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Removal of Basic Blue-9 Dye from Water by *Eugenia jambolana* Seeds and *Citrullus lanatus* Peels

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Sorption of basic blue 9 dye from aqueous solution on the surface of *Eugenia jambolana* seeds (Jamun seeds or J.S) and *Citrullus lanatus* peels (Watermelon peels or W.M.P) was accomplished under the optimize conditions of temperature, pH, contact time, agitation speed and adsorbent dose. Both adsorbents were characterized for seeking different functional groups and unsaturation that can act as possible active sites for biosorption. The values of q_{max} data for basic blue-9 dye sorption on W.M.P (35.714 mg g^{-1}) showed better removing capacity as compared to J.S. (4.902 mg g^{-1}). Thermodynamic parameter 'ΔG^o' indicated that basic blue-9 sorption on jamun seeds and watermelon peels exhibit spontaneous and exothermic behaviour. The results of these investigations suggested that these agro-wastes can be utilized as sorbent materials for basic blue-9 dye removal from waste-water streams.

Keywords: Basic blue-9 dye, *Citrullus lanatus* peels, *Eugenia jambolana* seeds, Sorption.

INTRODUCTION

Water is a spring of energy and life. Fast speeds of mechanization, growing population, industrialization and unforeseen development of towns and cities have largely added to the intense pollution of soil and water. The major sources of water pollution can be accredited to the dumping of poisonous industrial wastes and untreated sanitary wastes disposal, transfer of industrial fluids and agricultural fields, rivers and ponds *etc*. Mostly 70-80 % of all diseases in world are associated with pollution of water. Color is the first pollutant to be documented in water and has to be eliminated from wastewater before dumping off the industrial effluent into water bodies. Industries *viz*., paper, plastic, textile food, rubber, cosmetics and leather tanning are dislodging a massive volume of waste water effluents daily. Such effluents contain dyes, heavy metals and organic pollutants. Dyes retards light entrance, block photosynthetic activity, prohibits biota growth and their metal chelating capability is toxic for fish and fresh water organisms[1-4]. Presence of oxidizing agents in water degrades the dyes. Products of such degradation are metabolites that have mutagenic effects. Hence the dyes release in water greatly prohibits growth of phytoplankton by interrupting processes of photosynthesis which is eventually fatal for zooplanktons and fallout in ruining food web of life[5-9]. Present study has been planned to remove basic blue-9 dye from water.

Basic blue-9 (B.B-9, common name: Methylene blue) is a cationic dye. It is generally used for dying cotton, wood and silk. Its chemical formula is $C_{16}H_{18}N_3SCl{\cdot}3H_2O$ (Fig. 1). It is not treated as severely-poisonous[10], but its excess quantity has many adverse effects on human health. Like on inhalation, it causes paroxysms of difficult breathing. Whereas its swallowing or drinking along with food causes burning sensation and sometimes in severe cases results in vomiting, diarrhea, nausea, gastritis, abdominal and chest pain, severe headache, mental confusion, profuse sweating, urinary tract infection and methemoglobin anemia. It can infect eyes, which results in irritation. Hence the removal of basic blue-9 dye, from waste-water is essential due to its adverse effects[11-13].

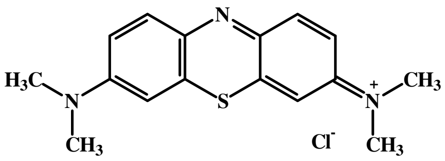

Fig. 1. Structure of basic blue-9

The management of waste-waters to remove the wastes and to make them acceptable for successive use requires biological, physical and chemical processes. But most of the techniques require financial inputs which overrides the budget of pollution control planning. Moreover there are many restrictions in following them on industrial scale. Coagulation process creates an enormous amount of sludge which leads to high costs when disposed off. Process of ion-exchange is beneficial because it has no loss of adsorbent due to modification. However, it is costly and cannot be accommodated for wide range of dyes and membrane discoloring problem also occurs side by side, therefore membrane separation application is constrained. Biological methods for dye treatment are not at all effective. Adsorption is a well-known surface phenomenon and an effective technique for water purification[14-17]. It provides an alternative solution, particularly if the adsorbent is occurring in large and amount being low cost as well. This process transfers the dye from the waste water to an adsorbent surface. It helps in reducing effluent volume and moreover, the used adsorbent can easily be disposed off in landfills as the disposal of solid waste is comparatively easy. Hence, adsorption treatment for removal of dyes from waste-water can be regarded as a superior technique to the other ones in accordance with the design simplicity, operationally handy, being low cost and is indifferent to toxic pollutants. Adsorption never corresponds to the formation of harmful substances. Therefore, many investigators have considered the practicability of using the low cost adsorbents for the exclusion of various pollutants and dyes from waste waters. Quite a lot of contemporary agricultural wastes have been used as adsorbents. The two main purposes of using agricultural wastes as adsorbents are: first is to substitute activated carbon with low cost alternatives and secondly to apply various waste products for this purpose so that re-use of waste materials can be accomplished. These low cost adsorbents at least have found use in laboratories for treatment of colored effluents with different degrees of accomplishment. Various adsorbents have been utilized for removing Basic blue-9 dye from water including rice husk[18], rice husk ash[19], spent tea leaves[20], tea waste[21], coconut bunch waste[22],coconut husk activated carbon[23], garlic peel[24], brazil nut shell and wood apple shell[25], papaya seed[26], pineapple stem waste[27], sunflower stalks[28] and pearl millet husk[29]. The present article deals the technical feasibility of removing basic blue-9 dye by low-cost and non-conventional adsorbents from waste-water. These include *Eugenia jambolana* seeds and *Citrullus lanatus* peels.

Eugenia jambolana (Common name: Jamun, family: Myrtaceae) seeds are used as a most recent adsorbent for treating basic blue-9 dye. It is native to locality of barren areas of Asian countries. Due to its impenetrable vegetation and rapidly growing nature, it is usually found along sides of roads. Its bark, fruit, leaves and seeds are used in medicines that are meant for controlling blood pressure, sugar and gingivitis. Its wood is strong and is water resistant therefore used for construction purposes[30]. It has marked action on diabetes mellitus as it causes marked weakening of sugar in urine. It also helps in treating old ulcers of skin related with diabetes mellitus.

Citrullus lanatus (Common name: Watermelon, family: Cucurbitaceae) is a vine like flowering plant. It is native to southern Africa and Asian countries. Its fruit 'pepo'is a berry, which has a thick rind that is usually wasted[31]. Its rindis a rich source of the non-essential amino acid called as citrulline, which contains copious amount of carboxyl and amino groups. Because watermelon peels is often thrown out and not used as food item, its biosorbing potential has been explored in this study for sorbing basic blue-9[32].

This study investigates the basic blue-9 dye biosorption from aqueous solution by jamun seeds and watermelon peels. The biosorbents were first characterized by applying different processes such as Boehm titration (for determination of acidic and basic sites), Iodine titration(for determination of micropores), determination of porosity/bulk density, determination of ash content and volatile matter, determination of moisture content, determination of pH and determination of zero point pH. The effect of different parameters on biosorption process was also studied.

EXPERIMENTAL

Basic blue-9 dye (λ_{max}: 662 nm, Scharlaw, C.I (52015), HCl (37 %, 11.6M), NaOH (m.w. 40 g/mol), NaCl (m.w. 58.5 g/mol), Iodine crystals (m.w. 253.81 g/mol, 99.8 + %), KI (m.w. 166 g/mol), Na_2CO_3 (m.w. 58.5 g/mol), $NaHCO_3$ (m.w. 84 g/mol), phenolphthalein, methyl orange, KCl (75.5 g/mol), $MgCl_2·6H_2O$ (95 g/mol), $CaCO_3$ (100 g/mol), $CuSO_4·5H_2O$ (249.68 g/mol), $CdCl_2·H_2O$ (201.32 g/mol), $ZnCl_2$ (136.28 g/mol), K_2CrO_4 (194.20 g/mol), $MnCl_2·H_2O$ (143.86 g/mol), $Pb(NO_3)_2$ (331.21 g/mol) and $NiSO_4·6H_2O$ (263 g/mol) chemicals were used. They were obtained from Riedel-de-Haen, Merck, Acros Organic and Friends laboratory chemicals and used as such. All glassware were washed with chromic acid and water before using for the experiments and sterilized at 70 °C for 0.5 h in an electrical oven.

Electric grinder, Weighing balance (VELP Scientifica 230 V, 50 Hz), Electrical furnace (ranging from 30-1200 °C) Naberthem B170,UV/VIS spectrophotometer (UVD-3500, Labomed) and orbital shaker (model OSM-747) Digiteck instruments.

Preparation of adsorbent: Jamun seeds and water melon peels were collected from a local market of Lahore and washed.They were soaked in 10 % ethanol solution separately for 2 h, in order to remove coloring material and microorganisms from them, filtered and dried in sunlight for 3 days. The samples were then oven dried at about 70-80 °C for 16 h. Then it was ground to a fine powder in a pin mill. The resulting material was sieved in the size range of 50 to 60 mesh (ASTM)[33].

Characterization of adsorbents: The biosorbents were characterized by applying different processes such as: Boehm titration (for determination of acidic and basic sites), Iodine titration (for determination of micro-pores), determination of porosity/bulk density, determination of ash content and volatile matter, determination of moisture content, elemental analysis, determination of pH and determination of zero point pH and results are given in Table-1 and in Figs. 2 and 3[34].

Synthetic wastewater solution of basic blue-9 dye: In order to make 1000 ppm stock solution of dye, its 1 g was dissolved per litre. Standard solutions (5-25 ppm) of dye were prepared from the stock solution by dilution.

Batch adsorption experiments: They were done separately using both adsorbents, in order to optimize adsorption parameters for removing basic blue-9 dye, like: contact time, pH of dye solution, adsorbent dose, temperature and agitation speed, followed by isothermal studies for determining mechanism of sorption and thermodynamic feasibility of this process on industrial scale. Same procedure is followed as described earlier[31,33]. The percentage adsorption of dye is calculated by eqn. 1:

TABLE-1
PHYSICOCHEMICAL ANALYSIS OF *Eugenia jambolana* SEEDS (J.S) AND *Citrullus lanatus* PEELS (W.M.P)

Property		J.S	W.M.P
pH		4	7
Particle density (g/cm^3)		0.476	0.479
Bulk density p_{wet}		0.980	0.952
Porosity %		0.165	0.185
Moisture %		11	8
Ash %		2.2	2
Volatile matter %		10	28
Iodine number (mg/g)		8.45	2.108
Carboxylic (acidic functions) (mmol)		1.987	1.9972
Phenols (mmol)		0	0.004
Lactones (mmol)		0.003	0 .006
Basic sites (mmol)		1.98	1.98
pH_{pzc}		4	6
Elemental contents (%)	K^+	0.952	14.807
	Na^+	2.387	21.10
	Mg^{2+}	0.304	0.342
	Ca^{2+}	1.122	0.30
	Fe^{2+}	0.001	0.038

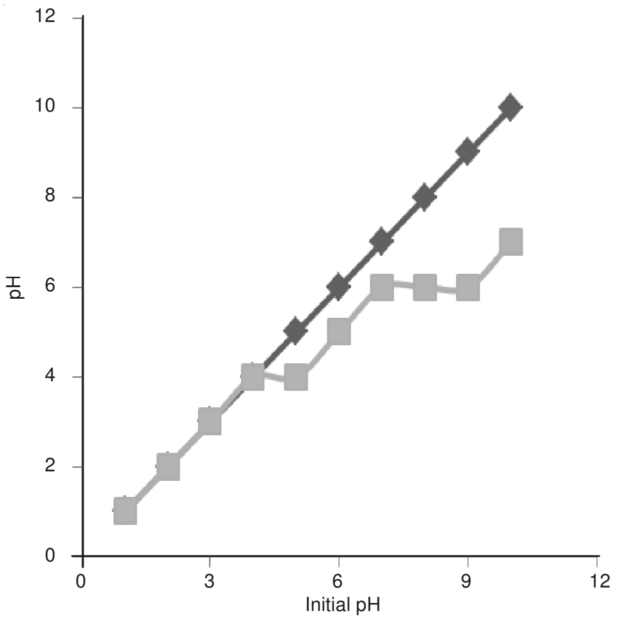

Fig. 2. pH_{pzc} of *Eugenia jambolana seeds*

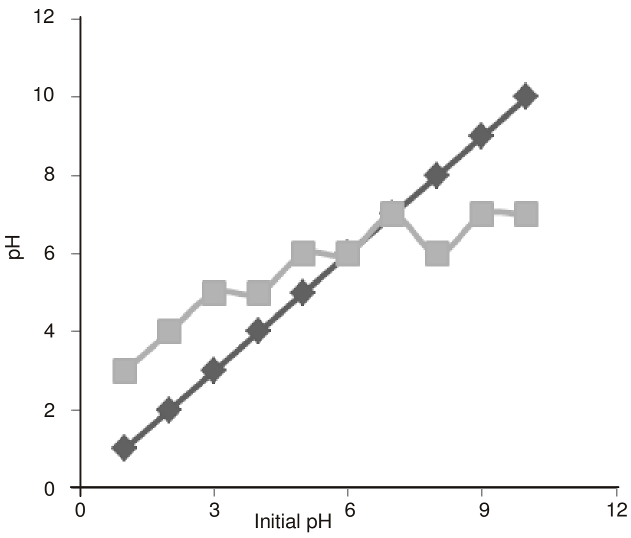

Fig. 3. pH_{pzc} of *Citrullus lanatus* peels

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

Initial concentration 'C_0' is 25 ppm, while remaining concentration 'C_e' is determined spectrophotometrically using standard solutions of dye at 662 nm λ_{max}. Optimized conditions were employed for isothermal investigations.

RESULTS AND DISCUSSION

Table-1 showed that *Citrullus lanatus* peels and *Eugenia jambolana* seeds have both acidic and basic functional groups, which can act as possible active sites for adsorption. Unsaturated functional groups in adsorbents enhance their chelating nature, in turns increasing sorption capacity. It is found that *Eugenia jambolana* seeds contain more unsaturated compounds, as indicated from its iodine value. *Citrullus lanatus* peels contain more acidic functional groups as compared to *Eugenia jambolana* seeds, as indicated from higher values of acidic contents like: carboxylic, phenolic and lactonic sites. Figs. 2 and 3 are showing that pH_{pzc} value of *Eugenia jambolana* seeds is 4 and for *Citrullus lanatus* peels, it is 7. It is indicating that they can work better for basic type of pollutants, instead of acidic type, because of having more acidic functional groups[32-35]. Elemental analysis indicated that they did not contain any harmful metal ions, so they can be employed for adsorption studies without any harm to environment in benign way.

Optimization of operational conditions for sorptive removal of basic blue-9 dye

Effect of sorbent dose: Adsorbent dose ranging from 0.3 to 3 g with a difference of 0.3 g each, was subjected to ten 100 mL conical flasks containing 25 mL of 25 ppm solution of basic blue-9 dye for 35 min at 100 rpm at 25 ± 1 °C. Solutions were then filtered off and their absorbance was noted through spectrophotometer. Optimum adsorbent dose for watermelon peel as shown in Fig. 4 was obtained at 0.6 g and for jamun seed at 2.4 g. For jamun seed, the increase in % age adsorption of dye was continuous upto 2.4 g but for watermelon peel the trend was irregular but maximum adsorption occurred at 0.6 g.

Effect of contact time: It was determined,ranging from 5 to 60 min 0.5 g of adsorbent was added in twelve 100 mL Erlenmeyer flasks containing 25 mL of 25 ppm solution of basic blue-9 dye and kept for above specified contact time at 100 rpm at 25 ± 1 °C. Then adsorbents were separated form solutions and remaining dye concentration was noted. Optimum contact time for both watermelon peels and janum seed as shown in Fig. 5 was found to be 60 min. For both the adsorbents the trend of % age adsorption was irregular. Initially it was increased due to availability of more empty binding sites, later on decreased and again increased due to passive transport into intra-particle diffusion[28-35].

Effect of agitation speed: It was determined in range of 25-200 rpm using 0.5 g of adsorbent in eight 100 mL Erlenmeyer flasks containing 25 mL of 25 ppm solution of basic blue-9 dye and kept for 10 min. Then adsorbents were separated form solutions and remaining dye concentration was noted. Optimum agitation speed for watermelon peels as shown in Fig. 6 was 75 rpm and for jamun seeds, it was 100 rpm. The % age adsorption was not vary very much with changing agitation speed.

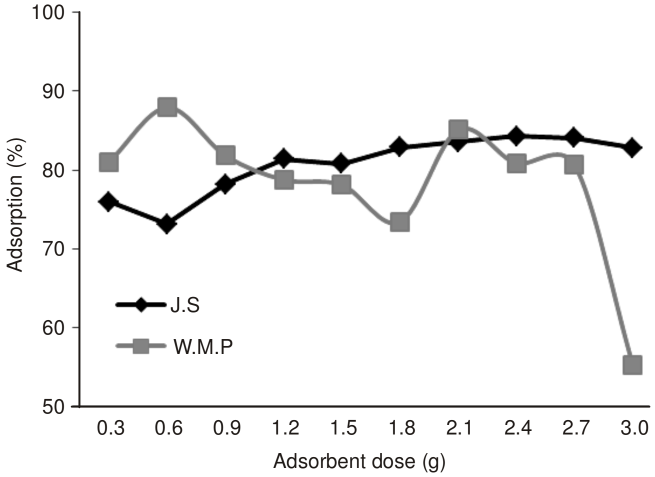

Fig. 4. Effect of adsorbent dosage on basic blue-9 dye comparative sorptive removal by *Eugenia jambolana* seeds (J.S) and *Citrullus lanatus* peels (W.M.P)

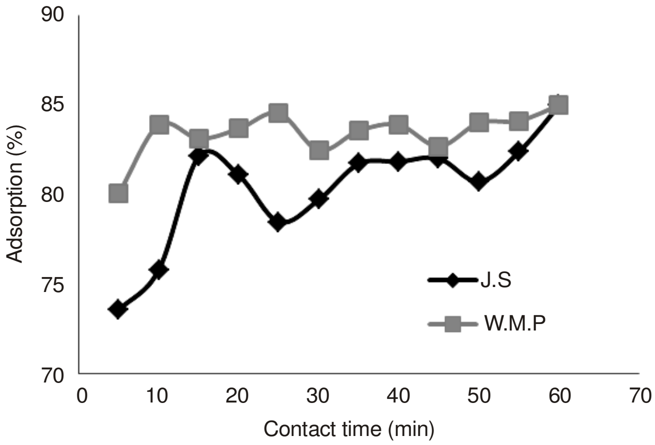

Fig. 5. Effect of contact time on basic blue-9 dye comparative sorptive removal by *Eugenia jambolana seeds* (J.S) and *Citrullus lanatus* peels (W.M.P)

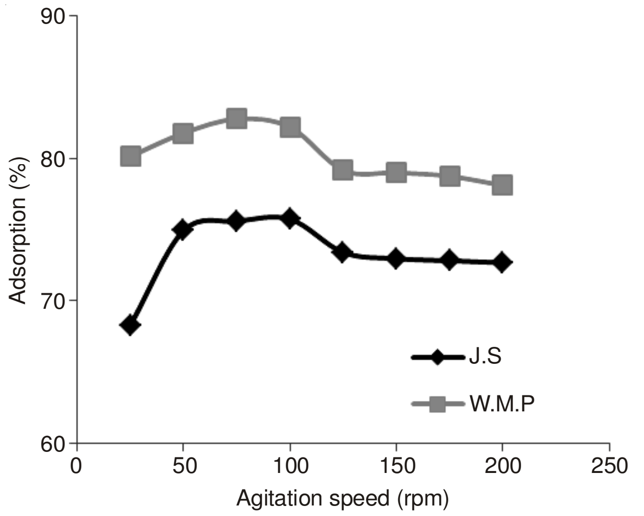

Fig. 6. Effect of agitation speed on basic blue-9 dye comparative sorptive removal by *Eugenia jambolana* seeds (J.S) and *Citrullus lanatus* peels (W.M.P)

Effect of pH: It was determined in range of 1-9 with a variation of 1 each. 0.5 g of adsorbent was added in ten 100 mL Erlenmeyer flasks containing 25 mL of 25 ppm solution basic blue-9 dye and kept for above specified pH for 25 min at 100 rpm at 25 ± 1 °C. Solutions were then filtered off and dye concentration was measured. Optimum pH for watermelon peel as shown in Fig. 7 was found to be 4,while for jamun seed, it was 6. On jamun seed, % age adsorption of basic blue-9 dye varied in a wave like manner with increasing pH values but on watermelon peel the dependence of adsorption is such that after an increase in pH upto 4, the % age adsorption was not increased or decreased sharply.

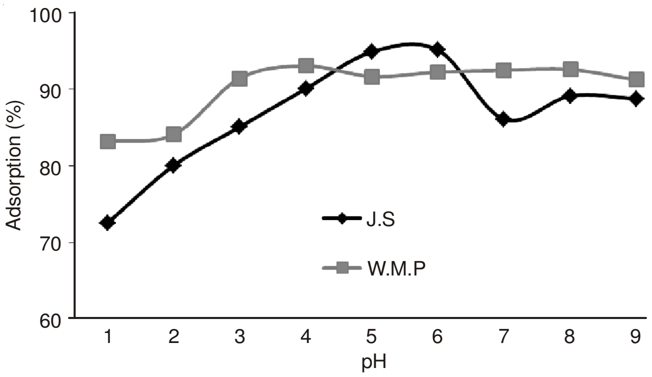

Fig. 7. Effect of pH on basic blue-9 dye comparative sorptive removal by *Eugenia jambolana seeds* (J.S) and *Citrullus lanatus* peels (W.M.P)

Effect of temperature: It was determined in range of 20-80 °C at an interval of 10 °C each. 0.5 g of adsorbent was added in six 100 mL Erlenmeyer flasks containing 25 mL of 25 ppm solution basic blue-9 dye and kept for above specified temperature for 25 min. Then adsorbents were separated form solutions and remaining dye concentration was quantified. Optimum temperature for watermelon peel as shown in Fig. 8 was found to be 30 °C and for jamun seed it was 50 °C. For watermelon peels, % age adsorption increased first reaching a maximum value and then decreased but for jamun seeds it was continuously increased but maximum adsorption occurred at 50 °C.

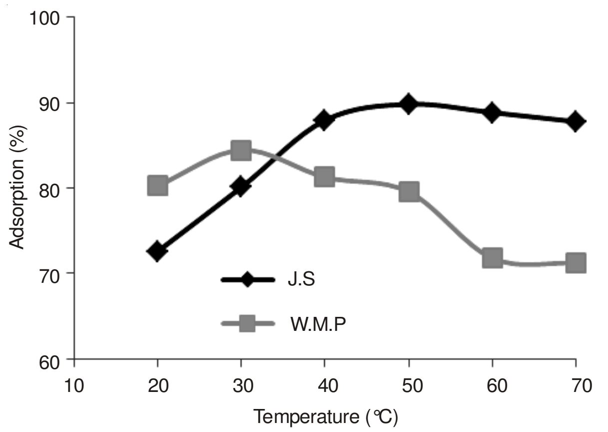

Fig. 8. Effect of temperature on basic blue-9 dye sorptive removal by *Eugenia jambolana seeds* (J.S) and *Citrullus lanatus* peels (W.M.P)

Study of adsorption isotherms: Seven Erlenmeyer flasks of 250 mL were washed, dried and labeled 1-7. Basic blue-9 dye solutions of concentration 10-40 ppm were added, with a difference of 5 ppm each. Isothermal study was done at optimum conditions of temperature, pH, adsorbent dose and contact time

TABLE-2
LANGMUIR ISOTHERMAL PARAMETERS FOR BASIC BLUE-9 DYE SORPTIVE REMOVAL
BY *Eugenia jambolana* SEEDS (J.S) AND *Citrullus lanatus* PEELS (W.M.P)

Adsorbent	Slope	Intercept	R^2	q_m (mg g^{-1})	b (L mg^{-1})	ΔG^0 (KJ mol^{-1})	R_L	*S* (nm)
J.S	0.694	0.204	0.918	4.902	0.294	-3.033	0.119	0.135
W.M.P	1.243	0.028	0.690	35.714	0.023	-9.346	0.635	0.984

for both adsorbents. Langmuir and Freundlich isotherms were applied to quantify maximum sorption capacity of adsorbents, mechanism of removal of dye, feasibility of process and enthalpy change for this process.

Langmuir isotherm: Langmuir isotherm was represented by eqn. 2

$$1/q = 1/(q_m\, b)C_e + 1/q_m \qquad (2)$$

The Langmuir isotherm theory assumes that the adsorbed layer is one molecule in thickness (monolayer adsorption). The values of the Langmuir constants are related to the physical properties of the system.

The value of q is calculated by using the formula:

$$q = \frac{(C_o - C_e)V}{m} \qquad (3)$$

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

$$\Delta G^o = -RT \ln K \qquad ...(4)$$

where 'q_m' is maximum adsorption capacity (mg g^{-1}), ΔG^o is in KJ mol^{-1}, 'V' (L) is volume of dye solution, 'm' (g) is adsorbent mass used, 'R' is gas constant, 'T' is temperature, *i.e.*, 298 K and 'K' is inverse of Langmuir constant 'b'[33]. The Langmuir isotherms for basic blue-9 dye adsorption using watermelon peels and jamun seeds are shown in Fig. 8 and the corresponding parameters are given in Table-2. Value of 'q_m' was 4.902 mg/g for jamun seeds and 35.714 mg/g for watermelon peels. Their comparison with other reported adsorbents (Table-3) indicated that jamun seed and watermelon peel are suitable for adsorption process.

TABLE-3
COMPARISON OF REMOVING CAPACITY OF REPORTED
ADSORBENTS FOR BASIC BLUE-9 (METHYLENE BLUE)
DYE WITH PRESENT STUDY [Ref. 18-29, 35-40]

Adsorbent	q_m (mg g^{-1})
Rice husk	4.41
Peanut husk	72.13
Garlic peels	8.62
Banana peels	20.8
Neem leaves	8.76
Orange peels	18.6
Madhuca longifolia leaves	3.66
Fly ash	13.42
Wheat shells	16.56
Eugenia jambolana seeds	4.902
Citrullus lanatus peels	35.714

ΔG^o values are totally dependent on ΔH^o values, when temperature is kept constant. As indicated from ΔG^o values, this process is spontaneous, feasible and exothermic in nature using both adsorbents.

Feasibility of process can also be predicted from R_L values, *i.e.* separation factor. It was calculated using Langmuir constant 'b' with formula: $R_L = 1/(1 + bC_o)$. Its value ranging between 0-1 reveals the feasibility of adsorption process, which is more for watermelon peel in this case[36].

The 'q_m' was used to estimate adsorbent specific surface area covered by the basic blue-9 molecule from the relationship: $S = q_m \times A_m \times 6.02 \times 10^{23}/M$. Here molecular surface of basic blue-9 (A_m) is 1.30 nm^2 and its molecular weight is 284 g mol^{-1}[37]. It also indicated the same trend that watermelon peels are better than jamun seeds for removing basic blue-9 dye, because of having more surface area.

Freundlich isotherm: It was shown in eqn. 5 and related parameters were tabulated in Table-4.

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad ...(5)$$

'K_F' ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1}) indicate the binding constant related to adsorption capacity. Its value for jamun seed was 0.774 and for watermelon peel, it was 0.719. It means jamun seed has more physiosorption capacity as compared to watermelon peel. It was also supported by its bulk density and porosity values, as given in Table-1.

Comparison of correlation coefficient 'R^2' values of Langmuir and Freundlich model indicated that this process is more following Langmuir model as compared to Freundlich model, because Langmuir model 'R^2' values are greater than Freundlich model. It means monolayer chemisorptive removal of basic blue-9 dye occurred more on homogenously distributed active sites on jamun seed and watermelon peel, as compared to intra-particle physiosorption on heterogeneously distributed active sites[38-40].

Conclusion

Comparative study of basic blue-9 dye adsorption was done using *Eugenia jambolana* seeds and *Citrullus lanatus* peels as biosorbents. After optimizing adsorption conditions, isothermal investigation were carried out, which indicated the feasibility of using these substances as adsorbents. Watermelon peels adsorption capacity was moreas compared to jamun seeds. Both the surface characteristics of adsorbents and chemical

TABLE-4
FREUNDLICH ISOTHERMAL PARAMETERS FOR BASIC BLUE-9 DYE SORPTIVE REMOVAL
BY *Eugenia jambolana seeds* (J.S) AND *Citrullus lanatus* PEELS (W.M.P)

Adsorbent	Slope	Intercept	R^2	K_F ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1})	n
Eugenia jambolana seeds	0.630	-0.111	0.707	0.774	1.586
Citrullus lanatus peels	1.053	-0.143	0.653	0.719	0.950

nature of dye are in synchronization with the results of isothermal study. Hence it is concluded that watermelon peels are more efficient adsorbent as compared to jamun seeds in removing basic blue-9 dye from aqueous medium. Both of them can be used for industrial waste-water treatment.

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