Kinetics and Isotherm of Sunset Yellow Dye Adsorption on Cadmium Sulfide Nanoparticle Loaded on Activated Carbon

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Abstract: The objective of this study was to assess the potential of cadmium sulfide nanoparticles loaded onto activated carbon (CdSN-AC) for the removal of sunset yellow (SY) dye from aqueous solution. Adsorption studies were conducted in a batch mode varying solution pH, contact time, initial dye concentration, CdSN-AC dose. In order to investigate the efficiency of SY adsorption on CdSN-AC, pseudo-first-order, pseudo-second-order kinetic models were studied. It was observed that the pseudo-second-order kinetic model fits better than other kinetic models with good correlation coefficient. Equilibrium data were fitted to the Langmuir model. It was found that the sorption of SY onto CdSN-AC is followed by these results.

Keywords: Adsorption; Sunset yellow dye; CdS nanoparticle; Activated carbon; Adsorption isotherm; Kinetic of adsorption

INTRODUCTION

The dyeing effluent discharged from textile industries is one of the largest contributors to textile effluent and is comprised mainly of residual dyes and auxiliary chemicals (Blackburn, 2004). Dyeing effluent has a serious environmental impact because disposal of this effluent into the receiving water body damages aquatic biota or humans by mutagenic and carcinogenic effects (Crini, 2006). Such colored effluent can affect photosynthetic processes of aquatic plants, reducing oxygen levels in water and, in severe cases, resulting in the suffocation of aquatic flora and fauna (Hu & Wu, 2001; Cheung et al., 2009). Treatment of effluent containing synthetic dyestuffs is very difficult, since the dyes are stable in conditions of light and heat, the presence of oxidizing agents and are resistant to aerobic digestion (Sun and Yang, 2003; Yee and Chin, 2005; Chatterjee et al., 2009).

Because of the low biodegradability of dyes, the conventional biological wastewater treatment processes were not efficient in the treatment of dyes contaminated wastewater (Mondal, 2008). Therefore, dyes wastewater was usually treated by physical and/or chemical methods, such as coagulation and flocculation (Zonoozi et al., 2009), membrane separation (Sachdevaand Kumar, 2009), activated carbon adsorption (Tan et al., 2008), electrochemical removal (Gupta et al., 2007a), and photochemical degradation (Gupta 2007b). However, for the developing countries, these methods are still too expensive to be used widely. Developing economical adsorbents to treat dyes wastewater has attracted great interest in recent years (KavithaandNamasiyam, 2007; Hua et al., 2010). Azo dyes are characterized by the presence of one or more –N=N–(azo) bonds and used in products such as textile, leather and foodstuffs (Engel, 2008).
Sunset yellow dye is one of azo dyes that are added to a wide range of products such as jam, jelly, jams, soup and sauces. It should be avoided by anyone suffering from existing allergic conditions, such as asthma or urticaria and a child who has signs of hyperactivity of ADHD. Disposal of untreated effluent to the surroundings often leads to the following consequences (a) makes the water bodies colored and creates aesthetic problem (b) limits the reoxygenation capacity of the receiving water and cuts-off sunlight which in turn disturbs the photosynthetic activities in the aquatic system and (c) causes chronic and acute toxicity. Thus it is mandatory to treat dye bath effluents prior to discharge into the surrounding aquatic systems. (Wood and Roger, 2004). There are many processes to remove SY molecules from colored effluents and the treatment methods can be divided into three categories: (1) physical methods such as adsorption (Namashivayam and Kavitha, 2002; Mall et al., 2005; Chatterjee et al., 2009); (2) chemical methods such as ozonation (Gharbani et al., 2008; Khadhraoui et al., 2009), photo degradation (Wahi et al., 2005) and electrochemical process (Elahmadi et al., 2009); and (3) biodegradation (Gopinath et al., 2009). Adsorption techniques have potential for removing organics from water due to their high efficiency and ability to separate a wide range of chemical compounds (Slejko, 1985; Suffet and McGuire, 1985; Jain and Sikarwar, 2008; Sari and Tuzen, 2008; Ulusoy et al., 2010). Nanoparticles have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area. It is a common behavior that nano particles would easily aggregate because of the magnetic property of nano particles themselves, so most of the particles exist in chain-like aggregates (Arami et al., 2005; Ardejani et al., 2007). The objective of the present work is to investigate the potential feasibility of CdsN-AC for the adsorption of Sunset Yellow (Fig. 1). The kinetic and equilibrium data were analyzed so that we can understand the adsorption mechanism and different models were applied to fit the experimental data.

![Chemical structure of sunset yellow](image)

**Fig. 1 Chemical structure of sunset yellow**

**EXPERIMENTAL**

**Chemical and apparatus**

All chemicals including NaOH, HCl and KCl with the highest purity available were purchased from Merck, Dermasdat, Germany.

Stock SY solution was prepared by dissolving its appropriate amount in double distilled water and the test solutions were prepared by diluting stock solution to the desired concentrations, while its concentration was determined at 417 nm. The pH measurements were done using pH/Ion meter model-686, and absorption measurements were carried out using Jusco UV-Visible
spectrophotometer model V-570 using a quartz cell with an optical path of 1 cm. A Hitachi H-800 TEM at an operating voltage of 200 kV determined the morphology and electron diffraction pattern of the Cds nanoparticles.

Preparation of sorbent

Cadmium sulfide nanoparticle loaded on activated carbon was produced by cadmium chloride, sodium hydroxide and hydrogen sulfide. This aqueous solution 0.01 M cadmium chloride (20 ml) and 0.01 M sodium hydroxide (100 ml) was prepared separately. Sodium hydroxide solution was slowly added to methanol and hydrogen sulfide gas was additional. Solution was stirred for one hour before the addition of cadmium chloride. After 3h stirring the yellow solution was obtained. The non-selective deposition was performed using acetone as solvent. The sediment was then evaporated at room temperature; cadmium sulfide nano-particle was obtained to form an orange powder.

Preparation of aqueous dye solutions

The concentrations of dye in solution were estimated quantitatively using the linear regression equations obtained by plotting its calibration curve over SY concentrations. The efficiency of SY removal was determined at certain time intervals in the range of 0-35 min and the equilibrium was established after 15 min. The effect of pH on SY adsorption was studied by adjusting pH of dye solutions (25 mg L⁻¹) in the pH range of 2–6 using 0.03 g L⁻¹ of Cdsn-AC, while the initial pH of solution was adjusted by addition of HCl or NaOH. Dye adsorption experiments were also accomplished to obtain isotherms in the range of 10-70 mg L⁻¹ SY concentration.

The amount of dye adsorbed on adsorbent (qe (mg g⁻¹)) was calculated by the following mass balance relationship:

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

where \( C_0 \) (mg L⁻¹) and \( C_e \) (mg L⁻¹) are the initial and equilibrium dye concentrations in solution, respectively, \( V \) the volume of the solution (L) and \( W \) is the mass (g) of the adsorbent.

Determination of the zero point charge pH

The pH corresponding to the point of zero charge, pHZPC for this new solid phase was determined by the final pH drift method previously reported elsewhere. The pH was adjusted to initial values between 2 and 6 by adding HCl or NaOH and the pHZPC of Cdsn-AC used for the adsorption experiment is determined by using solid to liquid ratio of 1:1000. For this, 0.03 g of Cdsn-AC is added to 50 mL of dye solution with varying pH from 2 to 6 and stirred for 15 min. The difference between the final pH and initial pH of the solution is plotted against the initial pH of the solution. The surface of the material was neutral when aqueous solution pH was equal to zero point charge pH. The surface was negatively charged at pH values greater than zero point charge pH, and positively was charged at pH values lower than pHzpc (Kiefer et al., 1997; Nandi et al., 2009).

RESULTS AND DISCUSSIONS

Characterization of adsorbent

The Cds nanoparticles solution showed a well-resolved absorption maximum of the first electronic transition indicating a sufficiently narrow size distribution of the Cds nanoparticles, which shifts to the shorter wavelengths with decreasing size of the nanoparticles as a consequence of the quantum confinement. Fig. 2 shows a TEM image of the Cds nanoparticles, the characteristic Cds nanoparticles are observed with a relatively narrow particle size distribution (12-50 nm range)
Ion into the bulk of the adsorbent. It was found that more than 80% of removal of SY occurred in the first 7.5 min and thereafter the rate of adsorption was found to be slow till up 90% at 15 min.

Effect of pH

The wastewater from textile industries usually has a wide range of pH values. Thus pH of the system plays an important role in the textile waste treatment. The value of pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of initial pH on the adsorption of SY was studied in the pH range of 2 to 6 at room temperature at initial dye concentration of 15 mg L⁻¹, adsorbent dose of 0.02 g and contact time of 15 min and respective results are presented in (Fig. 4a).

As it can be seen, the maximum uptake of the SY is obtained at pH of 3.0. It was observed, that the pH significantly affects the extent of adsorption of dye over the adsorbent and a decrease in the adsorption efficiency further this value was observed. At lower pH, probably surface of CdSN-AC has positive charge (protonation of functional group of CdSN-AC in highly acidic solution) which favors the adsorption of SY over CdSN-AC and lead to increase in adsorption. The pHZPC of CdSN-AC used for the adsorption experiment is determined as pH 2.0 and 6.0 (Fig. 4b).
Effect of adsorbent dosage

One of the most critical parameter for rapid and efficient dye removal is size and amount of adsorbent which must be optimized. The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. The effect of adsorbent dose on the dye removal percentage is shown in Fig. 5. It was observed that initially the removal percentage increased rapidly with the increase in adsorbent dose till 0.03 g and after the critical dose the removal percentage almost reached a constant value. This can be attributed to increased adsorbent surface area and availability of more adsorption sites with the increasing dosage of the adsorbent, while the adsorption density of dye decreased with increase in adsorbent dosage. Therefore, for subsequent work 0.03 g of CdSN-AC has been selected.

Figure 5. Effect of CdSN-AC dosage on SY removal at dye concentration of 15 mg L\(^{-1}\), at pH 3 and room temperature.

Effect of initial dye concentration on adsorption of SY

Effect of SY initial concentration on the efficiency of its adsorption was investigated in range of 10 to 70 mg L\(^{-1}\) and results are shown in Fig. 6.
It was seen that the SY adsorption efficiency increased with increase in its concentration and tended to attain saturation at higher concentrations. Although, by increasing the initial dye concentration the percentage of dye removal decreased, the actual amount of dye adsorbed per unit mass of CdSN-AC increased. In the process, the SY molecules had to first encounter the boundary layer effect and then diffused from boundary layer film onto adsorbent surface and finally diffused into the porous structure of the adsorbent that took relatively longer contact time. On the other hand, the percentage removal of dye was higher at lower initial dye concentrations and smaller at higher initial concentrations, which clearly indicated that the adsorption of SY from its aqueous solution was dependent on its initial concentration. For subsequent analysis the initial concentration of SY was adjust at 25 mg L⁻¹.

**Adsorption equilibrium study**

Adsorption isotherms are prerequisites to understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants. Successful application of the adsorption technique demands studies based on various adsorption isotherm models (Mittal et al., 2009) because adsorption isotherm models clearly depict the relationship of amount adsorbed by a unit weight of adsorbent with the concentration of adsorbent remaining in the medium at equilibrium. There are many equations for analyzing experimental adsorption equilibrium data. The equation parameters of these equilibrium models often provide some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent for adsorbate.

The parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and the two important isotherms, the Langmuir, Freundlich isotherms are applied in this study. Langmuir isotherm: The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature. The Langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites with negligible interaction between adsorbed molecules, is represented in the linear form as follows (Langmuir, 1916; Amin, 2009):

\[ \frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \]  

Where \( K_L \) is the Langmuir adsorption constant (L mg⁻¹) and \( Q_m \) is the theoretical maximum adsorption capacity (mg g⁻¹). The value of \( Q_m \) and KL constant obtained by the Langmuir plots (\( C_e/q_e \) vs. \( C_e \)) that these values and the correlation coefficient of this model is presented in Table 1. The isotherms of SY on CdSN-AC was found to be linear over the whole concentration range studies and the correlation coefficients were extremely high (R²>0.99) as shown in Table 1 and fig 7a and 7b.

Freundlich isotherm: The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of sorption heat over the surface was presented in the linear form as follows (Freundlich, 1906):

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

Where \( K_F \) (mg g⁻¹)/(mgL⁻¹)⁻¹ is the Freundlich constant related to the bonding energy and can be defined as the adsorption or distribution
coefficient and represents the quantity of dye adsorbed onto adsorbent. The \( 1/n_f \) factor is heterogeneity factor and \( n_f \) is a measure of the deviation from linearity of adsorption, which its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of \( n=1 \), the adsorption is linear; \( n<1 \), the adsorption process is chemical; if \( n>1 \), the adsorption is a favorable physical process (Crini et al., 2007). Slope and intercept plot of \( \log(q_e) \) versus \( \log(C_0) \) indicate the value of \( K_f \) and the slope of \( 1/n_f \) (Table 1). As it can be seen, Freundlich is an unsuitable model for interpreting whole isotherm interpretation.

Table 1. Isotherm parameters and correlation coefficients calculated by various adsorption models onto 0.03 g of CdsN-AC, pH 3, and room temperature.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.973</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td>( K_w )</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>( Q_m )</td>
<td>83.33</td>
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<tr>
<td></td>
<td>( 1/n )</td>
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<tr>
<td>Freundlich isotherm</td>
<td>( K_f )</td>
<td>9.54</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.943</td>
</tr>
</tbody>
</table>

**Kinetic study**

The rate as well as mechanism of adsorption process can be elucidated on the basis of kinetic study (Rengaraj et al., 2004; Anayurt et al., 2009). Dye adsorption on solid surface may be explained by two distinct mechanisms; (i) an initial rapid binding of dye molecules on the adsorbent surface followed by (ii) relatively slow intra-particle diffusion. The adsorption kinetic data were described by the Lagergren pseudo-first-order model that is the earliest known equation describing the adsorption rate based on the adsorption capacity. The Lagergren equation is commonly expressed as follows (Sari, 2008):

\[
dq/dt = k_1 (q_e - q_t)
\]

where \( q_e \) and \( q_t \) are the adsorption capacity at equilibrium and at time \( t \), respectively (mg g\(^{-1}\)), \( k_1 \) is the rate constant of pseudo-first order adsorption (1 min\(^{-1}\)). Integrating Eq. (4) for the boundary conditions \( t=0 \) to \( t = t \) and \( q_t=0 \) to \( q_t=q_e \) gives:

\[
\log(q_e/q_t) = (k_1/2.303) t
\]  

Eq. (5) can be rearranged to obtain the following linear form:

\[
\log(q_e - q_t) = \log(q_e) - (k_1/2.303) t.
\]  

By plotting the values of \( \log(q_e - q_t) \) versus to give a linear relationship from which \( k_1 \) and \( q_e \) can be determined from the slope and intercept (Table 2). If the intercept dose not equal \( q_e \) then the reaction is not likely to be first-order reaction even this plot has high correlation coefficient. The variation in the rate of adsorption should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. Experimental data show high degree of nonlinearity and poor correlation coefficients for pseudo first-order model.

The adsorption kinetic may be described by the pseudosecond order model (Lagergren, 1898), which is generally given as following:

\[
dq/dt = k_2 (q_e - q_t)^2,
\]  

Where \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the second-order constant of adsorption. Integrating Eq. (7) for the boundary conditions \( q_t=0 \) to \( q_t=q_e \) at \( t=0 \) to \( t = t \) is simplified as can be rearranged and linearized to obtain:

\[
(t/q_t) = 1/k_2 q_e^2 + 1/q_e t.
\]
The second-order rate constants were used to calculate the initial sorption rate, given by the following Eq.:

\[ h = k q_e^2. \]  

(9)

It was mentioned above that the curve fitting plots of \( \log q_e - t \) versus \( t \) (Table 2) do not show good results for the entire sorption period, while the plots of \( t/q_e \) versus \( t \) give a straight line confirming the applicability of the pseudo-second-order equation. Values of \( k_2 \) and equilibrium adsorption capacity \( q_e \) were calculated from the intercept and slope of the plots of \( t/q_e \) versus \( t \), respectively. The values of \( R^2 \) and \( q_e \) also indicated that this equation produced better results (Table 2) and (fig.8a and 8b) \( R^2 \) values for pseudo-second-order kinetic model were found to be high (0.993), and the calculated \( q_e \) values are mainly near to the experimental data. This indicates that the SY –CdSN-AC adsorption system obeys the pseudo-second-order kinetic model for the entire sorption period. Transportation of the dyes from the solution phase into the pores of the adsorbent may also be considered as the rate controlling stage in batch experiments under rapid stirring condition.

Table 2. Adsorption kinetic parameters at different initial SY onto CdSN-AC in 50 ml at pH3, room temperature and SY concentration of 25 mg L⁻¹

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Value</th>
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</thead>
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<td>Pseudo-first-</td>
<td>( K_1 )</td>
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<tr>
<td>order</td>
<td>( q_{cal} )</td>
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<tr>
<td></td>
<td>( R^2 )</td>
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<tr>
<td>Pseudo-first-</td>
<td>( K_2 )</td>
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</tr>
<tr>
<td>order</td>
<td>( q_{cal} )</td>
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</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>( Q_{exp} )</td>
<td>32.00</td>
</tr>
</tbody>
</table>

Figure 7: a) langmuir isotherm for SY uptake by CdSN-AC, pH 3 and room temperature, b) freundlich isotherm for SY uptake by CdSN-AC pH 3 and room temperature.

Fig. 8 a) Pseudo-first-order kinetic plot for the adsorption of SY onto CdS nanoparticle initial SY concentration = 25 mg L⁻¹, CdS-AC dose =0.03g, pH 3.0, at room temperature. b) Pseudo-second-order kinetic plot for the adsorption of SY onto Cadmium sulfide nanoparticle initial SY concentration = 25 mg L⁻¹, CdS-AC dose =0.03 g, pH 3.0, at room temperature.

CONCLUSIONS

The cadmium sulfide nanoparticle loaded activated carbon was identified to be an effective adsorbent for the removal of SY from aqueous solutions. It was observed that batch sorption using CdSN-AC was dependent on parameters such as initial
concentration of dye, time, pH, dose of adsorbent and type of dye. The equilibrium and kinetic studies were made for the adsorption of dyes from aqueous solutions onto SY. Adsorption parameters for the Langmuir, Freundlich isotherms were determined and the equilibrium data were best described by the Langmuir model. Its kinetics can be successfully fitted to pseudo-second-order kinetic model.

REFERENCES


