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Comparative Adsorption Studies of Methyl Orange Using Different Varieties of Melon Seeds as Adsorbents

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In the present study seeds of melon, watermelon and muskmelon were used for the removal of methyl orange from aqueous media. It was observed that the efficiency of the three adsorbents was dependant on various parameters such as concentration of analyte, concentration of adsorbent, particle size, pH, temperature, time and stirring. It was found that maximum adsorption occurred at 80 mesh with value of 40 % for melon seed, 33.3 % for muskmelon seed and 2.70 % for watermelon seed. It can be concluded from this study that low adsorbent dose, low dye concentration, low contact time, low pH, low temperature and low stirring are the most favourable conditions for the adsorption of methyl orange dye on all three adsorbents. The comparative behaviour of these three adsorbents further indicates that muskmelon seed is a better adsorbent than watermelon seed and melon seed.

Key Words: Adsorption, Methyl orange, Melon seeds, Adsorbent.

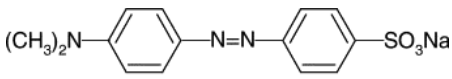
INTRODUCTION

The protection of environment is currently a significant concern throughout the world. The impact and toxicity of dyes that are released in the environment has been very important and extensively studied. The source of such pollution lies in the rapid increase of the use of synthetic dyes because of their ease use, inexpensive synthesis, stability and variety of colour compared with natural dyes. More than 10,000 chemically different dyes are being manufactured. These dyes are mainly consumed in textiles, tanneries, pharmaceuticals, pulp and paper, paint, plastics, electroplating and cosmetics industries.

Methyl orange is water soluble azo dye, which is widely used in textile, printing, paper manufacturing, food industries and also in research laboratories. Mostly it is used in research laboratories. It is used as an acid base indicator due to its ability to function as a weak acid[1-5]. It has been observed that methyl orange is the cause of increasing nitro reductase and azo reductase activities. Methyl orange when enters in the body by ingestion it is converted into aromatic amines by intestinal bacteria. Thus removal of such a dangerous dye is very necessary from the surroundings. Available methodologies in this regard such as flocculation combined with coagulation, nanofiltration, micellar enhanced ultrafiltration, membrane separation, oxidation or ozonation *etc.*, are either expensive or inadequate in removing dye from wastewater[6-8]. Therefore in continuation of our previous attempts[9], in this study we have used different types of melon seeds[10-13], which are abundantly available in Pakistan and are thus low cost for the removal of methyl orange.

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. Melon (MS), watermelon (WMS) and muskmelon (MMS) seeds used in the experiments were collected from local market of Lahore.



Methyl orange

Preparation of adsorbents: Seeds were washed first with water and then with deionized water to remove impurities. The dried seeds were ground and then passed through steel sieves having mesh size 80, 60, 40 and 20 and stored in airtight bottles for further use. No other physical or chemical treatment was used prior to adsorption.

All adsorption studies were carried out at room temperature at pH 2 (adjusted by 0.1 N HCl). A fix amount of three adsorbents (0.60 g) was added and allowed sufficient time for adsorption equilibrium. The mixture was then filtered by using Whatman filter paper (number 42). Uptake of adsorbate was

analyzed by spectrophotometer (Spectro UV-VIS double beam UVD-3500, lobomed.inco) at λ_{max} 465 nm. The effect of various parameters on the rate of adsorption was determined by varying adsorbent dose from (0.15-0.60 g), adsorbent size from (20-80 mesh), dye concentration from (5-25 ppm), contact time from (1-5 h), pH from (1-5), temperature from (34-75 ºC), stirring speed (200-1000 rpm). Percentage of dye adsorbed was determined by following formula:

$$\text{Methyl orange adsorption capacity } (\%) = \frac{C_o - C_e}{C_o} \times 100$$

where, C_o and C_e were the concentration of methyl orange 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

Effect of adsorbent size: The effect of variation in the adsorbent size on adsorption of methyl orange was studied with different adsorbent dose in the range of 20-80 mesh. The % age of adsorption increases with decrease in adsorption size because of the increase in the surface area. Similar results have been reported by Mittal *et al.*[14]. The comparative studies (Fig. 1) showed that the percentage of adsorption observed the order MS > MMS > WMS.

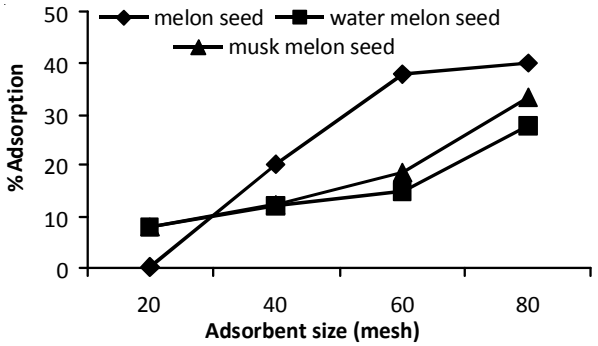


Fig. 1. Graph between adsorbent size and % age adsorption of methyl orange

Effect of adsorbent dose: The effect of variation in the adsorbent dose on adsorption of methyl orange was studied with different adsorbent dose in the range of 0.15 - 0.60 g. The % age of adsorption increases with increase in adsorption dose because of the increase in the number of surface area available for adsorption[15]. The comparative studies showed that the percentage of adsorption was maximum in MMS > MS > WMS and the results obtained are as follows (Table-1).

TABLE-1
EFFECT OF ADSORBENT DOSE ON % AGE ADSORPTION

Adsorbent dose (g)	% age adsorption		
	MS	WMS	MMS
0.15	11.5	7.3	2.8
0.20	12.5	10.7	3.0
0.25	12.9	15.5	11.9
0.30	17.6	18.4	16.3
0.35	18.3	19.7	16.8
0.40	19.7	20.1	21.5
0.45	19.8	21.1	21.69
0.50	22.6	22.7	24.62
0.55	23.0	25.3	25.4
0.60	28.0	27.8	33.48

Effect of dye concentration: The effect of variation in the adsorbent size on adsorption of methyl orange was studied with different concentrations of dye in the range of 5-25 ppm. The % age of adsorption decreases with increase in the concentration of dye (Fig. 2). The comparative studies showed that the percentage of adsorption was maximum in MMS > WMS > MS.

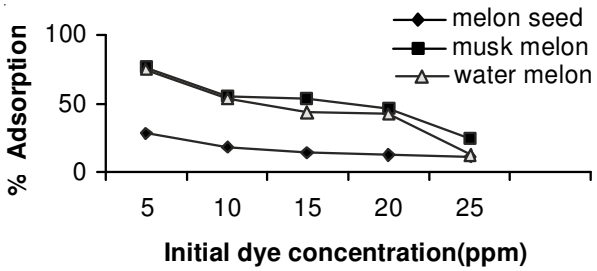


Fig. 2. Graph between initial dye concentration and % age adsorption of methyl orange

Effect of contact time: The effect of variation in the contact time on adsorption of methyl orange was studied with different contact time in the range of 1-5 h. The % age of adsorption decreases with increase in contact time because all available sites were covered and no active site available for binding as the time increased. Our results are in agreement with previous studies[14]. The comparative studies showed that the percentage of adsorption was maximum in MMS > WMS >MS. The results obtained are graphically represented as follows (Fig. 3).

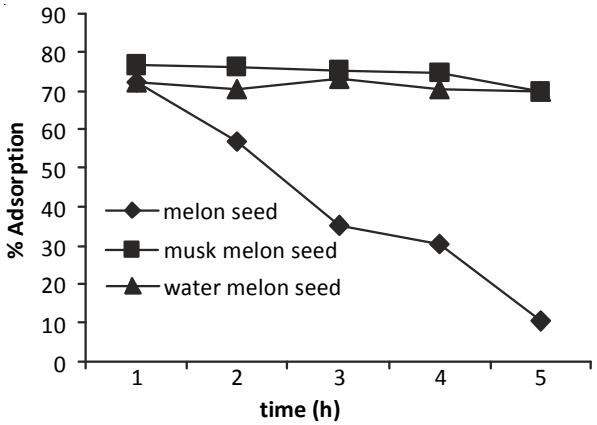


Fig. 3. Graph between contact time and % age adsorption of methyl orange

Effect of pH: pH of methyl orange was varied in the range of 1-5. The % age of adsorption decreases with increase in pH (Fig. 4). This might be due to the weakening of electrostatic force of attraction between the oppositely charge adsorbent and adsorbate[16].

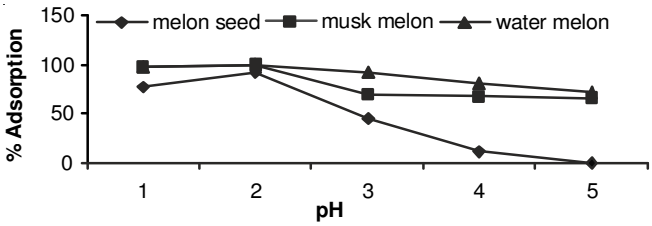


Fig. 4: Graph between pH and % age adsorption of methyl orange

Effect of temperature: Effect of temperature on adsorption of methyl orange was studied by varying temperature from 34 to 75 ºC. The % age of adsorption decreases with increase in temperature (Fig. 5) that proves the exothermic nature of the adsorption process[17]. The comparative studies showed that the percentage of adsorption was maximum in MMS > WMS > MS.

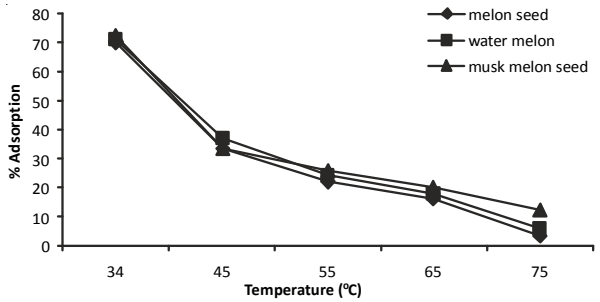


Fig. 5. Graph between temperature and % age adsorption of methyl orange

Effect of stirring speed: Stirring speed was varied in the range of 200-1000 rpm and it was observed that the % age of adsorption decreases with increase in stirring speed that might be because of no binding sites availabity at high stirring (Fig. 6)[9]. The comparative studies showed that the percentage of adsorption was maximum in MMS > MS > WMS.

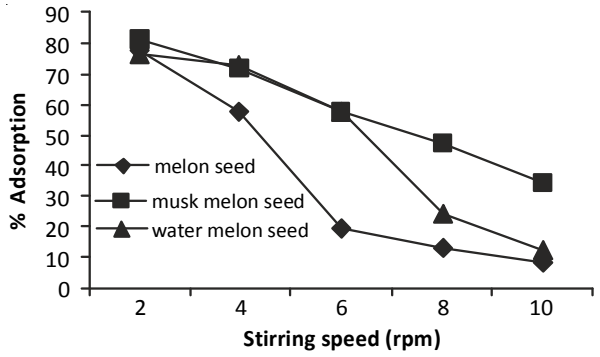


Fig. 6. Graph between stirring speed and % age adsorption of methyl orange

Adsorption isotherms: For all the adsorbents Langmuir and Freundlich isotherms were studied and Langmuir constants were calculated. The Langmuir isotherm is based on the assumptions that the molecules of the adsorbate are adsorbed at well-defined, energetically equal sites without interacting with each other and each site can hold only one molecule[18]. The validity of Langmuir adsorption mode was established using following relation:

$$1/q = 1/b\ Q_{max}\ Ce + 1/q_{max}$$

For Langmuir isotherm the plot of 1/qe against 1/Ce gives a straight line confirming that the adsorption of the dye follows the Langmuir isotherm model[19]. On the basis of slopes and intercepts of the straight lines Langmuir constants were calculated. Q_{max} is called Langmuir monolayer adsorption capacity, the value is 38.96 mg of dye per gram of MS, 40.90 mg of dye per gram of MMS and -70.49 mg of dye per gram of WMS. Maximum adsorption capacity of MMS indicates that more active sites of musk melon seeds are available for dye, b is Langmuir isotherm constant 0.036 dm^3/g for MS .041 for MMS dm^3/g and -0.007 dm^3/g. Value of R^2 shows correlation or linear relationship. Value of R^2 for all three adsorbent is 0.98, which indicate favourable adsorption for melon seed, watermelon seed and muskmelon seed.

The validity of Freundlich adsorption model was established using following relation[20-22].

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e$$

where, q_e is the amount adsorbed (g), C_e the equilibrium concentration of the adsorbate and K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Freundlich constants derived from these straight lines clearly indicate that the adsorption capacity decreases with increase in temperature. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The smaller value of 1/n for MMS is 0.296 and for MS is 1.483 indicates formation of relative stronger bond between dye and higher value for WMS is 2.272 indicates formation of relative weaker bond between dye and WMS.

Conclusion

It is concluded from discussion that the adsorbents are very cheap and effective materials for the removal of methyl orange dye because melon watermelon and muskmelon seeds are easily available in Pakistan. Removal of dye is higher at and optimum pH 2. The comparative study showed that muskmelon seed was found to be best adsorbent for removing methyl orange dye from aqueous solution as compared to watermelon and melon seeds.

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