REMOVAL OF ACID RED 1 FROM AQUEOUS WASTE STREAMS USING PEEL OF CUCUMIS SATIVUS FRUIT. EQUILIBRIUM STUDIES

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ABSTRACT

The utilization of Cucumis sativus fruit peel (CSP) as an efficient, copious and eco-friendly adsorbent has been explored as an alternative to expensive activated carbon for the removal of acid red 1 dye from textile wastewater. Batch adsorption method is followed in the present work and various parameters like adsorbent dose, pH, and initial dye concentration are optimized. Adsorption data fit best into Langmuir and D-R isotherm models of adsorption taking into consideration the high correlation coefficients values obtained (0.98381 and 0.97391 respectively). The adsorbent is characterized through SEM and FTIR techniques which identify its porous nature and the chemical groups present on its surface. The maximum adsorption capacity is found equal to 18.76 mg per gram of CSP. The values of K and Qm of the D-R isotherm are found equal to 4.21E-0.7 mol²/KJ² and 2.674 mg/g This study concludes that CSP could be used as a successful low-cost adsorbent in treatment of wastewater polluted with textile dyes.

Keywords: Cucumis sativus fruit peel, eco-friendly adsorbent, adsorption isotherms, textile dyes.

INTRODUCTION

Dyes contain two principal parts: (1) chromophores accountable for color production and (2) auxochromes increasing dye affinity towards the fibers [1]. Many dyes provide color through linking to the surface and are resistant to the activity of detergents. Man-made dyes are extensively used in many industries such as paper, textile, plastic, carpet, food, cosmetics and leather tanning to provide color to their yields [2 - 4]. These dyes are released in industrial effluents leading thus to disposal problems and pollution [5 - 8]. It is so because they are of non-biodegradable nature. Moreover, dyes may be toxic to aquatic plants as well as carcinogenic and mutagenic causing functioning problems in kidneys, liver, brain, the reproductive and central nervous system [9 - 11]. The degradation of dyes from in waste water effluents is of great importance because even a meager amount of it could be highly visible and poisonous [12]. A number of removal strategies such as adsorption, advanced oxidation, aerobic coagulation, anaerobic microbial degradation and membrane separation, are used to remove dyes from waste water streams. Amongst all these removal methods, adsorption is the most widely used procedure due to its cost effectiveness and efficiency. It is used in industries to decrease hazardous organic and inorganic pollutants from wastewaters [13]. Activated carbon is a well recognized adsorbent material because of its high and versatile adsorption capability and microporous structure [14]. But, due to its high cost, its commercial use is limited. Several domestic waste materials and residues have been recently employed as adsorbents to
remove dyes from wastewater effluents because of their low cost, low toxicity, and abundance [15]. They are otherwise discarded without any use to the community. As reported, rice husk [16, 17], peach gum [18], grass wastes [15], yellow passion fruit wastes [19], wheat shells [20], banana and orange peels [21] are tested for dye removal from aqueous wastewater. As observed, many of the reported low cost adsorbent materials show lesser adsorption capacity, thereby limiting their industrial use. New economical, easily accessible, environment friendly and efficient adsorbents are required.

Cucumis sativus (cucumber) is a widely cultivated plant throughout the world. It is used as a fruit and a vegetable, for salads and soups among the north Indian people. Cucumber oil, cucumber fruit water, and cucumber seed extract are the products made from the cucumber fruit. Cucumis sativus is a well known commercial plant and a common kitchen garden vegetable. Cucumbers are planted in all parts of India. The cucumber peel is a discarded material and of no use at all neither economically nor industrially. So it is freely available for the preparation of an adsorbent. Therefore the major aim of this study is to assess the prospects of using the peel of Cucumis sativus fruit to prepare a low-cost adsorbent carbon and to study its potential to remove Acid Red 1 dye from synthetic wastewater. It was previously investigated to remove cationic dyes [22]. The impact of various parameters like initial dye concentration, pH, and adsorbent dose are investigated. The isotherm and thermodynamic parameters were deduced.

**EXPERIMENTAL**

**Collection and preparation of the adsorbent**

The discarded cucumber peel powder (CSP) used in this study was collected from Panjab University hostel canteen and shops in and around the university campus. The CSP was gathered, rinsed properly with distilled water many times to eliminate all the dirt and pigments and was even boiled at 80°C. This was continued until the sieved water was clear and colorless. CSP was then dehydrated in hot air oven for 48 h at 70°C. The dried CSP was rumpled and sieved to achieve a particle size of 50 μm - 100 μm. The prepared adsorbent was put in storage in air tight containers for further use. It was used without any chemical or costlier pre-treatment in the dye removal experiments.

**Materials**

AR 1 (Fig. 1) was supplied by Sigma- Aldrich (C.I.18050; C₁₈H₁₇N₂Na₂O₈S₂ M.W. of 509.42, λmax = 532 nm). It was used as an adsorbent in the present study. 0.1 g of the dye investigated was dissolved in 100 mL distilled water for the preparation of a stock solution. The latter (1000 mg/L) was diluted further to the desired concentrations Analytical-grade chemicals were used throughout this work. All the solutions were prepared using distilled water. The initial solution pH was adjusted with 0.1 M HCl or 0.1 M NaOH and was determined using Systronics µ pH system 362. UV–VIS spectrophotometer (Systronics AU-2701 Double beam spectrophotometer) was used to determine absorbance at 532 nm (λ max of AR 1). All sorption experiments were done in an incubator shaker (IKA 4000 i control) at 30°C.

![Chemical structure of Acid Red 1](image.png)

**Batch sorption experiments**

The optimum values of the various parameters (an adsorbent dose, pH and an initial dye concentration) and their effect on dye removal were deduced by carrying out sorption experiments. 100 ml of the dye solution of a varying concentration (10 mg/L - 100 mg/L) was shaken for 24 h with different dosages (0.25 g - 1.25 g) of CSP adsorbent at different pH (2 - 10) at 30°C in an incubator shaker. At fixed time intervals, samples taken from the solution were filtered through Whatman filter paper no. 42 and analyzed using UV-VIS spectrophotometer. A calibration curve referring to the absorbance versus...
known AR 1 dye concentrations was plotted prior to the calculation of the final dye concentrations. The amount of AR 1 dye adsorbed at equilibrium, $q_e$ (mg/g), was calculated using the following mass balance relationship:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where $C_0$ and $C_e$ (mg/L) denote the liquid-phase initial and equilibrium concentrations of the dye, respectively, $V$ is the volume of the solution taken (L), while $W$ is the weight of the dry adsorbent used (g).

The dye removal percentage was calculated using the following formula:

$$\%\ \text{removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

**Characterization of adsorbent prepared**

FTIR spectra were recorded on Perkin Elmer-Spectrum 400 RX-IFTIR Spectrometer in KBr pellets to identify the chemical functional groups existing on the CSP samples prior dye adsorption. The IR absorbance data referred to wave numbers in the range of 450 cm$^{-1}$ - 4000 cm$^{-1}$. The SEM micrographs were collected via Scanning Electron Microscope (model JEOL, JSM-6490) to observe CSP surface morphology.

**RESULTS AND DISCUSSION**

**Effect of the adsorbent dose**

The adsorbent material quantity is an important sorption affecting factor.

Adsorption generally increases with adsorbent dose increase.

An optimum adsorbent dose is determined by batch sorption study aiming an effective adsorption. The effect of the adsorbent dose on dye removal is followed in this investigation by keeping the other parameters (solution pH, solution concentrations) constant. The quantity of CSP (0.25g to 1.25 g) varies. 100 ml dye solution of a concentration of 50 mg/L is shaken at natural pH at 30°C in an incubator shaker (at 200 rpm) for 24 h. Fig. 2 shows that amount of dye adsorbed at equilibrium ($q_e$) increases from 1.91 mg/g to 2.25 mg/g as the adsorbent dose increases from 0.25 g to 1.25 g.

This is attributed to the increase of adsorption sites and surface area availability. The optimum adsorbent dose is found equal to 1.25 g.

**Effect of pH**

AR 1 dye adsorption onto the CSP surface is mainly influenced by the surface charge on the adsorbent as it is a charged species. The surface charge in turn is influenced by the solution pH [23]. It is commonly known that the anions are favorably adsorbed at lower pH values due to H$^+$ ions and cations presence. Negative charges are found on the active sites of the adsorbent at high pH values [24]. The initial pH of the solution presence has a profound control on the adsorptive uptake of the adsorbate molecule because it influences the surface charge of the adsorbent, the degree of ionization of the adsorbate, the functional groups dissociation on the active sites of the adsorbent as well as the structure of

Fig. 2. Effect of adsorbent dosage on the removal of AR 1.

Fig. 3. Effect of initial pH on the removal of AR 1.
the dye [24 - 26]. In this study, the effect of pH on dye removal is studied by keeping the other parameters (the solution concentration and the contact time) constant. Varying the initial pH (2-10), 100 ml of a dye solution of a concentration of 50 mg/L is shaken with optimum CSP dose, i.e. 1.25 g at 30°C in an incubator shaker (at 200 rpm) for 24 h. Fig. 3 shows that amount of the dye adsorbed at equilibrium (qₑ) decreases from 2.69 mg/g to 1.35 mg/g as pH increases from 2 to 10. In an aqueous solution the sulphonate group (D-SO₃Na) of dye AR 1 dissociates to produce an anion:

\[ D - SO_3Na \rightarrow D - SO_3^- + Na^+ \] (1)

In acidic condition (low pH), the adsorption is well expressed because of the electrostatic attraction between the protonated DT surface and the negative anion groups (D-SO₃-) coming from the dye molecules. Conversely, in basic condition (i.e. at high pH), the adsorption is hindered due to the increase of the negative sites (OH ions) which compete with dye anions for active sorption sites. So the optimum pH is found equal to 2. This value is chosen for further experiments.

**Effect of the initial dye concentration**

The variation of the initial concentration of AR 1 provides an uneven driving force rising above all mass transfer resistances of dye molecules between the liquid and solid phase. Hence, the adsorption process is affected by the initial concentration of the dye [27]. So to find out the effect of the dye initial concentration on CSP adsorption capacity, 100 ml of the dye solution of a varying initial concentration (10 mg/L - 100 mg/L) are shaken with the optimum CSP dose, i.e. 1.25 g, at optimum solution pH for 24 h. Fig. 4 shows that the amount of the dye adsorbed per g of the adsorbent increases from 0.88 mg/g to 3.21 mg/g with initial dye concentration increase from 10 mg/L - 100 mg/L. This is due to increased adsorbate molecules diffusion at the higher initial dye concentration, increased resistance to dye uptake and dye to adsorbent ratio. The high initial dye concentration provides a higher driving force which facilitates the dye diffusion from the solution to the adsorbent. It is found that the dye removal efficiency depends on the initial dye concentration of AR 1.

**SEM characterization of the adsorbent prepared**

Fig. 5a shows the SEM micrograph of CSP adsorbent prior to dye adsorption. It is evident that CSP has a rough surface morphology with craters and cavity like pores in it. These irregular sized pores must have been acting as adsorption sites for the dye molecules. Fig. 5b shows the SEM micrograph of CSP adsorbent after adsorption. It is found that the dye removal efficiency depends on the initial dye concentration of AR 1.

![Fig. 4. Effect of initial dye concentration on dye removal.](image)

![Fig. 5. SEM micrograph of CSP adsorbent (a) before adsorption (magnification: 400x) and (b) after adsorption.](image)
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Fig. 5b shows the morphology of the CSP following the dye adsorption. It depicts some major changes in the adsorbent surface. The pores and cavities are filled with dye molecules which confirms adsorption occurrence.

**FTIR study of the adsorbent prepared**

FTIR spectra are recorded to identify the functional groups on the adsorbent surface responsible for adsorption proceeding. A large number of peaks are obtained indicating the complex nature of CSP. Fig. 6 shows the broad troughs observed in the range of 3166.6 cm\(^{-1}\) which are due to OH stretching. The bands obtained at about 2923.5 cm\(^{-1}\) and 2853.5 cm\(^{-1}\) could be assigned to C-H stretching of methylene and aromatic groups, respectively. The peak at 1646.5 cm\(^{-1}\) refers to C=O stretching within the carboxyl groups. The band shift at 1463.5 cm\(^{-1}\) is due to phenols O-H stretching. The stretching of carboxyl group C-O bonds (1161.4 cm\(^{-1}\)) are also clearly visible. The band at 609.7 cm\(^{-1}\) is due to stretching of C-Cl bonds of the alkyl halide groups. The results show that CSP biosorbent contains various functional groups such as hydroxyl, phenol, alcohol, carboxyl and alkyl halide which might be the sorption sites for AR 1 dye. After AR 1 sorption, the FTIR spectra show some shifts of the peaks which confirms that dye molecules and CSP adsorbent interact during the adsorption process.

**Sorption isotherms**

The experimental adsorption equilibrium data is analyzed using Langmuir, Temkin, Freundlich and D-R isotherms (Fig. 7). The linearized form of the isotherms pointed out is used. Models having high correlation coefficient (R\(^2\)) values are considered the best fit.

The Freundlich isotherm describes multilayer non-ideal adsorption on a heterogeneous surface. It is presented by the following equation:

\[
q_e = K_F C_e^{1/n}
\]

where \(K_F\) is the adsorption equilibrium constant (mg/g), \(1/n\) refers to the adsorption intensity of the dye onto the adsorbent, \(C_e\) is the dye equilibrium concentration (mg/L), while \(q_e\) is the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g). The linear form of the Freundlich equation (Agyei et al., 2000) is given below:

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

where \(K_F\) is an approximate indicator of the adsorbent capacity, while \(n\) is a function of the strength of adsorption. Values of \(n\) ranging from 2 to 10 refer to a favorable sorption capacity, those between 1 and 2 are indicative of a moderate sorption capacity and whereas \(n < 1\) denotes poor sorption capacity. The values of \(K_F\) and \(n\) are calculated from the intercept and slope of the plot of \(\log q_e\) v/s \(\log C_e\) respectively. The value of \(n\) found in this investigation is greater than 1. This indicates a
favourable sorption capacity of CSP. Because of the low value of the correlation coefficient ($R^2 = 0.95798$) obtained in case of Freundlich isotherm application, it is not further considered.

The Langmuir isotherm holds for monolayer sorption on a homogeneous sorbent surface. It is described by the following equation [28]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$

(1)

The linearization of Eq. (1) leads to:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_a} \times \frac{1}{C_e}$$

where $C_e$ is the dye equilibrium concentration (mg/L), $q_e$ is the dye amount sorbed per gram of an adsorbent (mg/g), $K_a$ is the adsorption equilibrium constant (L/g), while $q_m$ is the maximum monolayer capacity (mg/g).

The values of $q_m$ and $K_a$ are calculated from the intercept and slope of the Langmuir plot of $1/C_e$ v/s $1/q_e$. The required characteristics of the Langmuir isotherm are expressed through the equilibrium parameter $R_L$, which is a dimensionless constant considered as a separation factor or an equilibrium parameter:

$$R_L = \frac{1}{1 + K_a C_0}$$

where $C_0$ is the highest initial dye concentration, i.e. 100 mg/L in this investigation. The $R_L$ values described the adsorption nature type. The latter is irreversible in case
Table 1. Isotherms Constants and Correlation Coefficients for adsorption of AY 17 from aqueous solutions.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>( R^2 )</th>
<th>( N )</th>
<th>( K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Freundlich</td>
<td>0.95798</td>
<td>1.152</td>
<td>2.23</td>
</tr>
<tr>
<td>2. Langmuir</td>
<td>0.97391</td>
<td>-0.171</td>
<td>-18.76</td>
</tr>
<tr>
<td>3. Temkin</td>
<td>0.95783</td>
<td>0.5535</td>
<td>3.97</td>
</tr>
<tr>
<td>4. D–R</td>
<td>0.98381</td>
<td>2.674</td>
<td>-4.210E-7</td>
</tr>
</tbody>
</table>

\( R_l = 0 \), it is favorable if \( 0 < R_l < 1 \), linear when \( R_l = 1 \) or unfavorable if \( R_l > 1 \). The values of \( R_l \) are found to be in the range from 0 to 1 for 100 mg/L indicating a favorable adsorption process. The maximum monolayer sorption capacity determined from the linearized Langmuir isotherm is found equal to 18.76 mg/g, (Table 1). The results referring to AR 1 dye sorption on CSP show that the Langmuir isotherm model can be applied as the correlation coefficient \( (R^2 = 0.97391) \) has a high value (Table 1).

The Temkin isotherm model assumes that the decrease of the heat of sorption is linear rather than logarithmic. It is described by the following equation:

\[
q_e = Q_m \exp (-K \varepsilon^2)
\]

The linearized form of D-R isotherm is:

\[
\ln q_e = \ln Q_m - K \varepsilon^2
\]

where \( K \) is a constant related to the sorption energy \( (\text{mol}^2/\text{KJ}^2) \), \( Q_m \) is theoretical saturation capacity \( (\text{mg/g}) \), \( \varepsilon \) is the Polanyi potential, which can be calculated on the ground of the following equation:

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]

The values of \( K \) and \( Q_m \) are estimated from the slope and the intercept of the plot of \( \ln q_e \) versus \( \varepsilon^2 \), respectively. The mean free energy of sorption \( (E) \) is defined as the free energy change when one mole of an ion is transferred from infinity in the bulk of the solution to the surface of the adsorbent and is calculated from the \( K \) value using the following equation:

\[
E = \frac{1}{\sqrt{2R}}
\]

If the value of \( E \) is between 8 kJ/mol and 16 kJ/mol, the adsorption process studied is chemisorptive in nature. It is determined by physical interactions in case the value of \( E \) is smaller than 8. The high \( R^2 \) value (0.98381) found shows that this model is also applicable. The values of \( K \) and \( Q_m \) from the D–R isotherm are found equal to 4.21.10^{-7} \text{mol}^2/\text{KJ}^2 and 2.674 mg/g, correspondingly.

Table 1 shows the values of all important parameters obtained from the different isotherm models applied. It also lists the values of the correlation coefficients obtained for the different isotherms.
CONCLUSIONS

This work describes the development of a highly efficient, economical and abundantly available adsorbent on the ground of discarded cucumber peel. It is successfully tested for AR 1 textile dye removal from aqueous solutions. The results obtained show that the dye initial concentration, the solution pH and adsorbent dose affect significantly the process investigated. The adsorption capacity increases with increase of the initial dye concentration up to 100 mg/L. The adsorption equilibrium data fit better the Langmuir and D-R isotherm models when compared to those of Freundlich and Temkin. The results of this study provide the conclusion that the use of CSP can be a promising dye removal adsorbent with environmental benefits like waste material reduction and environmental degradation minimization.

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