Adsorption study for the Removal of Hazardous Dye Congo Red by Biowaste Materials as Adsorbents

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ABSTRACT

The present work aims to investigate the removal of dye Congo red from aqueous solution by using Green Peas Shell (GPS) low-cost biowaste adsorbent under various experimental conditions. The effect of contact time, temperature, pH, dye concentration, and adsorbent dose on the removal of Congo red dye was studied. The adsorption study reveals that Congo red has the affinity to get adsorbed on to the surface of GPS. Equilibrium isotherms were analyzed by Langmuir, Freundlich isotherm described the isotherm data with high-correlation coefficients. The results of the present study substantiate that GPS biowaste material is promising adsorbent for the removal of the dye Congo red.

Keywords: Adsorption, GPS, CR, Contact Time, Adsorption Isotherm.

1. INTRODUCTION

Dye is widely used in textile, paper, plastic, food, and cosmetic industries and is easily recognized pollutant [1]. It significantly affects photosynthetic activity in aquatic life due to the presence of aromatics, metals, chlorides etc in them [2]. Many of the dyes used in the industries are stable to light and oxidation, as well as resistant to aerobic digestion [3]. However, dyes usually have a synthetic origin and complex aromatic molecular structure which makes them more stable so they are not biodegradable and photodegradable and creates some difficulties for the treatment of these pollutants [4].

There are different physicochemical processes generally used to treat dyes laden waste water, which includes flocculation, electro flotation, precipitation, electokinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation, and ozonation. However, all these processes are costly and cannot be used by small industries to treat wide range of dye waste water [5].

Adsorption process provides an attractive alternative for the treatment of contaminated water and known to be a better technique, which has great importance due to the ease of operation and comparable low cost of application in decoloration process. [6]-[11].

The objective of the present work was to study the mechanism of adsorption of Congo red (CR) benzidine-based anionic disazo dye known to be human carcinogen, (1-naphthalenesulfonic acid, 3, 3′-(4, 4′-biphenylene bis (azo)) bis (4-amino-) disodium salt) also known to be metabolize to Benzidine [7]-[8] on readily and cheaply available adsorbent material prepared from locally available vegetable waste Green Peas Shell (GPS).

The characterization of adsorbent SEM and adsorption as a function of time, nature of adsorbent, concentration of Congo red solution, pH of solution and temperature of the system were studied. On the basis of isotherm studies, test for the Langmuir and Freundlich adsorption isotherms and various thermodynamic parameters such as ΔG, ΔH and ΔS to find out the possibility of using these biomaterials as low-cost adsorbents for the removal of dye CR.
2. EXPERIMENTAL

2.1. Materials and Methods

2.1.1. Adsorbent:
The adsorbent selected for the present work was Green Peas Shell (Pisum sativum.) (GPS) which is locally available biowaste collected in Aurangabad District of Maharashtra state (India). The biowaste waste GPS identified and authenticated by Dr. Anil Bhuktar, Associate Professor and Head of Botany Department, Vivekanand College, Aurangabad (M.S.).

The sample covering (Shell) of Green Peas Shell (Pisum sativum.) were dried in shadow, avoiding direct sunlight on them. The dried material of GPS were grinded into powder separately and were boiled in distilled water and filtered. The residue left of each was divided into five equal portions. One portion was considered as untreated where as Remaining four portions of each were treated with formaldehyde solution first and finally with very dilute solution of sulphuric acid, and sodium hydroxide respectively. All were then stirred for half an hour vigorously using mechanical stirrer at room temperature. Then all were filtered and washed with distilled water repeatedly to remove free acids and alkali.

After chemical treatment all residues were dried first in air and finally in oven at 90-100°C for 8-10 hours and powdered using electric grinder. The homogeneous powder of each was passed through mesh for desired particle size (125-250 µm). The adsorbents once prepared were used throughout the experimental work. The particle size of adsorbents selected for these experiments were on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernatant liquid [11]-[12].

2.1.2. Dye Solution Preparation
Congo Red (CR) (sodium salt of benzidinediazobis-1-naphthyl-amine-4-sulfonic acid) is a benzidine-based Azo dye and it was selected in this study as a model anionic dye because of its complex chemical structure, solubility in aqueous solution and its persistence, once it is discharged into natural environment. It is metabolized to benzidine, a known human carcinogen and exposure to this dye can cause some allergic responses. It mainly occurs in the effluents discharged from textile, paper, printing, leather industries, etc in wastewaters. [11]-[13].

Congo red determined by using UV-Visible spectrophotometer (SL 159) at λmax = 545 nm. The adsorption experiments were carried out in stirred batch mode. For each experiment, 50 ml of CR, dye solution of specified concentration was continuously stirred with 0.2 gm of powder at 303 ± 0.05 K. 12

2.1.3. Adsorption Experiments
Adsorption experiments were carried out by agitating 100 mg of adsorbent with 100 mL of dye solution, of the desired concentration and pH, at different temperatures (393,303,313,323 and 333,) in a thermostated metrex water bath shaker with a shaking of 120 rpm. The samples were withdrawn from the shaker at predetermined time intervals and dye solutions were separated from the adsorbent using Whatmann filter paper [12].

3. RESULTS AND DISCUSSION

3.1 Scanning Electronic Micrographic Studies (SEM)
A scanning electron microscope (SEM) images is widely used to study the morphological features and surface characteristics of the adsorbent material. It also reveals the surface texture and porosity of adsorbent. It also plays an important role in determining the surface availability for the adsorption of dye on adsorbents [14].

Scanning electron microscope (SEM) study shows that the presence of macro-pores on the surface which were irregularly distributed pores which enhance the adsorption of CR dye molecules onto the surface of GPS adsorbent.
3.2. Effect of Contact Time

The removal of dye by adsorption process using GPS was found to be rapid at the initial stage of contact time and then related with increase in contact time of adsorbent and adsorbate then it becomes constant. It may be attributed to the strong binding forces between dye molecules and the adsorbent GPSC which is in good agreement with Dandge et.al [14]. In present study removal of Congo red ranges from 53.657 % (Untreated GPS) to 87.287 % (H₂SO₄ treated GPS).

The mechanism for the removal of dye by adsorption may be attributed to the migration of dye from bulk of the solution to the surface of the adsorbent, Diffusion of dye through the boundary layer to the surface of the adsorbent and Intra-particle diffusion of dye into the interior pores of the adsorbent particle The boundary layer resistance affected by the rate of adsorption and with increase contact time, which will reduce the resistance and increase the mobility of dye during adsorption similar reports are also reported by Rathod et.al. [6]-[13].

3.3. Effect of pH

The pH of a solution is an important factor which controls any adsorption process. The dye binding sites on the surface of the adsorbent are often modified by change in the pH of the solution. Similarly the chemistry and the structure of the dye molecules is also pH dependent [12]. In present study the influence of pH on the time rate study of adsorption, the necessary precaution were taken while adjusting the pH of solution i.e. there was no change in colour appearance of the dye under these extreme conditions [13-14]. Therefore, for the present study as Congo red dyes are acidic dyes, the selection of the pH value were restricted with a conveniently small range 2 to 7. However the selection was based on trial experiments of colour appearance and change in concentration. The Increased solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and biosorbent surface. Generally, the net positive charge decreases with increasing pH value resulting in the decrease in repulsion between the adsorbent surface and the dye, thus improving the biosorption capacity [35]. As the pH increased from 2 to 7, there was increased in adsorption of dyes onto the surface of GPS, ranges from 52.275 % (Untreated GPS) to 93.844 % (H₂SO₄ treated GPS) and have a good support for the results reported by Ubale and others [11]-[15].
3.4. Effect of Temperatures

Temperature also plays an important role on the rate of adsorption. Generally rate is found to be increase with temperature [17]-[19]. For chemisorptions Taylor et.al. [20] described that the increase in rate proceeds exponentially.

In the present investigation the percentage Congo red removal increases with increase in temperature which ranges from minimum of 49.634% onto the surface of Untreated GPS and maximum of 94.446% onto the surface of H$_2$SO$_4$ treated GPS. Increased adsorption may be attributed to the increase in the mobility of the large dye ion with temperature. An increasing number of molecules may acquire sufficient energy to undergo an interaction with active site at the surface [14] and the increase in sorptive uptake of CR with increase in temperature may be partly attributed to chemisorptions [1].

3.5. Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of Congo red by GPS at initial concentration (Co = 65 mg L$^{-1}$) is illustrated in Figure 6. Results describe that CR removal increases up to a certain limit and then it remains almost constant. With increase in the amount of GPS i.e. adsorbent dose from 0.2 to 1.0 g, dye uptake increases from minimum of 58.867 % onto the surface of Untreated GPS) and maximum of 89.926 % onto the surface H$_2$SO$_4$ treated GPS) which may be attributed to increased adsorbent surface area and availability of more adsorption sites [14]-[21].
3.6. Effect of Initial Concentration

The adsorption of dyes onto the surface of GPS is rapid in the beginning, slow down later on and finally reached towards the equilibrium. A large fraction of the total amount of dye is found to be adsorbed within a few minutes of time. Minimum of Congo red adsorbed 44.563% onto the surface of Untreated GPS where as maximum of Congo red adsorbed 94.267 % on to the surface of H_2SO_4 treated GPS. Thus 40-45 % of the total amount of dye is observed to be removed from solution within 20-30 minutes which can be attributed to concentration, surface area, and active sites of the adsorbent were saturated and hence percentage removal decreases with increase in the concentration of Congo red [1]. The increase adsorption of the adsorbate onto adsorbent may be due to increase in surface activity and due to micelle formation or the aggregation of dye molecule in the concentration range studied. Similar results have also been reported by several workers [6].

Saiful et.al. [22] during their adsorption study of removal of dye from aqueous solution by using sugar bagasse reported that with increase in the concentration of dye solution, there was a decrease in percentage removal of dye even though the amount of dye adsorbed increased, the reported findings are in good agreement with our findings [6]-[14].

![Figure 4](image.png)

**Figure 4** Effect of initial concentration

3.7. Adsorption Isotherm

The equilibrium nature of adsorption can be described by various isotherm equations such as Langmuir, Freundlich Isotherm. These isotherms are empirical equation employed to describe heterogeneous system. Freundlich isotherm can be applied to plot the equilibrium data of the adsorption1. Freundlich [23] suggested that the ratios of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution are not constant at different concentration of solutions. If q_e is the amount of solute adsorbed mg per gram of adsorbent and C_e is the equilibrium concentration in the solution, the empirical relation is;

\[
\frac{X}{m} = q_e = K_f C_e^{1/n}
\]

Where,

- \( K_f \) = rough measure of adsorption capacity (intensity of adsorption)
- \( n \) = empirical constant.

The linear form of the equation is;

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]
The values of $K_F$ and $1/n$ are calculated from the intercept and slope of the plot of $\log q_e$ vs. $\log C_e$ respectively. The Freundlich isotherm was verified by using least square fit and regression analysis and computer programming in EXCEL. The value of regression co-efficient $r^2$ was calculated and the value found to be very close to 1.0 which indicates that good correlation exists, between $\log x/m$ and $\log C$.

3.8. Langmuir Isotherms

The Langmuir model [24] represents monolayer adsorption on a set of distinct localized adsorption sites having the same adsorption energies no interaction between adsorbed molecules. The plot yield a straight line for all the organics investigated, indicating that the Langmuir sorption model is followed by the sorption data very well. The values of maximum adsorption capacity calculated from the slopes of the linear plots whereas the values of enthalpy of adsorption (b) estimated from the intercepts of the plot. Hussain et.al. [25] during their adsorption study of organic acid on to the surface of chemically processed animal charcoal reported the data obtained during findings was fitted for Langmuir Isotherm and found to be linear indicative of applicability of Langmuir equation.

The essential characteristic of the Langmuir isotherm is expressed in terms of dimensionless constant separation factor or equilibrium factor $R_L$

$$R_L = \frac{1}{1 + bC_e}$$

This parameters indicates the nature of the isotherm as under,

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Type of Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
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The adsorption of Congo red is favorable onto the surface of GPSC as the $R_L$ value in the present study falls in the type $0 < R_L < 1$ and the range found to 0.009 to 0.010 and are in good agreement with findings of Lodha et.al[26]

3.9. Thermodynamic Properties

The adsorption isotherm data obtained at different temperatures were used to calculate important thermodynamic parameters such as changes in Gibbs free energy $\Delta G$, enthalpy change $\Delta H$, and entropy change $\Delta S$. The adsorption enthalpy ($\Delta H$) ranges between 6.970 to 8.075 in our findings for GPSC system found to negative indicative of exothermic process, $\Delta G$ decreases from -1.5 KJ to -14.562KJ/mole with increase in temperature from 293°C to 333 K. The negative value of $\Delta G$ indicates that the adsorption process is favorable and spontaneous in nature. The positive $\Delta S$ value which ranges between 28.670 to 74.907 is indicative of randomness at the adsorbent –adsorbate interface (GPSC-Congo red).

Our finding is in good agreement with the findings of Sivakumar et.al. [27]. The positive value of $\Delta S$ indicates increase in the randomness in the system [6]. The negative values of $\Delta G$ indicate the feasibility and spontaneity of the adsorption process. The $\Delta G$ value becomes more negative with increasing temperature supports that CR adsorption on GPSC is favored with the increase in temperature.

4. CONCLUSION

i. The adsorption of dye Congo red was examined at different experimental conditions. The results corroborate that adsorption increases with increase in temperatures, adsorbent dose, pH contact time and initial concentration of Congo red.

ii. The maximum adsorption capacity increases with increase in temperature and was found to be 87.481 % and 94.446 % for GPS at 293 K to 333 K.
iii. Equilibrium data fitted very well in a Langmuir and Freundlich isotherms equation, confirming the adsorption capacity of Dyes (Congo Red,) onto the surface of adsorbents GPS with a monolayer adsorption and intensity of adsorption, these isotherms model confirmed that adsorption of Dyes (Congo Red) is favorable

iv. The Freundlich isotherm was verified by using least square fit and regression analysis and computer programming in EXCEL. The value of regression co-efficient r² found to be very close to 1.0 which indicates that good correlation exists, between log x/m and log C

v. The adsorption of Congo red is favorable onto the surface of GPS as the RL value in the present study falls in the type 0 < RL < 1 and the range found to 0.009 to 0.010.

vi. Adsorption is favored at high temperature for GPS adsorbents is also evident by the high values of various constants at high temperature, for example, Freundlich constant, (adsorption capacity), Langmuir constant (affinity to binding sites), (monolayer concentration).

vii. The negative value of change in Gibb’s free energy implied that the reaction is spontaneous in nature, and values are more negative with temperature intimating that adsorption is favored with increase in temperature.

viii. The values also approve that biosorbents GPS can be used favorably for the adsorption of dye CR. The present research work established that GPS is an excellent low-cost bioadsorbents for the removal of dye Congo red and can be further explored for the design of an adsorbent for industrial effluents treatment.

References


AUTHOR

Dr. Milind Baburao Ubale presently working as Principal, Professor and Head, Research Centre of Chemistry, Vasantrao Naik Mahavidyalaya, Aurangabad. He completed his Post graduation from Dr. Babasaheb Ambedkar Marathwada University, Aurangabad and obtained PhD degree from same university in 1995. He has recipient of Adarsh Shikshak-2001 of Lions Club, Bharat Ratan Siksha Award, Global Society, New Delhi in 2011 and Rajeev Gandhi Excellence Award in 2013. He has twice elected among heads as Member, Board of Studies in Chemistry. Till date under his guidance Nine Students have been awarded with PhD degree and one student have submitted thesis for PhD and five students with M.Phil degree of Algappa University, Kairaikudi. In the field of Surface Chemistry, Biologically active heterocyclic chemistry he has published more than 140 papers in reputed Journals and still counting.He Chaired scientific/Technical session of National and International Conferences and attended fifty State, National and International Conferences/ Seminars/ Symposia and has the experience of Organizing Regional Workshop in 2005 and National Seminar in 2006, 2012 and recently one day seminar of ACTRA. He is Reviewer of fourteen reputed journal and editorial board member of twelve different National and International journals