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Research Article

Adsorption of Dyes from Aqueous Solution Using Orange Peels: Kinetics and Equilibrium Studies

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Abstract: The adsorption of dyes from aqueous solution has been investigated on Orange Peels (OP). The influence of pH, contact time, adsorbent dosage, dye concentration, agitation speed, temperature and particle size of biosorbent on the biosorption has been investigated. The biosorptive capacities of the biosorbents were dependent on the pH of the dye solution, with pH 2 and 4 being optimal. From the analysis of isotherm data obtained from the fittings of the Freundlich model fits better than the Langmuir model in case of acid blue MTR dye and in case of red 3BLS disperse dye Langmuir model fits better than Freundlich model. The adsorption capacities were found to be 19.48, 36.67, 16.69mg/g for FOP, IOP, DOP in case of Acid Blue MTR Dye and similarly 23.35, 29.36, 27.30mg/g respectively in the case of Red 3BLS Disperse Dye.

Keywords: Disperse Dye, MTR Dye, pH, Langmuir model, Freundlich model.

1. Introduction

Environmental pollution is contamination of air, water and land from man-made waste. Pollution leads to depletion of the ozone layer, global warming and climate change. Air pollution is the release of chemicals and particles into the atmosphere. Environmental pollution can have a deadly effect on humans and ecosystems. Water pollution is caused by the release of any type of foreign contaminants into a body of water or spilled in the watershed of a body of water. Perhaps the most common cause of water pollution is simply dumping of garbage and waste. Worse still is contamination from bacteria, worms and viruses present in sewage. Similarly, dye wastewater discharged from textile and dyestuff industries have to be treated due to their impact on water bodies and growing public concern over their toxicity and carcinogenicity in particular. Dyes usually have synthetic origins and complex aromatic molecular structures (1). Synthetic dyes are extensively used by industries including dye houses, paper printers, textile dyers, color photography and as additives in petroleum products (2, 3). The effluents of these industries are highly colored and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentrations as low as 1 ppm (3). Moreover, they may also affect the photosynthetic activity in aquatic systems by reducing light penetration (4). Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and/or chemical methods (5). Although these treatment methods are efficient, they are quite expensive and have operational problems (5, 6). Adsorption of the molecules onto various adsorbents is an ideal option for decolourization, which is evidenced by the effectiveness of adsorption for various dye types (6, 7). The main drawbacks which exist at the present time are the high costs involved in the regeneration of the adsorbent. This work studies the possibility of using a certain biological waste: orange peel, as an inexpensive sorbent for the removal of acid dyes from aqueous solutions. This material is abundantly available through our country and the world. The dyes used in this study were: Acid Blue MTR Dye and Red 3BLS Disperse Dye. The present study reports their sorption potential through kinetics tests and sorption isotherms, in batch conditions. The experimental data of dyes adsorption equilibrium were fitted by either the Langmuir (8) or Freundlich (9) equations.

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2. Materials and Methods

2.1 Preparation of biosorbents

All the materials were obtained from local market. The biowaste materials used for the study were OP with three types of treatments i.e. Formaldehyde Treated OP (FOP), Isopropyl Alcohol Treated OP (IOP) and D/W Treated OP (DOP).

Formaldehyde treatment consisted of mixing 1g of the NB biomass with 100mL of a 0.2% (v/v) aqueous formaldehyde solution for 24 hr at room temperature. Afterwards, it was filtered and washed with distilled water until no color was detected in the filtrate. The resulting biomass was designated as the treated biomass, the filter residue was dried in an oven and grinded, after that the adsorbent was obtained.

For the preparation of isopropyl treated orange peels, 20 grams of OP and 80% isopropyl alcohol were put together into a flask and were stirred for 24 hr at room temperature and then rinsed with 80% isopropyl alcohol for three times. At last, it was washed with distilled water until the filtrate was colorless. Thereafter, the filter residue was dried in an oven at 50°C for 24 hrs. Finally, 10.5gm of adsorbent were obtained.

Orange peel as an agricultural byproduct waste, It was used as a sorbent material after the following treatment: 10gm of orange peel was contacted with 2 Liters of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of 25°C during 4 hours, then continuously washed with distilled water to remove the surface adhered particles and water-soluble materials, and oven-dried overnight at 60-80°C for 24 hrs after filtration. This material was crushed and sieved to have particles of size 0.125 – 1.60mm for further batch sorption experiments.

2.2 Preparation of synthetic dye solution

For this study, synthetic Acid Blue MTR dye and Red 3BLS dye (disperse dye) were procured from the textile industry itself. An accurately weighed quantity of the dye was dissolved in distilled water to prepare stock solutions (1000 ppm). Experimental solution of desired concentration was obtained by successive dilution with distilled water. Dye concentration was determined by using absorbance values measured and after treatment with a Shimadzu UV Visible spectrophotometer (Model No: 1650). The wavelengths used for the dyes were 578 nm for Acid Blue MTR and 466nm for Red 3BLS disperse dye.

2.3 Batch sorption experiments of synthetic dyes with orange peels

The three types of biosorbent prepared were evaluated for dye removal efficiency by using synthetic dyes. Adsorption experiment was carried out in batch mode using a conical flask (250ml) which contains 0.4-0.6gm of orange peels, selected as biosorbent for treatment of synthetic dyes as well as optimization of process parameters for removal of dyes. The dye solution was agitated on a shaker at room temperature (30-35°C).

2.4 Dye removal Assay

Absorbance units were converted to concentration by using standard curves. The percentage dye removal was determined by using the following formula.

$$\text{Percentage age dyes removal} = \frac{\text{Initial concentration of dye} - \text{Final concentration of dye}}{\text{Initial concentration of dye}} \times 100$$

2.5 Optimization of process parameters to develop an effective treatment technology with orange peels

Various process parameters (pH, contact time, amount of adsorbent, conc. of dye, agitation speed, temperature, particle size) and their effect on dye removal activity of orange peels materials was observed.

3. Sorption Studies

3.1 Sorption Kinetics

The initial solution dye concentration was 100mg/L for all experiments except for that carried out to examine the effect of the initial concentration of dyes. For dyes removal kinetics studies, 0.6gm of adsorbent was contacted with 0.3 L of dye solutions in a flask agitated vigorously at a constant temperature of 25 ± 1°C. Their dye concentrations were determined with a UV-visible spectrophotometer. The dye uptake qt (mg dye/g adsorbent) was determined as follows:

$$qt = (Co - Ct)\frac{V}{m}$$

Where, Co and Ct is the initial and time dye concentration (mg/L), respectively, V is the volume of solution (mL), and m is the sorbent weight (gm) in dry form.

Blank runs, with only the sorbent in 100mL of distilled water, were conducted simultaneously at similar conditions to account for any color leached by the sorbent and sorbed by the glass container. Blanks were also run simultaneously, without any sorbent to determine the impact of pH change on the dye solutions. Each experimental point was an average of two independent sorption tests. Duplicate tests showed that the standard deviation of the results was ± 5%.

3.2 Sorption Isotherms

The equilibrium isotherms were determined by contacting a constant mass 0.5gm of sorbent material with a range of different concentrations of dye solutions: 20-100 ppm. The mixture obtained was agitated in a series of 250ml conical flasks with equal

volumes of solution 100ml for a period of 2-4 hrs at room temperature. The contact time was previously determined by kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 2-4 hrs, the final pH was measured. The equilibrium concentration of unbound dye was determined spectrophotometrically. The amount of dye adsorbed by the material was determined as the difference between the concentrations before and after adsorption.

4. Results and Discussion

4.1 Optimization of various process parameters

To study the effect of process parameters on decolourization of synthetic dye, various parameters were considered i.e. pH, contact time, amount of adsorbent, concentration of dye, agitation speed, temperature, particle size.

4.2 Effect of pH

The effect of pH on the amount of both the dyes adsorbed was investigated by contacting 100ml of dye solution with initial dye concentration i.e. 100 ppm at room temperature 30-35°C for 30-120 min. removal at different pHs (2, 4, 5, 7, 8) were 65% for Acid blue MTR Dye in case of FOP 45% in the case of IOP, 55% in case of DOP at pH 4, 4, 2 respectively and 67% for Red 3BLS Disperse Dye using FOP, 61% in the case of IOP, 50% in the case of DOP at pH 2, 2, 4 respectively.

The adsorption capacity increases with decreasing the pH of the solutions. Maximum adsorption of acid dyes occurs at acidic pH 2 and 4. Dyes dissociated to polar groups ($R\text{-}SO_3^-$), orange peel is comprised of various functional groups, such as hydroxyl and carboxyl groups, which could also be affected by the pH of the solutions. Therefore, at various pHs, the electrostatic attractions, as well as the structure of the dye molecules and orange peels, could play very important roles in dye adsorption on orange peels. At pH 2 and 4, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent due to the ionization of functional groups of adsorbent and negatively charged anionic dyes and in case of disperse dyes the adsorption of disperse dyes onto the orange peels also occurred at acidic condition. Solution pH would affect both surface binding sites of adsorbents and aqueous chemistry. In acidic condition, the positive charge dominates the surface of the adsorbent. Thus, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged dye species. This attractive force increases the adsorption chances of dyes species onto the surface of the adsorbents. As the pH of the system increases, the surface of the adsorbent tends to become negatively charged, which does not favor the adsorption of disperse dyes due to electrostatic repulsion. At the same time, the presence of excess OH^- ions in alkaline pH will compete with the dye anions for the adsorption sites. Low aqueous solubility of disperse dyes as reported by Ramakrishna and Viraraghavan will result in a higher affinity for solid surfaces than for water. Disperse dyes are hydrophobic. As the solubility of disperse dyes in the aqueous solution is low, they have a tendency to accumulate at the surface of adsorbents. Thus, the adsorption capacity will increase if the solubility of the dyes is low. At the alkaline pH, the excess of OH^- ions destabilizes anionic dyes and compete with the dye anions (Fig. 1.1).

4.3 Effect of contact time

Both the synthetic dyes were kept in contact with the biosorbent at adsorbent dosage 0.5g/100ml in shaking conditions (150 rpm) for 2 hrs at room temperature and removal of synthetic dyes were observed at regular time intervals i.e. After 30 min., 60 min., 120 min., 180 min. and 240 min. After a definite time interval, the samples were taken after filtration to know the optical density of residual concentration of the sample. After taking the O.D. it was observed that at 30–120 min. the maximum removal (75%) of both the dyes was achieved with the adsorbent dosage 0.5g/100ml of the three types of orange peel biosorbents. It was concluded from here that initially with an increase in time, adsorption increases but after 120 min. the equilibrium is achieved or we can say it has become stable (Fig. 1.2).

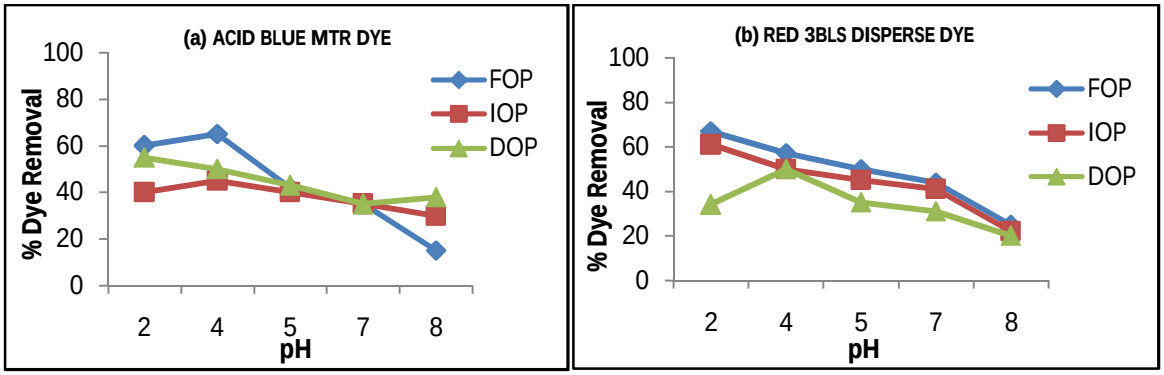

Fig. 1.1. Effect of pH on % Dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP. (b) IOP (c) DOP.

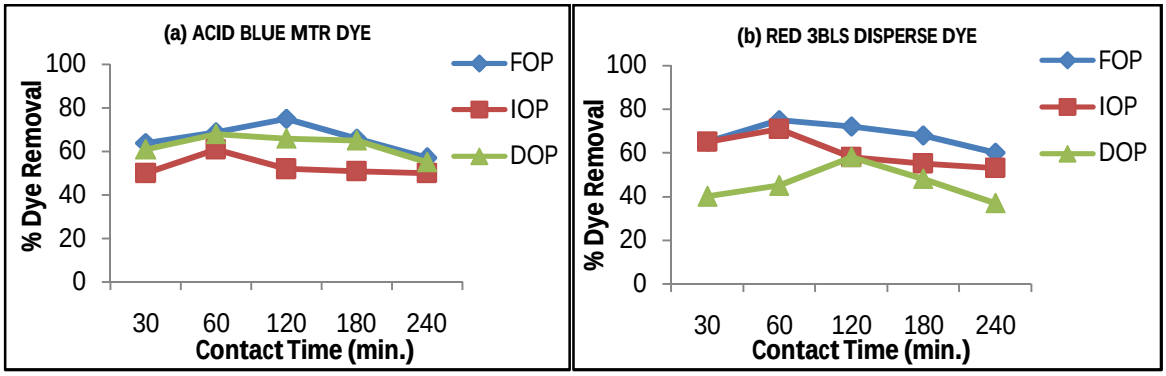

Fig. 1.2. Effect of contact time (min.) on % dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP (b) IOP (c) DOP.

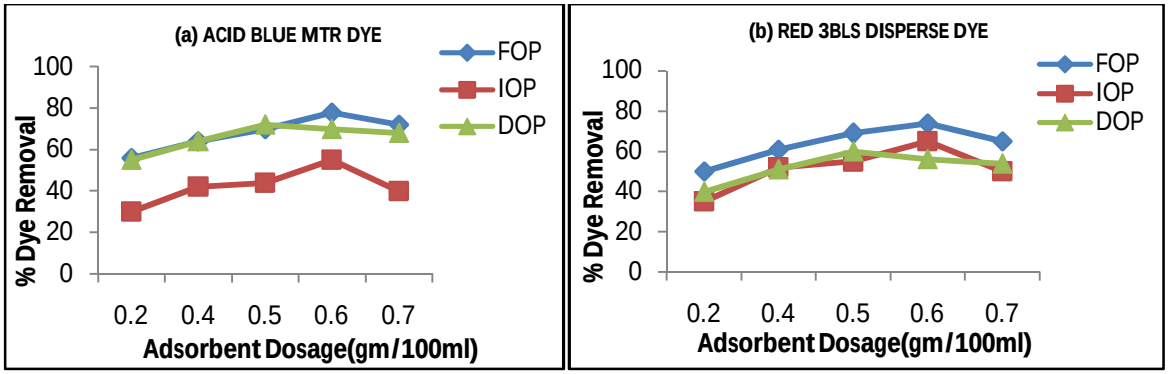

Fig. 1.3. Effect of Adsorbent Dosage (g/100ml) on % Dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP (b) IOP (c) DOP.

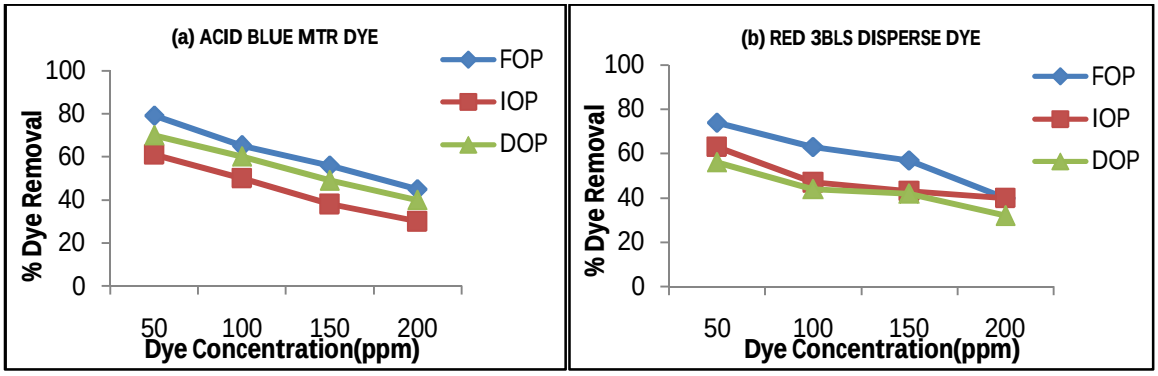

Fig. 1.4. Effect of dye concentration (ppm) on % Dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP (b) IOP (c) DOP.

4.4 Effect of adsorbent dose

Effects of adsorbent dose on removal of both the synthetic dyes were studied by mixing different amounts of adsorbents (0.2, 0.4, 0.5, 0.6 and 0.7gm) with a fixed volume of synthetic dyes (100ml) agitating. After a fixed time interval, the samples were taken after filtration to know the optical density and concentration of the sample. After taking the O.D. it was observed that at the adsorbent dose of 0.5 and 0.6g/100ml of three types of orange peel biosorbents the maximum removal (78% and 74%) of both dyes was achieved. This suggests that as the adsorbent dose increase, the extent of dye removal also increase but as the concentration reaches above 0.7gm the adsorption starts decreasing. The initial increase in adsorption with an increase in adsorbent dosages can be attributed to greater surface area and availability of more biosorption sites (Fig. 1.3).

4.5 Effect of dye concentration

To observe the effect of both the synthetic dyes concentrations i.e. 50, 100, 150, 200 ppm were investigated for their percentage dye removal with the procured biosorbents i.e. orange peels. These various

concentrations of dyes were treated with biosorbent agitating at room temperature and after definite time interval the samples were filtered and O.D. was taken. After taking the O.D. it was observed that at 50 ppm-100 ppm dye concentration the maximum dye removal (79% and 74%) of both the dyes was achieved. This indicates that the adsorption rate will increase with an increased initial dye concentration mainly due to the increase in the mass transfer from the concentration gradient, but after a certain concentration, the removal efficiency of adsorbent starts decreasing because of the limited adsorption sites available for the uptake of adsorbate (Fig. 1.4).

4.6 Effect of agitation speed

To observe the effect of agitation speed of both the synthetic dyes was mixed with adsorbent at the rate of 0.5g-0.6gm/100ml and kept on a rotary shaker at various agitation speeds i.e. 75, 100, 150 rpm at room temperature. The dye removal assay was performed, then after 30-120 min. the samples were filtered. Then O.D. was taken and percentage dye removal was calculated. It was observed that rate of removal of both the dyes was increased with increase in agitation speed i.e. at 75-100 rpms because resistance to mass transfer is broken down with increasing agitation speed due to which more amount of colour penetrate (71% and 78%) into the adsorbent but beyond a certain agitation speed there were decrease in dye removal but beyond 200 rpm there were decrease in colour removal were found (Fig. 1.5).

4.7 Effect of temperature

Based on the results of the effect of temperature on the fitting adsorption capacity, the main mode for the adsorption of acid dye and disperse dye onto ground orange peels were speculated to be strong dispersion forces and thus led to significant attraction between the dye molecule and the ground orange peels particles, which should be an endothermic process, showing that the amount of dye adsorbed onto adsorbent, increases with raising adsorption temperature. The effect of temperature on removal (68% and 74%) of both the synthetic dyes was studied by varying the temperature of the synthetic dyes in various ranges (25, 35, 40°C) with the help of incubator shaker. The experiment was run with adsorbent dose 0.5g/100ml of synthetic dyes in shaking conditions (150 rpm). After a definite time interval, the samples were taken after filtration and O.D. was taken. It was observed that at 30-35°C the maximum dye removal of Acid Blue MTR (λmax 578nm) and Red 3BLS Disperse Dye (λmax 466nm) was achieved (Fig. 1.6).

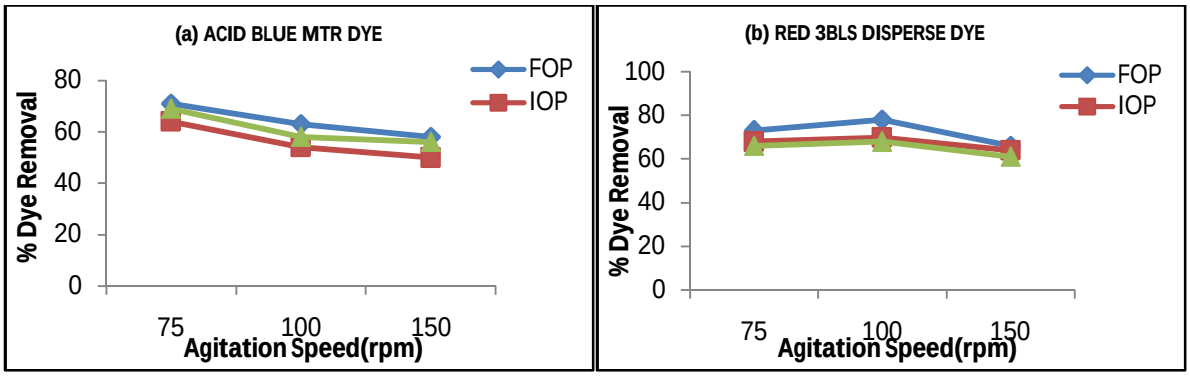

Fig. 1.5. Effect of agitation speed (rpms) on % Dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP (b) IOP (c) DOP.

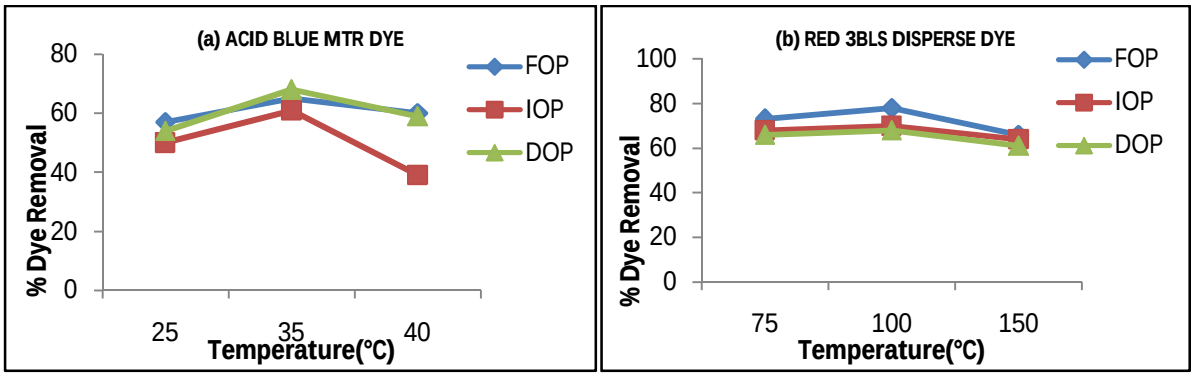

Fig. 1.6. Effect of temperature (°C) on % Dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP (b) IOP (c) DOP.

4.8 Effect of particle size

To observe the effect of particle size on both the synthetic dyes, the dye samples were mixed with adsorbent of various size ranges (1.1-0.5mm, 0.5-0.18mm, ≤ 0.18mm) at the rate of adsorbent dose of 0.5-0.6g/100ml of synthetic dyes in shaking conditions (150 rpm) at room temperature. After a definite time interval, the samples were taken after filtration to know the optical density and concentration of the sample. The dye removal assay was performed and percentage decolorization was calculated. It was observed that at the range of 0.5-0.18mm particle size the maximum dye removal (64 and 79%) of both the dyes was achieved.

The results showed that for both the dyes solutions, with decreasing the particle size, the adsorption is increasing to some extent. The rising in the dyes removal is the direct effect of the increase in surface area of the adsorbent by decreasing the particle size. All further studies were carried out choosing the appropriate particle size i.e. between 0.5 - 0.18 and ≤ 0.18 (Fig. 1.7).

4.9 Adsorption Kinetics of Acid Blue Mtr Dye

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount dye. As shown in Fig. 1.8, the kinetics of dye sorption were contacted time dependent. Sorption increases with time and it remains constant after a contact time i.e. the equilibrium time the response of the sorbent material used is not similar with all the pHs (2, 4, 5, 7, 8). The equilibrium is achieved after 2hrs. at pH 4 in case of FOP, 1 hr. at pH 4 in case of IOP, ½ hr. at pH 2 in case of DOP.

4.10 Adsorption Kinetics of Red 3bls Disperse Dye

Fig. 1.9 shows the change of dye adsorption with time goes up. As the contact time increases, dye uptakes also go up initially and then become almost stable, showing an attainment of equilibrium. The equilibrium was achieved after having been shaken more than 3 hrs. To assure the true equilibrium is established, all the subsequent sorption experiments are carried out about 3 hrs.

4.11 Adsorption Isotherms

To facilitate the estimation of adsorption capacities at various liquid-phase concentrations of acid blue MTR dye and red 3BLS disperse dye, the two well-known equilibrium adsorption isotherm models. Langmuir and Freundlich were employed as follows:

Langmuir: $qe = q_m K_L C_e / (1+K_L C_e)$ (1)

Freundlich: $qe = K_F C_e^{1/n}$ (2)

In Equation (1), C_e and qe are the concentration (mg dm^{-3}) and amount (mg g^{-1}) of acid blue MTR dye and red 3BLS disperse dye adsorbed at equilibrium, respectively, K_L is a direct measure for the intensity of the adsorption process (dm^3 mg^{-1}), and q_m is a constant related to the area occupied by a monolayer of absorbate, reflecting the adsorption capacity (mg g^{-1}). K_F is a constant for the system, related to the bonding energy. K_F can be defined as adsorption or distribution coefficient and represents the general capacity of acid blue MTR dye and red 3BLS disperse dye adsorbed onto adsorbents for a unit equilibrium concentration (i.e., C_e = 1mg dm^{-3}). The slope 1/n, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity. The results of the Langmuir and the Freundlich isotherms fitted by using the data of adsorption capacity from the regression of Equation (1) at 35°C.

It was indicated that the Freundlich model obviously yields a somewhat better fit than the Langmuir model over the experimental range with good coefficients of correlation 0.940 vs. 0.846, 0.811 vs. 0.963 and 0.840 vs. 0.932 respectively in Langmuir and Freundlich model. A high dyes sorption was observed by this sorbent material confirming the previous tendencies observed in the kinetics sorption. According to the coefficients of correlation, we deduct that the Langmuir model is only adequate for modelling isotherms in case of acid blue MTR dye by using FOP while in case of IOP and DOP Freundlich model fits better (Table 1).

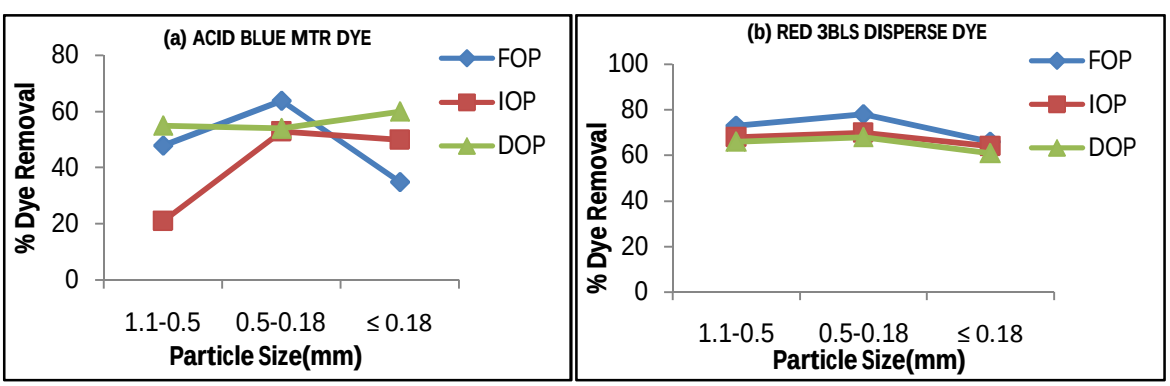

Fig. 1.7. Effect of particle size (mm) on % Dye removal of (a) Acid Blue MTR Dye and (b) Red 3BLS Disperse Dye by using (a) FOP (b) IOP (c) DOP.

Table 1. Langmuir parameters and Freundlich parameters of different types of treated orange peels biosorbents on adsorption of Acid Blue MTR dye.

S. No.	Sorbent type	Langmuir Parameters			Freundlich parameters		
		B_{max}	K_L	R^2	K_f	1/n(-)	R^2
1.	FOP	19.48	11.13	0.9406	0.5	0.420	0.846
2.	IOP	36.67	107.5	0.8118	0.4	0.596	0.963
3.	DOP	16.69	14.32	0.8407	0.3	0.504	0.932

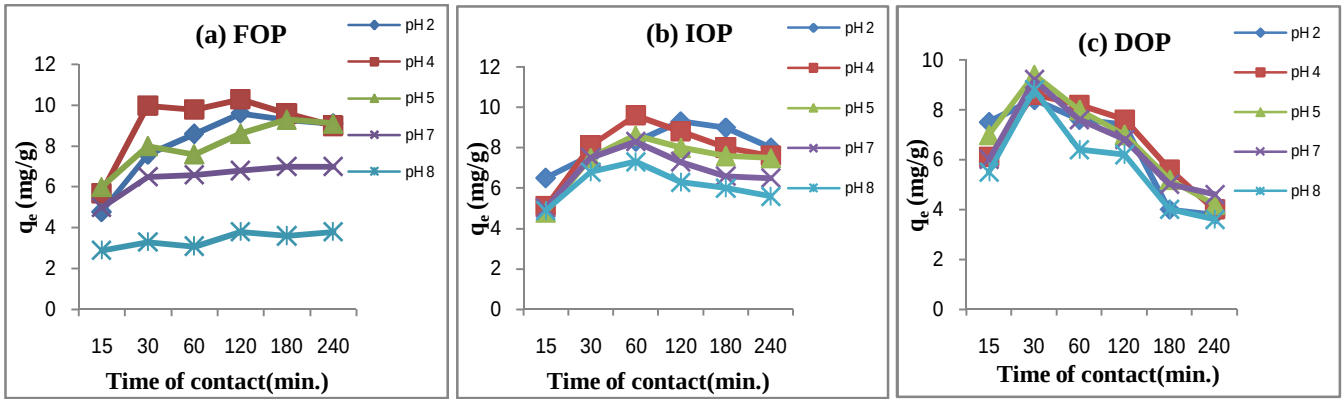

Fig. 1.8. Showing the adsorption kinetics of time Vs q_e for Acid Blue MTR Dye by using (a) FOP (b) IOP (c) DOP.

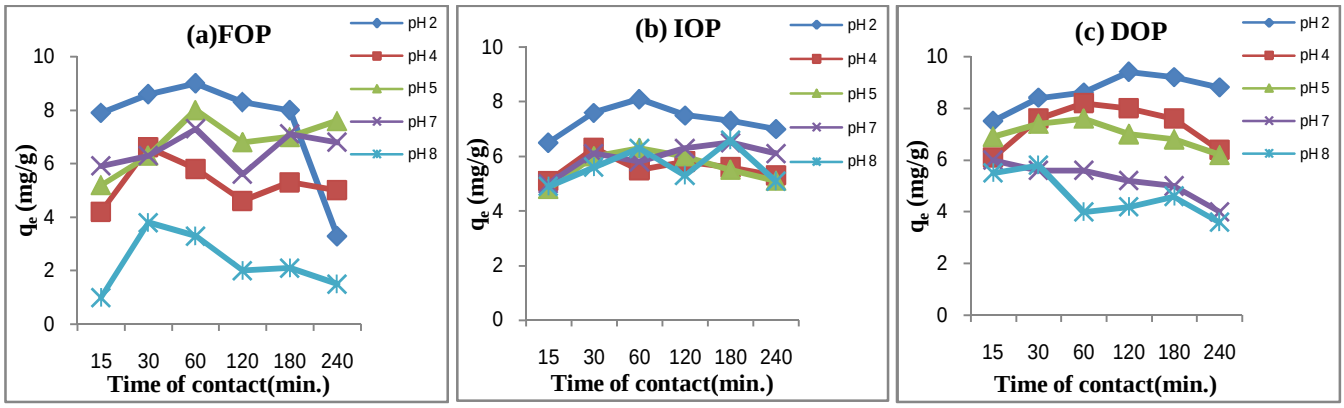

Fig. 1.9. Showing the adsorption kinetics time Vs q_e for Red 3BLS Disperse Dye by using (a) FOP (b) IOP(c) DOP.

Table 2. Langmuir parameters and Freundlich parameters of different types of treated orange peels biosorbents on adsorption of Red 3BLS Disperse dye.

S. No.	Sorbent type	Langmuir Parameters			Freundlich parameters		
		B_{max}	K_L	R^2	K_f	1/n(-)	R^2
1.	FOP	23.35	30.54	0.9624	1.8	0.321	0.841
2.	IOP	29.36	60.94	0.9336	0.41	0.512	0.923
3.	DOP	27.30	25.58	0.9926	1.6	0.294	0.647

In the case of red 3BLS disperse dye, the Langmuir model fits better than the Freundlich model over the experimental range with good coefficients of correlation 0.962 vs. 0.841, 0.933 vs. 0.923 and 0.992 vs. 0.647 respectively in Langmuir and Freundlich model. According to the coefficients of correlation, we deduct that the Freundlich model is not adequate for modelling isotherms in case of this dye for all the three biosorbents (Table 2).

5. Conclusion

The present study concludes that the OP and its treated types i.e. IOP and DOP could be employed as low-cost adsorbent for removal of acidic dyes and disperses dyes from wastewater at low concentrations. From the analysis of isotherm, data obtained from the fittings of the Freundlich model fits better than the Langmuir model in case of acid blue MTR dye and in case of red 3BLS disperse dye Langmuir model fits

better than Freundlich model. Further investigation is required to study the reusability of the biosorbent. An experiment can also be designed for the removal of dyes from the textile effluent. It may be concluded that orange peel may be used as a low-cost, natural and abundant source for the removal of dyes and it may be an alternative to more costly materials. It may also be effective in removing as well other harmful or undesirable species present in the waste effluents.

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