Biosorptive Treatment of Acid Yellow-73 Dye Solution with Chemically Modified *Eugenia jambolana S*eeds

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Summary: The removal of reactive Acid Yellow-73 textile dyes from wastewater through biosorption has been investigated in laboratory using seeds of *Eugenia jambolana* as biosorbent. Biosorption potential was enhanced by chemical modification and surface chemistry changes were studied by recording FT-IR spectra of biosorbent. Operational conditions of biosorption were optimized in batch mode to evaluate biosorption data by Langmuir and Freundlich isotherms. Maximum removal of dye occurred at 4.0 pH, within 20-30 minutes, shaking at 150 rpm on 30-40°C temperature, using 40-60 micron sized particles, giving 'q_m' values 28.93 and 33.44 mg.g^{-1} of biosorbent with simple and chemically modified seeds of *Eugenia jambolana*. Spontaneity of this process was confirmed by negative ΔG^o values. These results had pointed out that *Eugenia jambolana* seeds have potential to be used on industrial scale for wastewater treatment containing anionic reactive dyes.

Keywords: Eugenia jambolana seeds, Acid Yellow-73 dye, biosorption, Langmuir and Freundlich isotherms.

Introduction

Waste-water containing dyes are usually treated by many physiochemical, chemical and biological methodologies like chemical precipitation followed by filtration, coagulation, electrocoagulation, adsorption on activated carbon, membrane filtration, ozonation, fungal decolorization, ion-exchange, photo-degradation, biosorption etc. But treatment by biosorption has been investigated in recent years enormously using different waste materials of agricultural or industrial origin like coir pith, bottom ash, egg shells, fishery waste, leaves of neem, globe artichoke and pine, radish peels, peas waste, orange peels, cassava peel, saw dust, rice husk, eucalyptus bark, wheat husk etc. The main purpose of searching new biosorbents is to replace activated charcoal and ion exchange resins, which are very expensive to use on larger scale but more efficient. The researchers are trying to find as an alternative biosorbents of biodegradable origin and cheap nature with great biosorptive efficiencies, and searching new ways to modify biosorption capacities, either by physical or chemical modification [1-12].

Different industries like textile, paper, rubber, plastic, food, cosmetic and leather tanning are discharging a huge volume of wastewater effluents on daily basis containing dyes, organic pollutants and heavy metals. Various types of dyes are used in these industries like: anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [11]. Acid dyes are mostly organic sulphonic acids, which are commercialized usually in the form of sodium salts for increasing their water solubility. Dyes are mainly problematic due to aesthetically unpleasant color producing tendency and non-biodegradable nature. Their degradation in wastewater due to the presence of other oxidizing chemicals results in the production of mutagenic intermediates and metabolite products. Moreover, their release in water reservoir strongly inhibits phytoplankton growth by hindering photosynthetic processes, which is ultimately lethal for zooplanktons and results in annihilation of food web equilibrium of life on earth [13-17].

Acid Yellow-73 dye is a reactive, anionic, textile dye having general formula shown in Fig.1. It is usually employed in detergent, soap, textile, printing and cosmetic industries. It is also marketed with the other names like fluorescein or its sodium salt, uranin and D & C Yellow#8.

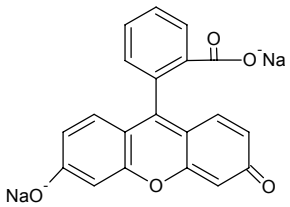

Fig. 1: Structure of Acid Yellow-73 dye.

It can harm respiratory system i.e. dyspnea, dermatitis and irritation to eyes, cardiovascular and nervous system of human beings and living organisms. Its thermal decomposition produces toxic fumes of oxides of carbon and nitrogen. It has

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mutagenic and tumorigenic effect on bacteria, yeast and somatic cells of mammalian, resulting in problem during reproduction and growth by affecting genetic material [18, 19]. Therefore, its removal from wastewater is a critical issue.

Eugenia jambolana (Jamun) seeds are used as a novel biosorbent for treating Acid Yellow-73 dye. *Eugenia jambolana* belongs to plant family Myrtaceae. It is very common plant in arid regions of Asian countries like Pakistan, India, Bangladesh and Sri Lanka. Due to its dense foliage and rapid growth nature, it is usually planted along side roads. Its fruit, seeds, leaves and bark are used in ayurvedic medicines for controlling diabetes mellitus, blood pressure and gingivitis. Its wood is used for construction because of strong and water resisting nature [20-22].

Results and Discussion

Surface Characterization

For investigating structural changes due to chemical modification in *Eugenia jambolana* seeds, FT-IR spectra were recorded and vibrational frequencies of different functional groups compared (Table-1). Broad and intense peaks at 3446 and 3421 cm^{-1} were due to stretching of O-H group of alcohols, phenols or carboxylic acids, which are commonly found in plant materials due to the presence of pectin, cellulose and lignin.

Table-1: Characteristic Vibrational absorption frequencies in FT-IR spectra of *Eugenia jambolana* seeds.

Biosorbent	Vibrational frequencies (cm^{-1})
S.B	**3446**, **2938**, **2740**, **2157**, **1737**, **1628**, **1448**, **1382**, **1256**, **1161**, **1119**
C.M.B	**3421**, **2918**, **2847**, **2722**, **2138**, **1732**, **1621**, **1443**, **1370**, **1246**, **1156**, **1112**

The bands at 2938, 2855, 2847 and 2918 cm^{-1} were due to C-H stretching vibration of aliphatic carboxylic acids. The bands observed at 1737 and 1732 cm^{-1} were due to stretching vibration of C=O bond of non-ionic carboxylic or methoxy ester functional groups and at 1448, 1443, 1382 and 1370 cm^{-1} were due to ionic carboxylic groups (-COO-) whereas peaks at 1628 and 1621 cm^{-1} were due to amino groups. The vibrations at 1256 and 1246 cm^{-1} were due to carbonyl and hydroxyl groups of carboxylic acids and phenols. The bands at 1161, 1119, 1156 and 1112 cm^{-1} were attributed to thionyl (>C=S) functional groups. It is clear from the study that vibrational frequencies shift to lower wave number values, showing that carboxyl, hydroxyl, phenolic, ester, amino and thionyl functional groups are active binding sites for biosorption in *Eugenia jambolana* seeds [23, 24].

Optimization of Biosorption Conditions

Different biosorption conditions like particle size of biosorbent, biosorbent dose, contact time, pH and temperature were optimized using simple biosorbent (S.B) and chemically modified biosorbent (C.M.B) *Eugenia jambolana* seeds. Effect of particle size on biosorptive removal of Acid Yellow-73 dye was shown in Fig. 2. It clearly indicated that maximum biosorption occurred when 40-60 micron sized particles were used. Larger sized particles have low surface area exposed for biosorption and very small sized particles coagulated in solution resulting in lower biosorptive removal of dye. The optimized conditions were used for isothermal investigation of equilibrium data. Chemical modification enhanced biosorption efficiency by exposing more sites that are binding.

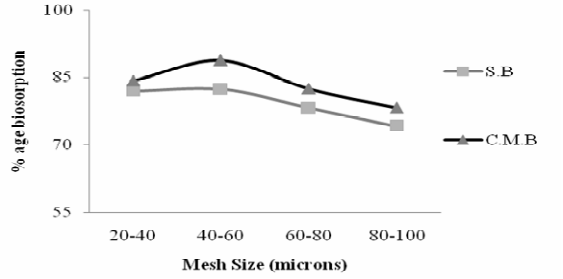

Fig. 2: Effect of biosorbent particle size of *Eugenia jambolana* seeds on % age biosorption of Acid Yellow-73 dye.

Effect of biosorbent dose on removing capacity of Acid Yellow-73 dye by *Eugenia jambolana* seeds was shown in Fig. 3.

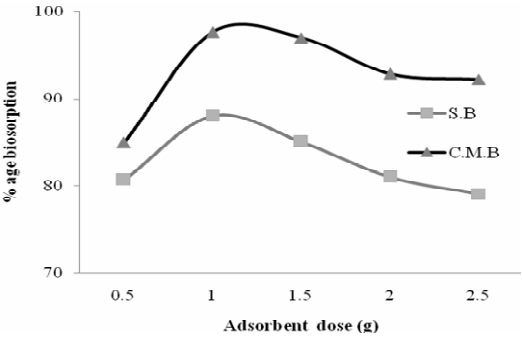

Fig. 3: Effect of adsorbent dose on % age biosorption of Acid Yellow-73 dye.

It shows that maximum removal of dye occurred at 1.0g of biosorbent dose. Chemical modification with tartaric acid resulted in enhanced removing efficiency of same quantity of biosorbent by enhancing the number of binding sites available for biosorption that was mainly due to protonation of carboxylic, hydroxylic and amino functional groups of seeds (as clear from FT-IR data in Table-1) [24].

The effect of contact time on biosorption capability of *Eugenia jambolana* seeds was graphically presented in Fig. 4. The maximum biosorption occurred within 30 and 20 minutes using simple and chemically modified *Eugenia jambolana* seeds. Chemical modification results in exposure of more binding sites for chelating adsorbate species in relatively shorter interval of time with even better efficiency.

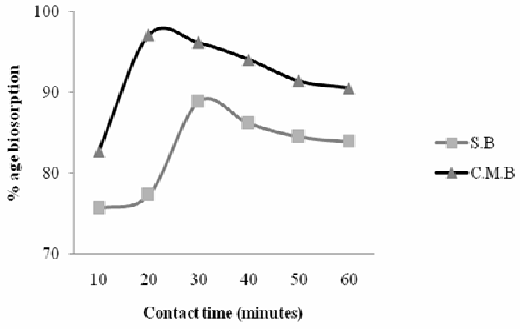

Fig. 4: Effect of various contact intervals of *Eugenia jambolana* seeds with Acid Yellow-73 dye solution on % age biosorption.

Greater biosorption of anionic dye occurred in pH range 3 to 4 using simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds (Fig.5). In highly acidic conditions of solution, the interfering anions compete with the anionic dye, lowering biosorption capacities of *Eugenia jambolana* seeds. It is, basically, surface adsorption mechanism of dye removal, in which a dye molecule is attracted to a charged surface of biosorbent without the exchange of ions or electrons. The functional groups of biosorbent are protonated at higher pH, so biosorption efficiency increases with increase in pH. Hence, electrostatic interactions are principally involved in Acid Yellow 73-dye biosorption [6, 17].

The effect of variation in agitation speed on the biosorption of Acid Yellow-73 dye was shown in Fig. 6.

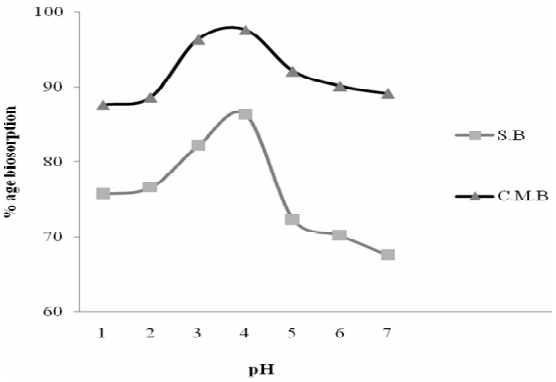

Fig. 5: Effect of initial pH of Acid Yellow-73 dye solution on % age biosorption by *Eugenia jambolana* seeds.

The maximum removal of dye occurred at 150 rpm using simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds. Agitation influences the distribution of the dye molecules in the bulk solution and formation of the external boundary film of dye molecules around the active binding sites of biosorbent surface. By further increase in agitation speed, biosorption efficiency was lowered down because all binding sites had been already utilized in this process [5, 15-18, 24].

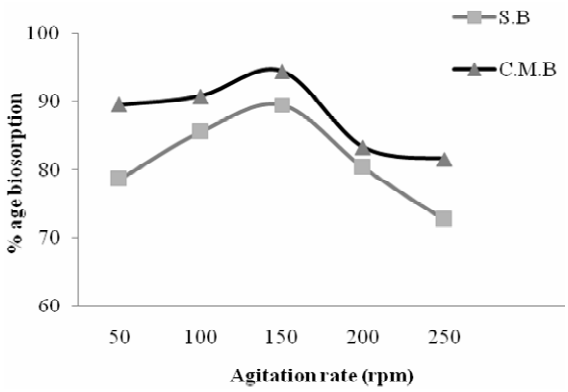

Fig. 6: Effect of agitation rate on % age biosorption of Acid Yellow-73 dye by *Eugenia jambolana* seeds.

The effect of temperature on biosorptive removal of Acid Yellow-73 dye by *Eugenia jambolana* seeds is shown in Fig. 7. It shows that maximum biosorption occurred at 30 and 40 ^{0}C using simple and chemically modified *Eugenia jambolana* seeds respectively. Biosorption is usually an exothermic process in most of the reported cases, so, it would be expected that decrease in biosorption be

caused by an increase in temperature of the dye–biosorbent system [15-24].

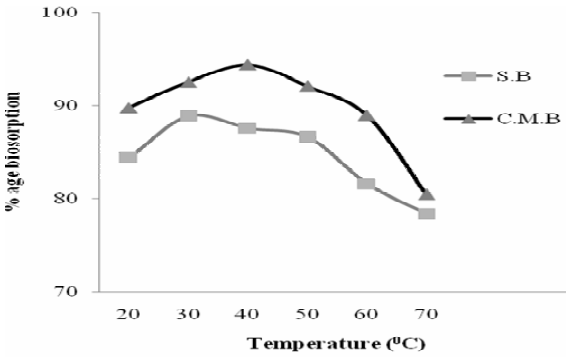

Fig. 7: Effect of temperature on % age biosorption of Acid Yellow-73 dye by *Eugenia jambolana* seeds.

Desorption Studies

The results of desorption experiment was shown in Fig. 8. It is clear from the graph that dilute nitric acid efficiently remove Acid Yellow-73 dye form simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds. After desorption, the biosorbent can be recycled with a little decrease in biosorption efficiency or employed as soil conditioner as organic manure.

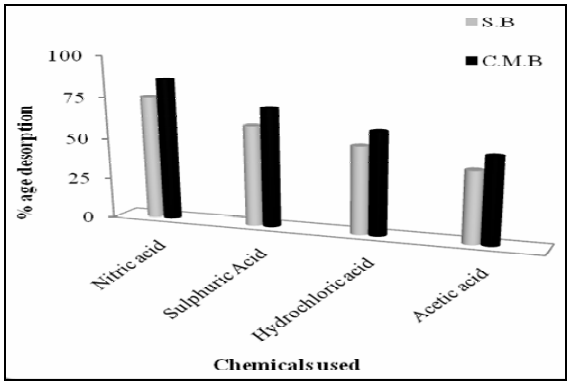

Fig. 8: Graph showing % age desorption of Acid Yellow-73 dye from biosorbent using various chemicals.

Isothermal Investigation of Equilibrium Data

Isothermal parameter constants were calculated using their standard straight-line equations and results of regression analysis were given in Table-2. The correlation coefficient (R^2) value is greater for Langmuir model suggesting that it is applicable to equilibrium data more than Freundlich model. It means that monolayer chemisorption of Acid Yellow 73-dye occurred on the homogenously distributed active binding sites on the surface of *Eugenia jambolana* seeds. Langmuir parameter 'q_m' values were 28.93 and 33.44 mg.g^{-1} simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds respectively, clearly showing the enhancement in biosorption capacity after chemical modification.

Other Langmuir parameter 'b' is used for thermodynamic calculations and separation factor constant 'R_L' [6, 22]. The value of R_L lies between zero and one for favorable biosorption process, while R_L>1 represents unfavorable process. Here its value for simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds was 0.145 and 0.303 respectively, indicating feasibility of the process of removal of Acid Yellow 73-dye.

The Freundlich isotherm parameter 'K_F' value was 4.23 and 1.52 L.mg^{-1} for simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds respectively. The second Freundlich isotherm parameter 'n' is an empirical parameter related to biosorption intensity, which varies with heterogeneity of the binding sites of biosorbent. Its value less than 8 shows the feasibility of the process at low concentration of adsorbate species, i.e. dye concentration [17].

Thermodynamical Studies

The feasibility of biosorption process in terms of spontaneous nature is indicated by ΔG^o values, which is determined with the help of Langmuir constant 'b'. It is -7.012 and -9.346 KJ/mol for simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds correspondingly. It shows that spontaneity of the process increases after chemical modification of biosorbent for removing Acid Yellow 73-dye with even better efficiency [25].

Kinetic Studies

Pseudo-second order kinetic model was employed in this study to equilibrium data and results are given in Tables-3. As can be seen from Table-3 that pseudo-second order kinetic model was applicable to biosorption data in both cases of simple (S.B) and chemically modified (C.M.B) *Eugenia jambolana* seeds, because regression coefficient values (R^2) were close to unity. The 'k_2' values of simple (S.B) and chemically modified biosorbents (C.M.B) led to the conclusion that the reaction taking place is pseudo-second order suggesting chemical sorption between the dye solution and biosorbent [25].

Table-2: Isotherm parameters for biosorption of Acid Yellow-73 dye on *Eugenia jambolana* seeds.

Adsorbents	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters			Thermodynamical parameter
	R^2	q_m (mg.g^{-1})	b (L.g^{-1})	R^2	K_F (L.mg^{-1})	n (L.mg^{-1})	ΔG^o (KJ.mol^{-1})
S.B	0.985	28.93	0.059	0.977	4.23	2.325	-7.012
C.M.B	0.972	33.44	0.023	0.966	1.52	1.574	-9.346

Table 3: Kinetic parameters for biosorption of Acid Yellow-73 dye on *Eugenia jambolana* seeds.

Adsorbents	Pseudo-second-order model		
	k_2 (|g.mg^{-1}|min^{-1})	q_e (mg.g^{-1})	R^2
S.B	0.019	2.427	0.995
C.M.B	0.096	2.391	0.989

Experimental

Chemical Reagents and Instrumentation Used

Acid yellow 73-dye, HCl, H_2SO_4, HNO_3. CH_3COOH, NaOH and tartaric acid were used in this study. All these chemicals were of analytical grade. Double distilled water was employed for solution preparations. Electric Balance ER-120A (AND), Electric grinder (Ken-Wood), pH meter (HANNA pH 211) and (Spectro UV-Vis Double Beam UVD-3500, Labomed spectrophotometer, FTIR spectrophotometer (Perkin Elmer RX-I) were used.

Preparation of Biosorbent Samples

The *Eugenia jambolana* seeds were purchased from local markets of Lahore, Pakistan and washed with water for removing dust and foreign impurities. They were sun dried and crushed into fine powder. This was the sample of the simple biosorbent (S.B). For chemical modification of biosorbent, 50 g of this powder was dipped into 500 mL of 10 % tartaric acid solution for 3-4 hours after wrapping beaker with aluminum foil. After that, it was filtered and first air dried followed by drying in oven at 80 ^oC for one hour. This was the sample of chemically modified biosorbent (C.M.B). Both these samples were stored in airtight flasks until further use.

Biosorption Experiments

For optimizing operational conditions of biosorption, various experiments were conducted by varying at a time one factor, keeping other constant in the following range: particle size of biosorbent (20-40 to 80-100 microns mesh size), adsorbent dose (0.5-2.5 g), contact time, (10-60 min), initial pH of the solution (1-7), agitation speed (50-250 rpm) and temperature (20-70 °C). The solution volume (V) was 50 mL in all batch experiments and initial dye concentration (C_o) was 15 mg.L^{-1}. pH of dye solutions were adjusted with 0.01 M HCl and 0.1 M NaOH. After biosorption experiment, dye solutions were filtered and remaining concentration of dye in filtrate was with UV-Vis spectrophotometer working at λ_{max} 488 nm. All the experiments were conducted in triplicate fashion and average values were considered for calculations [6, 17].

After completing biosorption experiments, desorption studies were carried out with all used biosorbents for their reusability. They were regenerated by dipping their 5 g in 50 mL of 10.0 mM solution of HNO_3, HCl, H_2SO_4 and CH_3COOH separately for 20 minutes, while stirring at 150 rpm in room temperature conditions, i.e. at 25 $^0C \pm 5$ [17].

Mathematical Modeling of Equilibrium Data

The biosorption (%age) at any instant of time was determined by the following equation:

$$\%\ age\ \ biosorption\ = \frac{C_o - C_e}{C_o} \times 100 \quad \text{(Eq.1)}$$

Optimized conditions of biosorption experiments were applied to higher concentration of dye solution for isothermal studies, keeping other factor constant. Langmuir isotherm parameters were calculated by regression analysis of equation-2:

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad \text{(Eq. 2)}$$

The value of q is calculated by equation-3:

$$q = \frac{(C_o - C_e)V}{m} \quad \text{(Eq. 3)}$$

Separation factor 'R_L' was calculated with equation-4:

$$R_L = \frac{1}{(1_o + bC_o)} \quad \text{(Eq. 4)}$$

Freundlich isotherm parameters were calculated by regression analysis of equation-5:

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad \text{(Eq. 5)}$$

In these equations, C_o and C_e are the initial and final concentrations of dye respectively, 'q' (mg/g) is the amount of dye removed by biosorbent, 'q_m' (mg.g^{-1}) and 'b' (L.g^{-1}) are Langmuir isotherm parameters. Whereas 'K_F' (L.mg^{-1}) and 'n' (L.mg^{-1}) are Freundlich isotherm constants [6, 17].

Thermodynamic parameter 'ΔG^o' was calculated from equation-6:

$$\Delta G^o = -RT \ln K \qquad \text{(Eq.6)}$$

where 'ΔG^o' is in KJ.mol^{-1}, *'R'* is the universal gas constant, *'T'* is the absolute temperature in Kelvin and '*K'* is the reciprocal of Langmuir constant '*b*'. 'ln' is the symbol of natural logarithm. [25-30].

For kinetic modeling of equilibrium data, optimized conditions of biosorption experiments were employed by varying time and keeping other factor constant. Pseudo-second order kinetic model was employed using equation-7:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e t} \quad \text{(Eq. 7)}$$

The % age desorption was calculated by using equation-8:

$$\%\ age\ \ desorption = \frac{q_{des}}{q} \times 100 \quad \text{(Eq.8)}$$

Here *'q_e'* , 'q_t' are the biosorption capacity at equilibrium and at time t, 'q_{des}' is the amount of dye desorbed in mg.g^{-1} of biosorbent and 'k_2' is the overall rate constants of pseudo-second order sorption ([g.mg^{-1}].min^{-1}) [17, 25].

Conclusion

It is evident from the study that *Eugenia jambolana* seeds can efficiently remove Acid Yellow 73-dye from water. Chemical modification of biosorbent with tartaric acid further enhances its biosorption capabilities for removing anionic dyes due to protonation of active binding sites. Isothermal and kinetic modeling shows that chemisorption occurred during biosorption of dye. Negative ΔG^o values confirmed the spontaneous nature of biosorption. Desorption studies showed that biosorbent can be efficiently recycled by regenerating it with dilute nitric acid. So, chemically modified *Eugenia jambolana* seeds can be effectively employed for anionic dye removal processes by biosorption.

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