 g and for eosin B their values are: pH = 5, contact time = 1 h, temperature = 60 ºC, adsorbent dose = 0.3 g following dominantly chemisorptive pseudo-second order kinetics with maximum removing efficiency of 100 and 7.69 mg g^{-1}, respectively. The used *Opuntia dillenii* seeds can be recycled by desorbing with ethanol. So, *Opuntia dillenii* seeds can be used for dyes removal from water on larger scale.

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