Biosorption of Auramine O and Drimarene Dyes from Aqueous Solutions using the Seed Powder of Diospyros lotus

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Abstract. In the present study, the prospects of Diospyros lotus seed powder (DLSP) for biosorption of Auramine O and Drimarene Blue from simulated aqueous solutions were investigated. The surface characterization was done by FTIR spectroscopy and SEM technique. The optimum conditions for adsorption of 20 ppm AO at equilibrium were found to be 0.1g of DLSP, pH 6.0–6.0, 150 rpm speed for 2 hrs at 25–30 °C. Similarly, the effective conditions for optimal uptake of 20 ppm aqueous solution of DB were found to be 0.1g of DLSP, pH 0.0–2.0, 200 rpm speed for 2 hrs at 30 °C. The data followed the Langmuir, Freundlich and Temkin isotherm models but the Langmuir isotherm was the most consistent one with $q_m = 26.95 \text{ mg g}^{-1}$ and $34.36 \text{ mg g}^{-1}$ respectively for AO and DB dyes. The kinetic models showed that adsorption of DB and AO followed the pseudo second-order rate of reaction. The values of $\Delta G$, $\Delta H$ and $\Delta S$ for AO, and DB revealed the process as an exothermic and spontaneous one. These results indicate that DLSP is a cost-effective and environment-friendly sorbent that can be used for effective removal of Auramine O and Drimarene Blue dyes from aqueous solutions.

Keywords. biosorption, Diospyros lotus, auramine O, Drimarene Blue, Langmuir isotherm

1. Introduction

Everything that surrounds us is termed as “environment.” Every living organism interacts with the environment and gets benefit from it. With the advent of modern technology, life has entered a new era of development. The latest technology has increased the concern about the safety of our environment; as the addition of waste substances is increasing day by day at an alarming level (Sajwan et al., 1996). The sources of pollution may involve the origination from a single point or more than one point. Organic compounds are used daily for many purposes but their direct release causes water pollution (Ali et al., 2004). The main sources of organic pollution involve household waste, industrial waste, and waste from agriculture. Organic waste materials are of primary concern because they remain persistent in nature. They have a long residence time, which causes more lethal effects. In addition, they can be transported from one place to another with retention of configuration. End fate of all compounds is that they are becoming part of our ecosystem and are affecting us.

The compound which binds any fiber or substance and imparts color to it is termed as “dye” (Tan et al., 2008). These compounds are characterized by the class of compounds having an aromatic ring, and these compounds have a high degree of unsaturation which is responsible for their stable nature and they impart color to fibers more effectively. These synthetic dyes are prepared extensively because of their use in different industries (Crini et al., 2005). As the waste of unused dyes is directly released in water, they...
are decomposed with the help of microorganisms. During this process, the aquatic organisms use the oxygen to utilize these dyes. This results in depletion of oxygen in the water which is threatening to the other aquatic organisms (Burkhard et al., 2008).

Dyes are prepared synthetically with a wide range of colors and their toxicity levels vary depending upon the composition of dye (Crini et al., 2005). The dyes are usually difficult to degrade and have long-range effects. They disturb the odor/appearance of water and stop the entrance of light and other soluble gases which are required for life. The colored waste materials are released in rivers and streams. They disturb the original appearance of water bodies and make them unfit for use. The azo dyes usually enter a hydrolysis phase, instead of dying, leading to residual dyes making water bodies colored and unfit for aquatic organisms. The exposure of dyes may cause dermal and eye infections. The prolonged exposure may result in a respiratory disorder because these dyes release toxic gases on heating. In extreme cases, they may cause skin inflammation, indigestion, difficulty in breathing and respiration.

The treatment of wastewater has been a matter of major concern for centuries; several methods have been used for the solution of wastewater treatment (Lee et al., 2013). Traditional methods have disadvantages as they consume high energy, are expensive, the ions removal is incomplete, and after removal, the sludge obtained is toxic which still remains an issue and causes serious threats when discharged (Nezamzadeh-Ejhieh et al., 2010). “Biosorption” is a process in which the sorbates are removed by surface interaction with sorbent functional groups (Aksu et al, 2005; Oporto et al., 2008). The sorption phenomenon is a surface adsorption phenomenon, requires low energy, and is economical as sorbents are usually derived from waste materials and can be used again and again without loss of efficiency (Chakraborty et al., 2005; Chen et al., 2011). The plant biomass such as leaves, roots, shoots, seeds, and bark can be used for this purpose (Mack et al., 2007). The adsorbent used in this study was date plum persimmon (Diospyros lotus) seeds (DLS). Date plum grows abundantly in northern areas of Pakistan and contains 5 to 6 seeds per fruit. Seeds of Diospyros lotus were collected in bulk from the dried fruit in winter for sorption studies.

The Auramine O (AO) belongs to the group of cationic basic dye. It is also known as Auramine hydrochloride. The dye has a yellow needle like appearance. The dye works effectively in aqueous media. The wavelength for maximum absorption is 435 nm. The effective pH for working with an aqueous solution of dye is in the range of 7–8. AO is characterized by having an amino group. They have a tremendous fluorescence property and can be washed away easily. It is widely employed for the coloring of fabric, having a negative charge on its surface because it is a cationic dye and adheres to the surface well. It is used as an antimicrobial agent, as it can interact with proteins so harmful for the living organisms. The molecular weight of the dye is 303 grams per mole. The C.I. for the dye is 41,000 (Mall et al., 2007).

![Chemical structure of Auramine O dye](image1)

Drimarene Blue (DB) belongs to the group of reactive dyes and remains stable both in powder and liquid form. This dye is characterized by having azo group as shown in Figure 2. The dye is very effective for fast dying. It is employed on a large scale for dying at room temperature. The pH of the dye is 2 and its maximum absorption wavelength is 615 nm. The molecular weight of dye is 631 grams per mole. The dye forms a covalent bond with surface functional groups mainly –OH and –NH₂ groups. This property makes the dye permanent in nature and due to this reason, these are not faded easily and can be washed without decolorization (Jović et al., 2013). This is an anthraquinonic dye, so resistant to degradation. It is a toxic, carcinogenic, and mutagenic chemical. Its C.I. is Reactive Blue 52 (Siddiqui et al., 2010).
The adsorbent used in this study was date plum persimmon (Diospyros lotus) seeds (DLS). This is a deciduous tree and belongs to the family Ebenaceae and its fruit has many medicinal properties (Uddin et al., 2011).

2. Material and Methods

Auramine O (C.I. Basic yellow 2, C.F=C_{17}H_{21}N_{3}.HCl) dye was purchased from Matrix pharmachem. Drimarene Blue (C.I. Reactive Blue 52, C.F=C_{19}H_{14}ClCuN_{7}O_{8}S_{2}) dye was bought from Sandoz Pakistan Ltd. List of Salts including iron (II) chloride, manganese (II) chloride, potassium iodide, and magnesium sulfate heptahydrate were purchased from Riedel-de Haen chemicals. Aluminum sulfate octadecahydrate, calcium (II) chloride, and sodium chloride were bought from a friend’s chemical laboratory. Hydrochloric acid, nitric acid, sodium hydroxide, and ethanol were purchased from BDH laboratory supplies. A Fourier transform Infrared spectrophotometer (IR Prestige-21), SEM, UV-visible spectrophotometer (UV-1601 Shimadzu), Analytical balance (AX 200 Shimadzu, max capacity=200g), pH meter (Lab pH meter Crison), Orbital shaker (OS-752 Optima), centrifuge machine (800 electronic centrifuge), and an electric furnace (Muffle furnace) were used. The adsorbent used in this study was date plum persimmon (Diospyros lotus) seeds (DLS). Seeds of Diospyros lotus were collected in bulk from northern areas of Pakistan. The seeds were washed with distilled water, pulverized, and collected in a glass jar for the sorption study.

2.1 Modification of Sorbent

The sorbent was modified by two ways. Mechanical modification was done by grinding the sorbent seeds in a laboratory mill. The modification aided in increasing the surface area for rapid uptake and uniform distribution of ions. Moreover, the equilibrium was reached rapidly. The DLS was modified chemically by soaking the sorbent in 1M NaOH and 1M HCl overnight to modify the sorbent (Gong et al., 2005). Meanwhile, it enhanced the exposure of active sites which facilitates interaction with sorbates. The modified powder was filtered and washed with distilled water many times for the removal of residual sodium and chloride ions. Lastly, it was heated in an oven at 50 °C for drying. The acid modification effectively increased the positively charged sites which effectively uptake the anionic dye by electrostatic attraction. Similarly, base modification increased the negatively charged sites which facilitated the uptake of the cationic dye.

2.2 Characterization of Diospyros lotus Seed Powder

“Characterization” is a scientific understanding of substance structure and functional groups identification. For example, for identification of DLS functional groups, FTIR spectra were obtained. The identification of functional groups helps in the fingerprint profile. This profile of functional groups is unique and specific to DLS. Similarly, surface morphology of DLS was determined by using SEM. It facilitates in the interpretation of DLS surface structure and morphology.

2.2.1 FTIR Spectroscopic Analysis

Analysis of functional groups of DLS was done with the help of FTIR spectroscopy. The absorption of a specific wavelength of IR radiation identified the types of functional groups. 0.05 g of DLS was mixed with 0.2 g of potassium bromide and spectra were obtained using the FTIR spectrophotometer. The spectrum was recorded for the untreated and treated DLS, prior to interaction with dyes.

2.2.2 SEM of DLS

SEM is a type of microscope that uses beam of electrons, which are focused on the atoms present on the surface of sample. The interaction of electrons helps in determination of surface
structure. These electrons stimulated the production of secondary electrons which help in the surface analysis. As electrons are used, the image can be resolved up to a nanometer. The SEM of DLSP was done with the NOVA NANO SEM 450 electron microscope by FEI, Thermo Fischer Scientific for the examination of surface morphology.

2.3 Biosorption Batch Study

In the present context of research, the biosorption study was carried out to check the prospects of DLSP (sorbent) for removal of AO and DB dyes from waste water. The adsorption capability of DLSP was studied by variation of factors affecting the sorption efficiency and optimized conditions were attained for maximum uptake of the dyes. The optimization study was followed by isothermal, kinetic, and thermodynamic studies which comprehend the ability of DLSP for passive uptake of these dyes.

The ability of DLSP for uptake of dyes was investigated on a batch scale. The experiment was carried out by taking the 15-ml solution from 20 ppm DB solution. 0.1 g of DLSP was added to it at room temperature. The pH maintained was 2. The flasks were shaken by adjusting the shaking speed of the orbital shaker at 200 rpm for 1 hour. The sorbent after sorbing the dyes, was separated by centrifuging at 4,000 rpm for 10 minutes. The efficiency of sorbent was investigated by studying the absorbance of dye concentration left in the solution, through which the concentration of dye at equilibrium was studied. The unknown concentration of dye was determined from the calibration curve established at 615 nm for DB. A similar study was done for AO dye at 435 nm and 7 pH. Optimization studies were carried out by varying the factors of sorbent concentration, sorbate dosage, pH, temperature, time, and effect of ions by establishing a multisystem. The other equations used in these studies are shown below Equation 1 and Equation 2.

2.4 Isothermal Studies

Graphical analysis of data was done at a fixed temperature by taking the optimized values of the experimental study, in order to check the validity of data. The isothermal models were applied by obtaining the absorbance of solutions having varied sorbate concentration. From these concentrations, other isothermal parameters were calculated. Langmuir, Freundlich, and Temkin models were used to evaluate the process. The Langmuir model explains the uniform distribution of ions in form of a single layer. The Freundlich model describes the accumulation of dyes ions on a non-uniform surface in the form of multilayers. The Temkin isotherm explains that heat of adsorption decreases uniformly with the progress of sorption phenomena. The validity of data for the adsorption of AO onto DLSP was checked with the application of the following equations.

2.5 Kinetic Studies

The rate of reaction is determined by analyzing the speed of interaction between sorbate and sorbent (Kumar et al., 2012). The study involves the investigation of rate of transfer of ions from the solution to the layer surrounding the sorbent and from the layer to the surface on the basis of ion mobility and ion-exchange phenomena. The rate is obtained by preparing the solution of known concentration and taking out the small portion of solution at regular intervals of time. The sorbent is filtered off and remaining residual concentration of the ionic dye was determined with the help of UV-spectrophotometer. The rate of reaction facilitated the designing of proper sorption mechanism by finding the conditions which best fit the models for a particular sorbent-sorbate system.

\[
\text{Amount of dye adsorbed (q) = } (\text{Initial Conc. of dye (Co) - Equilibrium Conc. of dye (Ce)}) / (\text{Mass of sorbent added (W)}) \times \text{Volume of solution (V)} \quad [1]
\]

\[
\text{Percent sorption of dye (%) = } (\text{Initial Conc. of dye (Co) - Equilibrium Conc. of dye (Ce)}) / \text{Initial Conc. of dye (Co)} \quad [2]
\]
### 2.6 Thermodynamic Studies

Study of heat changes was done by analysis of the biosorption process under the influence of varying temperature. Temperature was varied while the other system variables affecting the efficiency of the system were kept constant. The value of free energy, enthalpy change, and entropy was calculated from a straight-line equation, which gives us the insight into the nature of the thermodynamic process.

### 3. Results and Discussion

#### 3.1 Functional Groups Identification

Analysis of the functional groups of DLSP was done with the help of FTIR spectroscopy. The absorption of a specific wavelength of IR radiation identified the types of functional groups. 0.05 g of DLSP was mixed with 0.2 g of potassium bromide and spectra were obtained using a FTIR spectrophotometer. The spectrum was recorded for the untreated DLSP, prior to interaction with dyes. It is evident from Figure 3 that wide peaks obtained at 3358.07 cm\(^{-1}\) and 3294.42 cm\(^{-1}\) might be due to the stretching of the -OH or -NH groups. Similarly, the peak at 2924.09 cm\(^{-1}\) may be due to the stretching of the CH bond, which might belong to the alkyne, alkene, or alkane family. The variable peak at 1639.49 cm\(^{-1}\) indicated the possibility of presence of either C=C, C=N groups respectively.

The stretching vibrations of the 1527.62 cm\(^{-1}\), 1442.75 cm\(^{-1}\), 1369.46 cm\(^{-1}\) and 1323.17 cm\(^{-1}\) wave numbers might be due to the stretching of -OH groups, while the last peak may be due to C=N groups. The peaks at 1247.87 cm\(^{-1}\), 1143.79 cm\(^{-1}\) and 1037.70 cm\(^{-1}\) indicated the likelihood of the C-O group, which might belong to the ester group.

Two spectra were recorded after chemical modification of DLSP; by using sodium hydroxide (1M) and hydrochloric acid (1M) separately. Figure 4 shows the spectrum, obtained after base modification of DLSP. The band at 3506 cm\(^{-1}\) indicated the possibility for interaction of acid with the carbonyl group. The band at the 2304 cm\(^{-1}\) wave number might be due to the stretching of the Si-H group. The peak at 2156 cm\(^{-1}\) might be due to the alkyne CH group stretching vibration. Similarly, the stretching vibration at 1703 cm\(^{-1}\) showed the possibility of the carbonyl group. The peak at 1369 cm\(^{-1}\) might be due to the -OH group stretching. Similarly, the disappearance of the peak at 1323 cm\(^{-1}\) in comparison to untreated DLSP is due to the interaction of acid with the hydroxyl group.

The spectrum noted in Figure 5 after acid treatment of DLSP exhibited the presence of a wide peak at 3305.99 cm\(^{-1}\). This peak indicated the possibility for interaction of acid with the carbonyl group. The band at the 2304 cm\(^{-1}\) wave number might be due to the stretching of the Si-H group. The peak at 2156 cm\(^{-1}\) might be due to the alkyne CH group stretching vibration. Similarly, the stretching vibration at 1703 cm\(^{-1}\) showed the possibility of the carbonyl group. The peak at 1369 cm\(^{-1}\) might be due to the -OH group stretching. Similarly, the disappearance of the peak at 1323 cm\(^{-1}\) in comparison to untreated DLSP is due to the interaction of acid with the hydroxyl group.
It is evident from Figure 6 that the presence of wide peaks at 3471.87 cm\(^{-1}\) and 3253.9 cm\(^{-1}\) might be due to the stretching of the free -OH group (without H-bonding) of DLSP or due to the -NH group of AO. The interaction of dye broke down the hydrogen bonding associated with functional groups due to which the peak became wide. The wave number of 2912.51 cm\(^{-1}\) was obtained due to the stretching of the -CH group, which may belong to the alkene or alkane family. Peaks of alkyne carbon-carbon triple bond stretching were observed at wave numbers of 2324.2 cm\(^{-1}\) and 2140.99 cm\(^{-1}\) respectively.

The spectrum obtained as shown in Figure 8 after adsorption of AO by DLSP exhibited that peaks recorded at 3720.69 cm\(^{-1}\) and 3842.20 cm\(^{-1}\) might be due to the presence of free hydroxyl groups. The presence of free hydroxyl group is due to the fact that AO has interacted. The peak at 3305 cm\(^{-1}\) wave number indicated the possibility of the alkyne -CH group stretching. The peak at 3417.86 cm\(^{-1}\) wave number could be due to the presence of free -OH or -NH groups. Series of consecutive bands at 3290.56 cm\(^{-1}\), 3246.20 cm\(^{-1}\), 3232.70 cm\(^{-1}\), and 3211.48 cm\(^{-1}\) might be due to the stretching or bending of the -NH groups which are not free, rather hydrogen bonded. These bands may be due to vibrations of the AO -NH groups. Stretching vibrations at 2160 cm\(^{-1}\) and 2270 cm\(^{-1}\) wave numbers might be due to the alkyne carbon-carbon triple bond vibrations. The wave number at 2420.66 cm\(^{-1}\) might be due to background noise.
The interaction of base treated DLSP with DB could be interpreted from the FTIR spectrum as shown in Figure 9. Wavenumbers at 3392.79 cm\(^{-1}\) and 3304.06 cm\(^{-1}\) were obtained due to the stretching of -OH groups, which might be hydrogen bonded. Similarly, the band at 3290.56 cm\(^{-1}\) might be due to the stretching of the -NH group. In this spectrum, no prominent shift in peaks was observed, and this showed that the interaction of DB with DLSP is of electrostatic type and no bond breaking and making was observed.

The peaks at 3909.71 cm\(^{-1}\), 3894.28 cm\(^{-1}\), and 3828.70 cm\(^{-1}\) wave numbers were recorded after interaction of acid treated DLSP with AO. These peaks exhibited the presence of free -OH groups (without hydrogen bonding). The vibrations at 2148.7 cm\(^{-1}\) and 2276 cm\(^{-1}\) wave numbers indicated the possibility of carbon-carbon triple bond stretching. The adsorption of AO on the surface of DLSP freed the -OH groups and no hydrogen bonded was indicated by the involvement of these hydroxyl groups as shown in Figure 10.

The interaction of DB dye with acid treated DLSP is purely electrostatic in nature. It can be studied from Figure 11 as no appreciable change in wavenumber of peaks was observed. The peaks obtained were similar to those found for spectrum of untreated DLSP.

3.2 SEM of DLSP
The SEM images of DLSP as shown in Figure 12 showed the presence of hollow spaces, which facilitated the adsorption of dyes through physisorption.
3.3 Factors Affecting Adsorption of Dyes onto DLSP

3.3.1 Influence of Dyes’ Concentration:
Concentration of the dye greatly influences the sorption efficiency, as it provides the driving force to start the process. The influence of dye dosage was studied by varying the concentration of dye from 10 to 50 ppm. The concentration of DLSP taken was 0.1 g and other system variables affecting the sorption efficiency were kept constant. The data was analyzed as shown in Figure 13 and Figure 14. It was found that maximum uptake of 94.20% AO was obtained for 20 ppm of the dye with NaOH treated DLSP while maximum uptake of 89.92% was found for 10 ppm and 20 ppm of DB with the untreated DLSP. With further increase in concentration, the percent uptake decreased due to occupation of all DLSP active sites. The decrease in uptake at higher concentrations is due to the reason that with the rise in amount of AO, the interaction between the dye ions increased and it decreased the interaction between the DLSP active sites and the dye ions.

3.3.2 Influence of Sorbent Dose
The concentration of DLSP is a decisive factor in scrutinizing the efficiency of dye biosorption. The influence of sorbent dose was studied by shaking 20 ppm solution of the dyes. The dosage of DLSP was varied from 0.1 to 0.5 g. The experiment was carried out for the uptake of AO and DB by using untreated and chemically treated forms of DLSP. The analysis of data with the help of a graph showed that the maximum uptake of 91.5% AO took place with the base treated DLSP while 99.52% of DB took place with 0.1 g of untreated DLSP. With the increase in concentration of DLSP, a decline in percent sorption was observed and this may be due to the fact that all the dye ions were adsorbed and a further increase in amount of DLSP results in the overlapping of active sites and it decreased the availability of active sites as shown in Figure 15 and Figure 16.

3.3.3 Influence of Contact Time
The contact time was found to be a controlling factor, influencing the establishment of equilibrium state during sorption process. As the contact time between the DLSP and dye was increased, the percent sorption increased. This may be attributed due to the fact that the interaction between the ions of dyes and active sites of DLSP increased with time. A batch study was carried out by using 0.1 g of DLSP, 20 ppm of AO
and DB dyes, shaking speed was adjusted to 150 rpm, pH adjusted was 7, and reaction was studied at room temperature. The graphical representation explains that initially the percentage uptakes of AO and DB were low and maximum values were obtained for the base treated DLSP for 97.93% of AO and for acid treated DLSP 99.95% of DB when the time approached 120 minutes. Further rise in contact time had no effect as equilibrium had already been achieved as shown in Figure 17 and Figure 18.

Figure 16: Influence of sorbent dose on adsorption of DB by using Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP

Figure 17: Influence of contact time on adsorption of AO by using untreated and treated forms of DLSP

3.3.4 Influence of Temperature

Temperature provides the energy to overcome the mass transfer barrier between the solution of dye and sorbent active sites. Influence of temperature also depends upon the thermodynamics of the sorption process, which may be endothermic or exothermic in nature. The effect of temperature on uptake of AO and DB was studied by establishing the system in which all the variables except temperature were kept constant. The temperature was varied from 10 to 50 °C. The graphical analysis in Figure 19 and Figure 20 shows that uptake was increased as the temperature increased from 10 to 30 °C, because the temperature provided the activation energy which facilitated the interaction between the dye and the sorbent. With the further rise in temperature, the sorption efficiency was reduced due to denaturation of active sites. The decrease in sorption at high temperature is also due to the exothermic nature of reaction (Gupta et al., 2012).

Figure 18: Influence of contact time on adsorption of DB by using untreated and treated forms of DLSP

As is evident from Figure 19 and Figure 20, percent sorption of AO (91.55%) and DB (97.29%) increased up to 30 °C and then decreased due to the denaturation of surface sites which are responsible for binding with the ions of the dyes.
3.3.5 Influence of pH

The chemistry of a solution largely depends upon the pH, as it affects the degree of ionization and chemistry of functional groups active sites. The basic or acidic nature of dyes is determined by the pH of a solution. At a low pH from 0 to 6, the solution becomes acidic and interaction between anionic species increased. While from pH 7 to 14, a solution becomes basic and uptake of cationic species increases. Influence of pH was studied by mixing the solution of 20 ppm of AO and DB with 0.1 g of DLSP. The pH values of the solutions were adjusted by using 0.1 m solution of sodium hydroxide and 0.1 m solution of hydrochloric acid. The solutions were shaken at 150 rpm for 120 minutes. After shaking, the absorbance values were noted for determination of equilibrium concentration of the dyes. From Figure 21, it is evident that the adsorption of AO decreased as pH became more acidic while percent sorption increased for the basic value of pH up to 93.90%. The optimum value of the dye uptake was obtained for pH 7. The decrease in sorption percent when the pH became acidic is due to fact that AO is a cationic dye and when the pH becomes acidic, the number of positively charged species increases. Hence, electrostatic repulsion at low pH leads to a decrease in sorption (Hu, 1996).

The analysis of data was done by plotting a graph between percent sorption and pH. It is clear from Figure 21 that the uptake of DB increased as the pH became more and more acidic and the maximum value 99.66% was obtained at pH 0.0–2.0. While in basic medium, the percent sorption reduced due to the repulsion between the anionic species present in the solution and the negatively charged ions of dye. Hence, it is evident from perusal that the AO is a cationic dye while DB is an anionic dye. The pH of the solution effectively explained the nature of the dye through percent sorption.

3.3.6 Influence of Shaking Speed

Influence of shaking speed was studied by changing the rpm of an orbital shaker and keeping other system variables constant. The shaking speed was changed from 100 to 300 rpm and influence was studied for the adsorption of AO and DB. It was found that the maximum percent sorption of 85% of AO took place at 150 rpm while the maximum removal of 91.30% DB took place at 200 rpm as shown in Figure 22. The adsorption increased with the increase in speed due to the increase in kinetic energy, but after 150 and 200 rpm, the sorption efficiency reduced because at higher speeds the desorption of ions takes place from the surface.
Table 1
Isothermal parameters for the adsorption of AO onto untreated, base and acid treated DLSP.

<table>
<thead>
<tr>
<th>Sorbent used</th>
<th>Langmuir Isothermal parameters</th>
<th>Freundlich Isothermal parameters</th>
<th>Temkin Isothermal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mg g$^{-1}$)</td>
<td>$k_L$ (L g$^{-1}$)</td>
<td>$R_L$</td>
</tr>
<tr>
<td>Un T DLSP</td>
<td>11.11</td>
<td>0.86</td>
<td>0.052</td>
</tr>
<tr>
<td>T1 DLSP</td>
<td>26.95</td>
<td>0.040</td>
<td>0.357</td>
</tr>
<tr>
<td>T2 DLSP</td>
<td>21.41</td>
<td>0.042</td>
<td>0.352</td>
</tr>
</tbody>
</table>

Table 2
Isothermal parameters for the adsorption of DB onto untreated, base and acid treated DLSP.

<table>
<thead>
<tr>
<th>Sorbent used</th>
<th>Langmuir Isothermal parameters</th>
<th>Freundlich Isothermal parameters</th>
<th>Temkin Isothermal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mg g$^{-1}$)</td>
<td>$k_L$ (L g$^{-1}$)</td>
<td>$R_L$</td>
</tr>
<tr>
<td>Un T DLSP</td>
<td>22.831</td>
<td>0.116</td>
<td>0.231</td>
</tr>
<tr>
<td>T1 DLSP</td>
<td>30.03</td>
<td>0.038</td>
<td>0.362</td>
</tr>
<tr>
<td>T2 DLSP</td>
<td>34.36</td>
<td>0.058</td>
<td>0.316</td>
</tr>
</tbody>
</table>

3.4 Isothermal Studies
It is evident from the experimental data as shown in Table 1 and Table 2 that the adsorption of AO and DB by untreated and treated forms of DLSP followed the Langmuir, Freundlich, and Temkin models effectively. The graphical analysis justifies the experimental data of all the models, as the value of $R^2$ is close to one in all the cases as shown in Figures 23–28 (Alkan et al., 2004; Dada et al., 2012).

3.4.1 Langmuir Model
This model is based upon a single metal system, the adsorption of a single metal ion is being discussed by a process in which the uniform layer is formed on the surface of the sorbent without any chemical change (Dada et al., 2012). The following formula best describes the model (Equation 3):

$$\frac{1}{q_e} = \frac{1}{bq_mC_e} + \frac{1}{q_m}$$  \[3\]

The “$q_m$” is the ability of the sorbent to adsorb the sorbate at its full limit, means it states the stage when saturation takes place and indicates the optimum adsorption of ions when the system is at equilibrium. The $q_e$ shows the concentration in milligram per gram of metal ions being adsorbed. The factor “$b$” shows the reactivity of the biosorbent or its effectiveness, and $C_e$ is the equilibrium concentration of sorbate. This model is based upon the following facts:
- The sorbate being adsorbed just forms a single layer
- The sorbates just react with one site at a time.
- The energies of dye ions sorbed on sorbent active area did not affect the other ions’ sorption.

This model is less effective when differences in energies of sites occur due to difference in structure. Another factor which describes the adsorption process is the separation factor $R_L$ which is dependent on the Langmuir constant “$b$” (Equation 4).

$$R_L = \frac{1}{1 + bC_e}$$ \[4\]

If $R_L > 1$, then the adsorption process is unfavorable, if $R_L = 1$, then it is linear, if $0 < R_L < 1$, then the process is favorable and if $R_L = 0$, then it is irreversible (Rauf et al., 2016).
3.4.2 Freundlich Model

The model describes the binding of metal ions to the surface containing different structural regions (Dada et al., 2012). Equation 5 describes the model:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]  

The \(q_e\) describes the concentration of sorbate ions being taken up by the sorbent and \(C_e\) is the amount of metal ions remaining in the solution and \(K_f\) is a constant and indicates the capacity of sorbent while reciprocal of “\(n\)” shows how intense is the process of sorption. If value of “\(1/n\)” is closer to zero, i.e. greater the value of “\(n\)”, then there is more heterogeneity on the surface. In all the cases except in the case of AO with base treated DLSP, the value of “\(1/n\)” is less than 1, which shows heterogeneous energy distribution on the surface (Rauf et al., 2016). This model describes the data more effectively when the concentration of ions at rest position of the system is large. Both models best describe the data when single dye ions are being studied for removal but when the system involves many ions then other factors operate which do not follow these models. In a system containing multi ions, selectivity and interference by ions accounts for the use of other models.

3.4.3 Temkin Model

In this model, the energy is distributed smoothly throughout the sorption sites (Dada et al., 2012). The energy of sorption shows decline with rise in the coverage of sites. The model is best described by Equation 6 as:

\[
q_e = B_T (\ln A + \ln C_e)
\]  

The \(A\) is constant, corresponding to the value, when the system is at equilibrium and sorbates are being bound to sorbent. Its value is in L/g. The \(B_T\) is Temkin constant, whose value is based upon energy released during the process of biosorption. The magnitude of both constants is obtained from the graphical representation between \(q\) and \(\ln C_e\). The former value is obtained from slope and intercept gives the value of latter.

**Figure 23:** Langmuir isotherms for adsorption of AO onto Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP

**Figure 24:** Freundlich isotherms for adsorption of AO onto Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP

**Figure 25:** Temkin isotherm for adsorption of AO onto Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP
Figure 26: Langmuir isotherms for adsorption of DB onto Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP

Figure 27: Freundlich isotherms for adsorption of AO onto Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP

Figure 28: Temkin isotherms for adsorption of DB onto Un T (untreated), T1 (NaOH treated), and T2 (HCl treated) forms of DLSP

3.5 Kinetic Studies

The rate of reaction facilitates the designing of proper sorption mechanism by finding the conditions which best fit the models for a particular sorbent-sorbate system. The systems usually follow the pseudo first- and second-order rate of reaction. Equation 7 shows the pseudo first order while the pseudo second order is shown as Equation 8 as given below (Juang et al., 2007; Kumar et al., 2006).

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \\
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

Figure 29: Pseudo first-order model for sorption of AO and DB onto DLSP

Figure 30: Pseudo second-order model for sorption of AO and DB onto DLSP

The data reveals that the pseudo second-order model was more applicable to the biosorption of AO and DB dyes on DLSP as the \( R^2 \) values were closer to 1 in the case of pseudo second order than the pseudo first-order models.

3.6 Thermodynamic Studies

The study of heat changes involved in the process of sorption was carried out and data obtained is presented in Figure 23 and Table 3.
Table 3
Thermodynamic parameters for sorption of AO onto DLSP

<table>
<thead>
<tr>
<th>Dye</th>
<th>∆G (KJ mol⁻¹)</th>
<th>∆H (KJmol⁻¹)</th>
<th>∆S(Jmol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO</td>
<td>-0.531</td>
<td>-12.883</td>
<td>0.477</td>
</tr>
<tr>
<td>DB</td>
<td>-1.446</td>
<td>-14.182</td>
<td>1.157</td>
</tr>
</tbody>
</table>

The negative values of free energy indicated that the process is spontaneous. The value of enthalpy change obtained was negative, which indicated that the process is exothermic. The positive value of entropy indicated the disordered nature of sorbate ions at the contact point of sorbent surface and solution of the dye. The Equations (9–11) used for calculating the thermodynamic parameters are shown below:

\[
\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{9}
\]

\[-\Delta G^o = -RT \ln K_d \tag{10}\]

where

\[
K_d = \frac{c_0}{q_e} \tag{11}
\]

The characterization of surface functional groups indicated that carboxyl and hydroxyl groups are responsible for the uptake of ions of dye through electrostatic interactions. The dyes are removed from the waste water in steps: firstly, ions are transported from the solution to the layer surrounding the sorbent and then ions are transported from the layer to the surface of the DSLP sorbent. The ions then form an inner sphere complex when we are studying the single ion. The -CO, -OH, and -NH groups are responsible for the formation of interaction with ions. The surface morphology was studied by using SEM, which indicated the presence of hollow spaces which facilitates the passive uptake of dyes. The mechanism followed the pseudo second order kinetically.

In the biosorption process, the adsorption capability of DLSP was studied by a variation of factors affecting the sorption efficiency and optimized conditions were attained for maximum uptake of dyes. The optimum conditions for adsorption of 20 ppm AO at equilibrium was found by using 0.1 g of DLSP at pH 6 to 7 by shaking the solutions at 150 rpm for 2 hrs at 25–30 degree centigrade. Similarly, the effective conditions for optimal uptake of 20 ppm aqueous solution of DB was found by using 0.1 g of DLSP at pH 0–2, keeping the temperature at 30 degrees centigrade and by shaking the solutions at 200 rpm for 2 hrs.

Isothermal models were applied for the adsorption of AO and DB in order to check the consistency of data. The data followed the Langmuir, Freundlich, and Temkin models effectively but the most consistent one being followed was Langmuir. The calculation of isothermal parameters indicated that value of q_max for the adsorption of AO by base treated DLSP was found to be 26 mg g⁻¹, while by that of untreated DLSP was 11 mg g⁻¹. This explained that base treatment increased the sorption of AO to double. Similarly, the q_max for the sorption of DB by acid treated DLSP was found to be 34 mg g⁻¹ as compared to

4. Conclusions

It is evident from the perusal of the study that DLSP is proved to be a low-cost, eco-friendly agrowaste for the removal of AO and DB from the aqueous waste water by designing the system simulated to the real one. The adsorbent was modified by using base (1 M NaOH) and acid (1 M HCl). The modification facilitates the removal of dyes in a way that the acid treatment envisages the removal of DB effectively while the base treatment improved the sorption of AO. The acid treatment increased the positively charged sites while the base treatment enhanced the availability of the negatively charged sites.
untreated DLSP, where the maximum sorbed amount was 22 mg g\(^{-1}\). The isothermal study indicated that experimental data followed the Langmuir and Freundlich isotherm more effectively but the Langmuir model was more consistent. The kinetics studies revealed that the pseudo second-order rate of reaction was more applicable to AO and DB dyes than the first-order rate of reaction. Thermodynamic studies also prove it to be a spontaneous and exothermic process. The capability of DLSP for removal of dyes was done for the first time in order to explore its ability to remove the dyes for the treatment of textile waste water.

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