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Comparative Studies on Adsorption of Congo Red (CR) by Low Cost Adsorbents Prepared from Different Varieties of Melon Seeds

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The comparative ability of melon, water melon and musk melon seeds as adsorbents for Congo red dye in aqueous solution was studied. The experiments were done as batch processes. The main objective of the study was to investigate the influence of adsorbent dose, contact time, stirring speed, pH and temperature on adsorption process performance. Acidic pH (2), low temperature (20-30 ºC) and low stirring speed (100-200 rpm) were found to be favorable conditions for the adsorption of Congo red dye by all the three adsorbents. The maximum adsorption 98.5 % at 50 min, 98.2 % at 30 min and 98.1 % 40 min has been observed for melon, musk melon and water melon seeds, respectively at low adsorbent dose (0.15 g). The adsorption capacity of melon seed was found to be 23.10 mg, 21.23 mg/g for musk melon seed and 3.08 mg/g for water melon seed. The adsorption equilibrium process has been described well by using Langumir and Fruendlich adsorption isotherms. It can be concluded from this study that melon seed can best be used as an adsorbent for the removal of Congo red dye from its aqueous solution as compared to watermelon and musk melon seeds.

Key Words: Adsorption capacity, Congo red, Melon seeds, Langmuir isotherm.

INTRODUCTION

The protection of environment is currently a burning issue throughout the world. The impact and toxicity of dyes that are discharged in the environment has been very imperative and broadly studied. The tremendous use of synthetic dyes as compared to natural dyes is a key source of such pollution because of their ease use, inexpensive synthesis, stability and variety of colour. More than 10,000 chemically different dyes are being manufactured. These dyes are chiefly used in textiles, tanneries, pharmaceuticals, pulp and paper, paint, plastics, electroplating and cosmetics industries[1]. During the process of manufacturing and application, more than 15 % of the used dyestuff is released in effluents[2,3]. Dyes and pigments are intense colored material and even their minor release into the environment may impart intense

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colour to wastewater streams causing reduced photosynthesis of aquatic plants due to inhibition of the sunlight penetration[4,5]. Most of the dyes are toxic, carcinogenic and can cause allergic dermatitis, skin irritation, mutation, *etc.*[6-8].

In this regard the available technologies like flocculation combined with coagulation[9], nanofiltration[10], micellar enhanced ultra filtration[11], membrane separation, oxidation or ozonation[12,13], *etc.*, are either costly or insufficient in removing dye from wastewater[14-17]. Adsorption has proven to be one of the most effective physio-chemical methods for textile wastewater treatment and most frequently the adsorption beds containing activated carbon are commonly used in industry to remove organics from water and air. One of the major disadvantages of this method is the difficulty of regeneration of the saturated carbon. There is a growing concern search alternatives for activated carbon, the conventional and pricy adsorbent recommended to remove dyes from colored effluents. Fruits seeds have not received serious attentions to be used as sorbents. Therefore in the present study an attempt has been made to search melon, water melon and musk melon seeds as low cost adsorbents for the removal of Congo red dye as model anionic and basic dye which is prepared by coupling of tetrazotised benzidine with two molecules of naphthonic acid. This dye has been chosen due to its chemical structure (Fig. 1) and environmental concern. It is frequently found in the effluents of textile, paper, printing and plastic industries. This dye can be decomposed into benzidine which is a well known human carcinogen[18]. The effect of various factors such as adsorbent dose, contact time, stirring speed, pH and temperature has also been investigated.

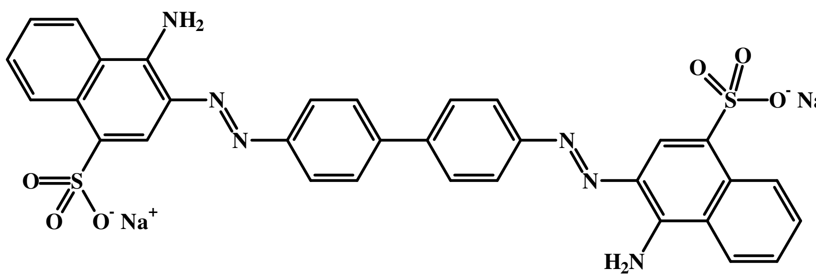

Fig. 1. Structure of Congo red

EXPERIMENTAL

All chemicals used were of analytical grade and were obtained from E-Merck/BDH/Fluka. All the apparatus used throughout the experimental work had standard quick fit joints and were dried at 110 ºC. The melon, water melon and musk melon seeds used in the experiments were collected from local market of Lahore, Pakistan.

Preparation of adsorbent: The seeds were washed thoroughly with distilled water followed by deionized water repeatedly to remove dust and soluble foreign impurities and were allowed to dry first at room temperature in a shade and then in oven at 110 °C until all moisture is evaporated. The dried seeds were crushed into fine powder by mechanical grinder and particle size between 50-80 mesh were obtained by passing seeds material through standard steel sieves. The resulting fractions were further washed with double distilled water till the washings were free of colour and turbidity. After drying for several hours at room temperature, these fractions of seeds were preserved in glass bottles for use as an adsorbents.

Preparation of aqueous dye solution: The dye, Congo red (CR) (60910) was used without further purification. A stock solution of Congo red was prepared in distilled water by dissolving 1 g of dye in 1000 mL of distilled water. A number of standard solutions were made from the stock solution in the concentration range 5-25 mg/L and a calibration curve was drawn by measuring the absorbance at λ_{max} = 495 nm (Spectro UV-Vis Double Beam UVD-3500, Labomed. inco).

Adsorption experiments: The adsorption studies were carried out at 25 ± 1 °C. pH of the solution was adjusted with 0.1 N HCl or 0.1 N NaOH. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture was filtered through Whatman No. 42 filter paper and dye concentration were determined in the filtrate using (Spectro UV-*vis* Double Beam UVD-3500, Labomed.inco) at λ_{max} = 495 nm.

The effect of various parameters on the rate of adsorption process were observed by varying contact time, t(10-140 min), initial concentration of dye Co(5-25 mg/L), adsorbent amount (0.15-1.05 g), initial pH of solution (1-5), agitation sped (100-500 rpm) and temperature (20-50 °C). The solution volume (V) was kept constant (25 mL).

The dye adsorption (% age) at any instant of time was determined by the following equation.

$$\text{Congo red adsorption}\,(\%) = \frac{\text{Co} - \text{Ce}}{\text{Co}} \times 100$$

where Co and Ce were the concentration of Congo red at initial condition and at any instant of time respectively. To increase the accuracy of the data, each experiment was repeated 3 times.

RESULTS AND DISCUSSION

In the present study seeds of melon, water melon and musk melon are used for the removal of Congo red from aqueous solution. The adsorbent capacity of various reported adsorbents for the removal of Congo red is given in Table-1. When the results of present study are compared with some non-conventional adsorbents, it indicates that adsorbents prepared from melon, water melon and musk melon seeds have better adsorption capacity for Congo red in many cases.

Effect of contact time: Contact time was one of the effective factor in adsorption process. The percentage of Congo red adsorption was studied as a function of contact time in the range of 10-100 min. The results obtained are presented in Table-2 and Fig. 2. The adsorption characteristic indicated a rapid uptake of the absorbate. The adsorption rate however decreased to a constant value with increase in contact time.

The contact time for musk melon seeds (MMS), water melon seed (WMS) and melon seeds (MS) were observed to be 30, 40 and 50 min, respectively. The comparative study showed that effect of contact time on the % age adsorption of dye by the three adsorbents is as follow: WMS > MMS > MS.

TABLE-1
ADSORPTION CAPACITY OF VARIOUS ADSORBENTS FOR CONGO RED

Adsorbent	Maximum adsorbent capacity, q_m (mg/g)	Reference
Coal based mesoporous carbons	52-189	21
Chitosan hydrobeads	92.59	22
Melon seeds	23.10	Present study
Waste orange peel	22.44	23
Musk melon seeds	21.22	Present study
Bagasse fly ash	11.88	24
Activated red mud	7.08	25
Activated coir pitch carbon	6.72	26
Red mud	4.05	27
Water melon seeds	3.80	Present study
Fe(III)/Cr(III) hydroxide	1.43	28
Walnut Shell	1.33	29

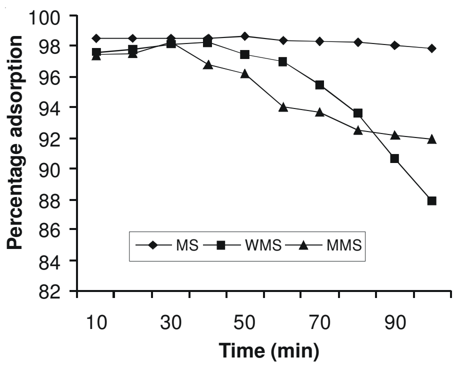

Fig. 2. Effect of contact time on percentage adsorption of Congo red by musk melon seeds (MMS), water melon seed (WMS) and melon seeds (MS)

Effect of adsorbent dose: The effect of variation in the adsorbent amount on the process adsorption of Congo red was studied with different adsorbent amount in the range of 0.15-1.05 g. The results obtained are given in Table-2 and are graphically represented in Fig. 3.

The percentage adsorption increases at low adsorbent amount 0.15 g for MS, MMS and WMS due to the availability of more adsorption sites. Another reason may be due to the particle interactive behaviour, such as aggregation, resulted from high adsorbent dose. Such aggregation would lead to decrease in total surface area of the adsorbent. The comparative study showed that the effect of adsorbent amount on the percentage adsorption of dye decreases in the following order: MS > MMS > WMS.

TABLE-2
EFFECT OF VARIOUS PARAMETERS ON PERCENTAGE ADSORPTION

Adsorbent dose (g)	Extent of adsorption (%)			Time contact (min)	Extent of adsorption (%)		
	MS	WMS	MMS		MS	WMS	MMS
0.15	98.6	98.1	98.2	10	98.5	97.6	97.4
0.25	97.9	97.3	94.3	20	98.5	97.8	97.5
0.35	97.6	95.8	92.1	30	98.5	98.1	98.2
0.45	95.3	90.1	86.7	40	98.5	98.2	96.8
0.55	94.2	88.3	80.6	50	98.7	97.4	96.2
0.65	92.0	81.4	71.1	60	98.4	97.0	94.0
0.75	91.9	76.4	65.4	70	98.3	95.5	93.7
0.85	91.3	72.7	58.4	80	98.2	93.6	92.5
0.95	90.2	64.0	44.4	90	98.0	90.6	92.2
1.05	88.5	52.5	35.5	100	97.9	87.9	91.9

MS = Melon seed, MMS = Musk melon seed, WMS = Water melon seed.

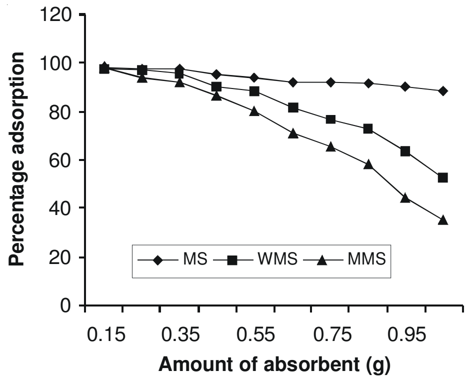

Fig. 3. Effect of adsorbent amount on percentage adsorption Congo red by musk melon seeds (MMS), water melon seed (WMS) and melon seeds (MS)

Effect of initial dye concentration: Initial dye concentration affected the adsorption efficiency (Table-3). The percentage of Congo red adsorption was studied as a function of initial dye concentration in the range of 5-25 mg/L. The results obtained are shown in Fig. 4. It has been observed from the results that the percentage adsorption increases with increase in initial concentration of the dye for all the three adsorbents. However, WMS was affected more as compared to MMS followed by MS. This may be attributed to available active sites and increase in the driving force of the concentration gradient.

Effect of pH: The pH of the aqueous solution is the important parameter that controls the adsorption process. The percentage of Congo red adsorption was studied as a function of pH in the range of 1-5. The results obtained are given in Table-3. It can be concluded from these results that percentage adsorption and pH has inverse relationship with each other (Fig. 4) and is might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent

TABLE-3
EFFECT OF VARIOUS PARAMETERS ON PERCENTAGE ADSORPTION

Initial dye concentration (mg/L)	Extent of adsorption (%)		
	MS	WMS	MMS
5	76.4	86.2	86.5
10	93.6	95.6	91.9
15	93.8	97.1	96.6
20	94.2	98.2	97.1
25	98.2	98.5	98.31
Temperature (ºC)	Extent of adsorption (%)		
	MS	WMS	MMS
20	98.5	98.5	97.3
30	98.2	98.5	98.2
40	97.2	95.1	96.5
50	97.4	87.9	94.6
pH	Extent of adsorption (%)		
	MS	WMS	MMS
1	98.2	96.4	96.7
2	98.5	98.5	98.1
3	98.0	96.8	97.6
4	86.4	38.1	81.1
5	65.9	36.3	36.3
Stirring speed (rpm)	Extent of adsorption (%)		
	MS	WMS	MMS
100	97.3	98.1	96.7
200	98.1	96.5	95.5
300	97.9	95.3	93.6
400	97.7	89.1	92.1
500	96.9	83.9	91.2

MS = Melon seed, MMS = Musk melon seed, WMS = Water melon seed.

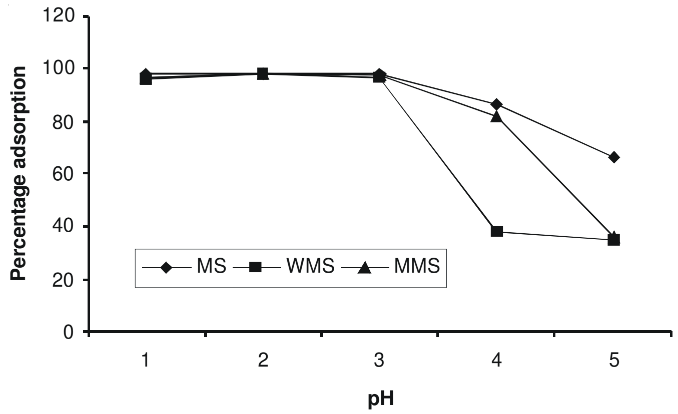

Fig. 4. Effect of pH on percentage adsorption of Congo red by musk melon seeds (MMS), water melon seed (WMS) and melon seeds (MS)

that ultimately lead to the reduction in percentage adsorption[19]. However maximum percentage adsorption has been observed at pH 2 for all the three adsorbents. The comparative study showed that effect of pH on the percentage adsorption of dye was maximum in MS as compared to WMS followed by MMS.

Effect of stirring speed: Fig. 5 presents and explains the effect of variation in the stirring speed on the adsorption process of Congo red on all the three adsorbents. It has been observed that for MMS and WMS the dye was best adsorbed at low as compared to MS where it is faster at 200 rpm than at lower ones. The comparative study showed that the effect of stirring speed on the percentage adsorption of dye by three adsorbents follows the following order: MS > WMS > MMS

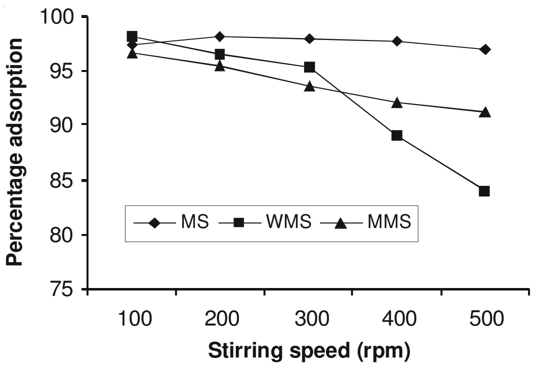

Fig. 5. Effect of stirring speed on percentage adsorption of Congo red by musk melon seeds (MMS), water melon seed (WMS) and melon seeds (MS)

Effect of temperature: The results in Fig. 6 and Table-3 show the influence of temperature on the adsorptive efficiency of all the three adsorbents. The percentage adsorption of Congo red was studied as a function of temperature in the range of 20-50 °C. The adsorption of dye is found to decrease with increasing temperature from 20-50 °C there by indicating that the adsorption process is thermodynamically stable. Similar results have been reported by Hong *et al.*[20] suggesting that at the high temperature molecules move with great speed and less time of interaction was available for dye anions with adsorbent material. Comparatively it is found that MS has been affected more by higher temperature as compared to WMS followed by MMS.

Adsorption isotherm: The interaction of adsorbate molecules with adsorbent surface can be described by using well known Langmuir and Freundlich isotherm models (eqns. 1-2). Langmuir adsorption isotherm is applicable to explain the equilibrium data for many adsorption processes. The basic assumption of this process is the formation of monolayer of adsorbate on the outer surface of adsorbent and after that no further adsorption takes place[21]. Freundlich model is an indicative of the extent of heterogeneity of the surface of adsorbent. The relationship between equilibrium data and either theoretical or practical equations is essential for interpretation and prediction of the extent of adsorption process.

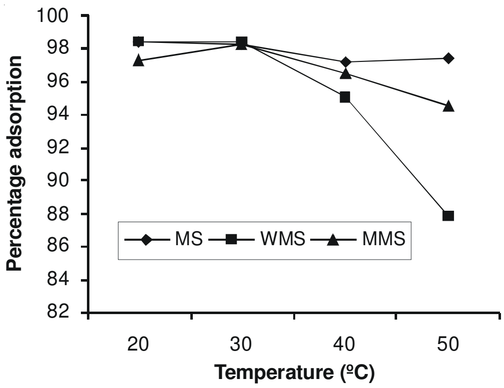

Fig. 6. Effect of temperature on percentage adsorption of Congo red by musk melon seeds (MMS), water melon seed (WMS) and melon seeds (MS)

$$\frac{1}{q} = \frac{1}{bQ_{max}} Ce + \frac{1}{q_{max}} \quad (1)$$

$$\log q = \log K_f + \frac{1}{n} \log Ce \quad (2)$$

Q_{max} is called Langmuir monolayer adsorption capacity, the value is 23.10 mg/g for MS and 21.22 mg/g for MMS, while Q_{max} value for WMS is found to be 3.80 mg/g (Table-4). Maximum adsorption capacity in case of MS suggests that melon seed (MS) possess more active sites and hence show more adsorption of dye. Similarly the value of b which is Langmuir isotherm constant found to be 0.011 dm^3/g for MS, 0.015 dm^3/g for MMS and 0.156 dm^3/g for WMS. Value of R^2 shows correlation or linear relationship. More that value is near to 1, more linear relation is there. R^2 value indicates the type of Langmuir isotherm, *e.g.*, $R^2 = 0$ means irreversible, $R^2 =$ 0-1 means favourable for adsorption, $R^2 = 1$ means linear and $R^2 > 1$ mean unfavo-

TABLE-4
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS FOR ADSORPTION OF CONGO RED ON MS, MMS AND WMS

Langmuir adsorption isotherm					
Seed	Intercept	Q_{max} (mg Congo red /1 g seeds)	Slope	b (dm^3/g)	R^2
MS	0.0430	23.10	3.12	0.014	0.98
WMS	-0.2630	3.80	17.60	0.015	0.96
MMS	0.0471	21.22	0.30	0.156	0.99
Freundlich adsorption isotherm					
Intercept	Slope	K_f	1/n	n	R^2
-0.3968	0.84	0.4010	0.84	1.19	0.97
-2.0477	1.73	0.0090	1.72	0.58	0.97
0.5543	0.56	3.5834	0.56	1.75	0.93

MS = Melon seed, MMS= Musk melon seed, WMS = Water melon seed urable. Value of R^2 = 0.98 (MS), 0.96 (WMM) and 0.99 (MMS) given in Table-4. It can be concluded that for Langmuir isotherms (Figs. 7-9) the Congo red dye indicates favorable adsorption for all the three adsorbents. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface (Figs. 10-12). The smaller value of 1/n 0.56 for MMS and 0.84 for MS indicates the formation of relative stronger bond between dye and MMS and MS while higher value of 1/n (1.72) for WMS indicates a relative weaker bond formation between dye and WMS.

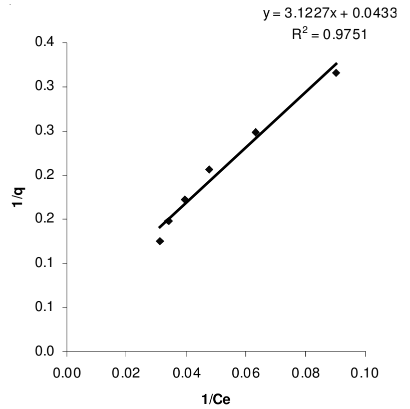

Fig. 7. Langmuir plot for the adsorption of Congo red by melon seed

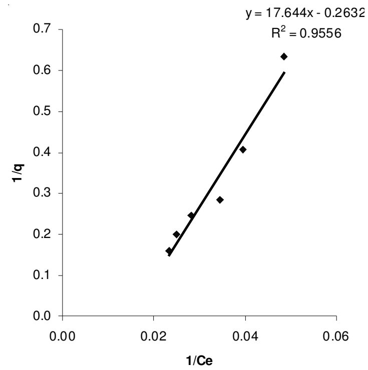

Fig. 8. Langmuir plot for the adsorption of Congo red by water melon seed

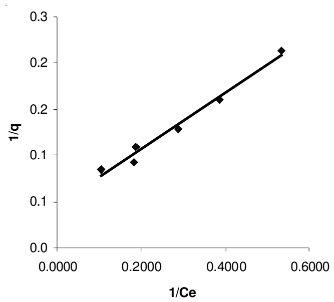

Fig. 9. Langmuir plot for the adsorption of Congo red by musk melon seed

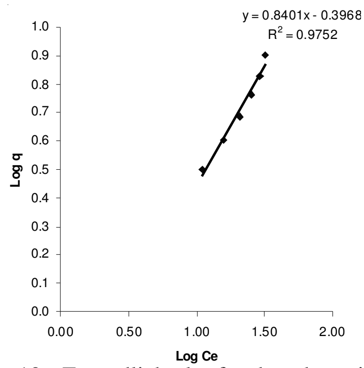

Fig. 10. Freundlich plot for the adsorption of Congo red by melon seed

Conclusion

Melon, water melon and musk melon seeds are very cheap and cost effective materials for the removal of Congo red dye because they are easily available in Pakistan and are widely consumed and the wasted during summer season. The comparative study among all the three adsorbents showed that melon seed can safely be used as best adsorbent for the removal of Congo red dye from its aqueous solution as compared to water melon and musk melon seeds.

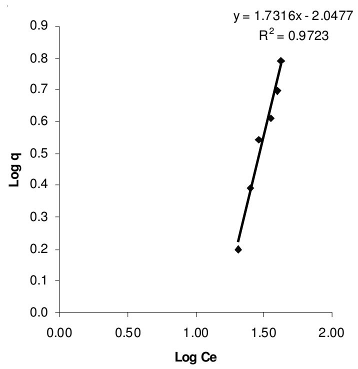

Fig. 11. Freundlich plot for the adsorption of Congo red by water melon seed

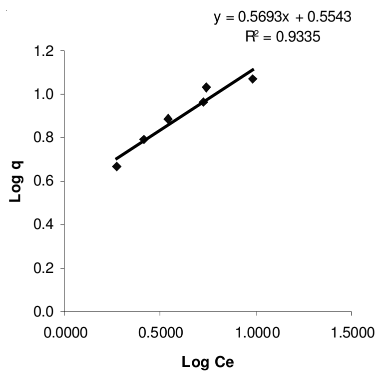

Fig. 12. Freundlich plot for the adsorption of Congo red by musk melon seed

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