Film-pore diffusion modeling for sorption of azo dye on to exfoliated graphitic nanoplatelets

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Exfoliated graphitic nanoplatelets (xGnPs) have been utilized as a potential adsorbent for toxic textile dye Acid Orange 7 (acid dye). The effects of major variables governing the efficiency of the process, such as temperature, initial dye concentration and pH are studied. The kinetic measurements have been used for determining the specific rate constant, confirming the applicability of pseudo first-order rate expression. Plausible mechanism of ongoing adsorption process involved is obtained by carrying out kinetic measurements. To identify whether the ongoing process is particle diffusion or film diffusion, the treatments given by Boyd and Reichenberg have been employed. The influence of different factors on the adsorption of Acid Orange 7 from solution is explained in terms of electrostatic interaction by considering the dye species and the surface character of the xGnPs. The developed system for the removal of acid dye is found to be very useful, economic, rapid and reproducible.

Keywords: Acid Orange 7, Adsorption, Film diffusion, Graphitic Nanoplatelets, Particle diffusion

The adverse effects of discharge of organic pollutants of dyeing industry waste on health have been already proved. Textile effluents are known toxicants, which inflict acute disorders in aquatic organisms. Uptake of textile effluents through food chain in aquatic organisms may cause various physiological disorders like hypertension, sporadic fever, renal damage and cramps¹. The release of colored waste water into the eco-system is a dramatic source of the aesthetic pollution, eutrophication and perturbation in aquatic life.

Brightly coloured and water soluble acid dyes, being sodium salts of organic sulphonic acids, are composed of ionisable anionic groups such as sulphonates, carboxylates or sulphates. They have direct affinity for polyamide and protein in an acidic bath and hence are commonly used for dying polyamide, as well as nylon, silk, wool and modified acrylics; also used to some extent for paper, leather and cosmetics. Acid dyes with higher molecular weight are one of the most problematic groups of dyes which tend to pass through conventional treatment system unaffected. Various physical and chemical methods of treatment of industrial waste water have been suggested. These include adsorption method, coagulation process, photo catalytic degradation and hypo chloride treatment of dye waste effluents²-⁴. Among these approaches, adsorption is regarded as an easy and economic process. This is attributed to its easy availability, simplicity of design, ease of operation, various materials, such as commercial activated carbon, natural materials, bio adsorbents and wastes from agriculture, have been used for such processes⁵.

The rapid development in nanotechnology sheds light on the waste water treatment. Nano materials have been studied for the adsorptions of metal ions⁶, dyes⁷, and antibiotics⁸. Exfoliated graphitic nanoplatelets (xGnPs) and graphite nano sheets⁹ have been successfully utilized as sorbents to extract oils⁹ and dyes¹⁰ from their aqueous solutions. In the present work, exfoliated graphitic nanoplatelets (xGnPs) have been used as an adsorbent for Acid Orange 7 (AO7) removals and the adsorption capacity of xGnPs is regulated by many influencing factors, such as temperature, pH variations and initial dye concentrations.

Experimental Procedure

xGnPs (with average diameter of 15 µm and average length of <0.01 µm) were procured from xG Sciences Inc., USA. Detailed information on fabrication, geometrical and surface characteristics

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of this material is already available. The textile dye (AO7) was purchased from Sigma - Aldrich (Germany), and characterization of the dye are summarized in Table 1. All the chemicals used were obtained as research grade chemicals and used without purification.

Characterization

Morphological structure of as-received xGnPs was characterized by the scanning electron microscopy. The sample was directly coated on the conductive surface and SEM images were obtained with a field-emission scanning electron microscope (FESEM, JEOL JSM-6700F). BET measurements were performed by using ASAP 2020 volumetric adsorption analyzer (Micrometrics, USA). The surface functional groups on the adsorbents were quantitatively measured by Boehm’s titration method. The Boehm titration is based on the principle that oxygen groups on graphite surface have different acidifies being neutralized by bases of different strengths. In our procedure, 20 mg of xGnPs (as-received) were stirred in 10 mL of 0.05 M base solution (NaOH, Na₂CO₃, and NaHCO₃), aqueous solution under Ar for 48 h, (in order to equilibrate with the NaHCO₃ solution). The mixtures were filtered (on 0.20 µm pore size membrane filters), 10 mL volume from each mixture being further titrated with 0.05 M hydrochloric acid. Three samples of each base solution were titrated; a blank sample without xGnPs is being titrated with the same procedure. NaOH solution neutralizes all acidic sites (carboxyl, lactonic and phenols) from the surface of xGnPs; NaHCO₃ neutralizes only carboxyl groups, Na₂CO₃ reacts with carboxyl, lactonic groups. The quantity of the possible surface groups is estimated through the difference between the calculated amount of surface functionality. The pH of the point of zero charge (pHpzc) was determined using the pH drift method. The Acid Orange 7 dye was used without purification. The characteristics of dye are shown below:

Batch adsorption studies were carried out in 250 mL tight lid glass bottle (Borosil R). Standard stock solution (1000 mg/L) containing Acid Orange 7 was prepared by dissolving appropriate amount of it in water. 50 mg of adsorbent was added to 100 mL of aqueous dye solution, initial concentration of AO7 ranging from 20 mg/L to 60 mg/L. The contents of the flasks were agitated by placing them in temperature controlled orbital shaker. The mixture was withdrawn at specified intervals then centrifuged using electrical centrifuge (universal make) at 3000 rpm for 10 min and un adsorbed supernatant liquid was analyzed for residual dye concentration using Elico make Bio UV-Visible spectrometer (BL-198) at a wave length of 484 nm. All the experiments were conducted in duplicate and mean of the two values were taken for calculation. Maximum deviation is 4%. The amount of AO7 adsorbed in mg/L at time t was computed by using the following equation:

\[ q_t = \frac{C_0 - C_t}{m_s} \times V \] ...

where \(C_0\) and \(C_t\) are the AO7 concentration in mg/L initially and at a given time t respectively; \(V\), the volume of the AO7 solutions in mL; and \(m_s\), the weight of the xGnPs. The removed AO7 (%) in solution was calculated using the following equation:

\[ \% \text{ Removal} = \frac{C_0 - C_t}{C_0} \times 100 \] ...

Adsorption dynamics and equilibrium studies

The study of adsorption dynamics describes the solute uptake rate, and evidently this rate controls the residence time of adsorbate uptake at the solid-

<table>
<thead>
<tr>
<th>Concentration mg/L</th>
<th>Pseudo first-order values</th>
<th>Elovich values</th>
<th>Pseudo second-order values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_{Lang} \times 10^2 \min^{-1} )</td>
<td>( R^2 )</td>
<td>( \alpha ) mg/g min</td>
</tr>
<tr>
<td>20</td>
<td>1.7306</td>
<td>0.986</td>
<td>0.869</td>
</tr>
<tr>
<td>40</td>
<td>1.7186</td>
<td>0.982</td>
<td>0.768</td>
</tr>
<tr>
<td>60</td>
<td>1.7094</td>
<td>0.985</td>
<td>0.667</td>
</tr>
</tbody>
</table>
solution interface. The kinetics models of AO7 adsorption on the xGnPs were analyzed using pseudo first-order\(^1\), pseudo second-order\(^2\), kinetic models and Elovich equation\(^3\). The isotherm models of AO7 adsorption on the xGnPs were analyzed using Langmuir and Freundlich equation\(^4\).

### Results and Discussion

#### Characterization of xGnPs

The dye adsorption on xGnPs depends on many factors, such as surface functional groups, specific surface area and composition of the solution, the most important factor being the surface area. BET surface area measurement of xGnPs asserts the large hysteresis area of N\(_2\) adsorption-desorption isotherm (Fig.1), suggesting the wide distribution of pores. The specific surface area of xGnPs calculated using BET equation is found to be 112.67 m\(^2\)/g. Large hysteresis area indicates a near uniform distribution of pores and large surface area of xGnPs, suggesting the high quality of graphene sheets. The SEM image reveals that the flat surface of xGnPs is homogeneous (Fig. 2), the property being responsible for this selectivity. The large layer of carbon containing delocalized \(\pi\) electrons can explain the different retention mechanisms such as electron transfer, ion-pairing and hydrophobic interaction. The surface area and \(pH_{pzc}\) are consistent with the literature\(^5\). The properties of xGnPs specific surface area (\(S_{BET}\)), \(pH_{pzc}\), carboxylic acid, lactone groups, and phenolic groups values are 112.67 m\(^2\) g\(^{-1}\), 8.1, 0.25 meq g\(^{-1}\) 0.48 meq g\(^{-1}\) and 0.36 meq g\(^{-1}\) respectively.

#### Effect of \(pH\)

The \(pH\) value of the solution being an important controlling parameter in adsorption is mainly influenced by the two factors, namely (i) distribution of the dye ionized species in the solution phase, and (ii) overall charge of the adsorbent. Therefore, the interaction between dye molecule and adsorbent is basically a combined result of charges on the dye molecules and the surface of the adsorbent\(^6\). The effect of \(pH\) on the adsorption of AO7 by as-received xGnPs has been evaluated in \(pH\) range 2-11. Which reveals that the removal of dye slightly decreases, when the \(pH\) is increased from 2-4 and then remain almost constant up to \(pH\) 8. A large decrease in adsorption capacity for this dye is observed as the \(pH\) approaches \(pKa\) of AO7 under basic condition. When the solution \(pH\) is above the \(pKa\) of dye (\(pKa\) for AO7 is 8.86), the adsorption decreases due to the electrostatic repulsion between dissociated adsorbate and adsorbent surface. Below the isoelectric point (\(pH_{pzc}\) of the xGnPs is 8.1), surface of adsorbent may acquire positive charge leading to an increased anionic dye adsorption due to electrostatic attraction\(^7\).

#### Effect of initial concentration of dye solution

The initial concentration of AO7 solution was varied (20 40 and 60 ppm) and batch adsorption experiments were carried out with 100 mg of the adsorbent at 30°C and \(pH\) 7. An increased percentage removal of AO7 from 75 to 90 is observed with 100 mg of the adsorbent, when the initial concentration of the AO7 solution is increased from 20 ppm. The higher uptake of AO7 at low concentration may be attributed to the availability of more active centers on the surface of the adsorbent for lesser number of adsorbate species.
Effect of temperature

Temperature influences the AO7 adsorption properties on xGnPs. The temperature effect on the sorption capacity of xGnPs was examined at 30, 45 and 60°C using initial dye concentration of 20 mg/L at pH 7. The adsorption capacity of the xGnPs increases with decreasing temperatures from 60°C to 30°C, which indicates that the adsorption process is exothermic. The optimum temperature for dye adsorption of the adsorbent, within the temperature range studied, is found to be 30°C.

Kinetic modeling

Pseudo first-order model

Figure 3 shows a plot of pseudo first-order equation for the results of adsorption of AO7 from 20 mg/L to 60 mg/L between log \((q_e - q_t)\) and agitation time over whole sorption period with high correlation coefficient (>0.986) for all the lines (Table 1). It is clear that the pseudo first-order equation may be used to describe the kinetics of sorption of AO7 on to xGnPs. Although the pseudo first-order equation does not provide any mechanistic evidence, it has been proved suitable for highly heterogeneous systems of which the adsorption of AO7 onto xGnPs is undoubtedly such a case.

Elovich model

The results of the sorption of AO7 on to xGnPs have been represented in the form of Elovich equation in Fig. 4 at various initial dye concentrations (20, 40, and 60 mg/L). From the plot a linear relationship between the amount of AO7 adsorbed, \(qt\) and \(\ln(t)\) are established. These plots show different distinct linear regions within individual sets of data. In these cases, it is thus necessary to perform multiple regressions on different ranges of the data. The kinetics could not be approximated using Elovich model.

Pseudo second-order model

The same data are shown as pseudo second-order equations in Fig. 5. These plots show that the data fits has good correlation coefficients (>0.962) when the pseudo second-order equation is employed. It is possible to ascertain from them whether the rate determining process is a chemical reaction. Thus, increasing the initial dye concentration from 20 mg/L to 60 mg/L, the AO7 sorbed at any contact time increases. This is obvious for higher initial concentration values, as a more efficient utilization of the sorption capacities of the adsorbent would be expected due to greater sorption driving force.

Isothermal modeling

The Langmuir adsorption isotherm obtained in 160 min of agitation time is shown in Fig. 6.
The values of $R_L$ obtained in this study lie within the range 0.127-0.151 indicating the favorable case of adsorption for the present adsorbent-adsorbate system. The Freundlich adsorption isotherm obtained in 160 min of agitation is shown in Fig. 7. The values of absorption intensity $1/n << 1$ reveal the applicability of the Freundlich adsorption isotherm in Fig. 7. The values of $1/n$ and $k_f$ are given in the Table 2. The study of temperature effects on the Freundlich parameters reveals a decreasing trend in the adsorption capacity with increase in temperature. However, the variation in the adsorption intensity is negligible. These data are useful for practical design purposes. Langmuir adsorption isotherm provides a best-fit description for the sorption of AO7 on to xGnPs relative to Freundlich isotherm model.

Table 3 shows the adsorption capacity of some of the adsorbents used for the adsorption of Acid Orange 7. It is observed that the adsorption capacity of exfoliated graphitic nanoplatelets is comparatively good when compared with some of the adsorbents already reported in the literature for the adsorption of Acid Orange 7 in aqueous solution. The differences in maximum adsorption efficiencies of various sorbents might be due to different structures and sorption mechanisms of various sorbents and experimental conditions.

**Mechanism for sorption of AO7 onto xGnPs**

Because of the high correlation coefficients obtained using pseudo first-order, pseudo second-order and Elovich kinetic models, it is impossible to conclude which adsorption mechanism actually occur and is responsible for the ability of adsorbent to review other sources of information in an attempt to identify the specific adsorption mechanism.

In adsorption process of dye on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceeds till the concentration of the adsorbate species, adsorbed on to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solution stops. Under this situation, it is possible to measure the magnitude of the distribution of the solute species between the liquid and the solid phases. The magnitude of this kind of distribution is a measure of the efficiency of the chosen adsorbent and the adsorbate species.

When graphene platelets are made to contact with a solution containing dyes, the dyes first migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore,
the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusion.

The adsorption of adsorbent on graphene layer is remarkably different from other conventional porous carbons in several aspects. First, due to their two-dimensional nano structure, the external surface available for adsorption is considerably larger than the surface area arising from inner cavities. The predominance of outer cavity surface area to inner cavity surface area determines the adsorption characteristics of dyes on xGnP. The adsorption on the external surface of graphene nanoplatelets is more important than the adsorption inside micro/mesoporous cavities. Another noteworthy difference should be ascribed to the interstitial space between individual graphene sheets. The dimension of this space is determined by the relative positions among individual graphene sheets.

In the batch mode contact time adsorption experiments, rapid stirring is maintained. This induces AO7 from the solution to the external surface of the adsorbent material and this step may control the rate of the adsorption process. To interpret the experimental data it is necessary to recognize the steps involved in the process of adsorption that govern the overall rate of removal of dye. The ingenious mathematical treatments recommended by Boyd et al. have been applied. These mathematical treatments are found to be useful to distinguish between particles diffusion and film diffusion. The successive steps in the adsorption dyes by adsorbents are:

(i) transport of adsorbates to the external surface of adsorbent (film diffusion);

(ii) transport of adsorbates within the pores of the adsorbent, except for a small amount of adsorption, which occurs on the external surface (particle diffusion); and

(iii) adsorptions of the ingoing ion (adsorbate) on the interior surface of adsorbent.

Out of these three processes the third process is considered to be not the limiting step in the uptake of dyes on to xGnP. The remaining two steps impart the following three possibilities:

Case I – External transport < internal transport, where rate is governed by particle diffusion.

Case II – External transport > internal transport, where rate is governed by external diffusion.

Case III – External transport ≈ internal transport, where the transport of the adsorbate ions to the boundary may not be possible with significant rate, this may result into a possibility of formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

In the present study, the quantitative treatment of the sorption dynamic is found in accordance with the observation of Reichenberge, as described by the following equation:

\[ F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -n^2 \beta_i \right) \]  \quad (3)

where \( F \) is the fractional attainment of equilibrium at time \( t \); and \( n \), the constant.

\[ F = \frac{Q_t}{Q_{\infty}} \]  \quad (4)

where \( Q_t \) and \( Q_{\infty} \) are the amounts adsorbed after time \( t \) and after infinite time respectively.

\[ B = \pi^2 \frac{D_i}{r_o^2} = \text{time constant} \]  \quad (5)

where \( D_i \) is the effective diffusion coefficient of adsorbate in the adsorbent phase; and \( r_o \), the radius of adsorbent particles.

For energy observed values of \( F \), corresponding values of \( B_i \) are derived from Reichenberg’s table. In each case the plot of \( B_i \) vs time distinguishes between the processes involved film diffusion and particles-diffusion controlled rate of adsorption.

Typical \( B_i \) vs time plots at the concentration 20 mg/L of AO7 adsorbed on xGnP at different temperature are represented in Fig. 8. It is found to be non-linear throughout the temperature 30, 45 and 60°C, thus the process involved can be represented as film diffusion. At 30°C the adsorbent exhibits linearity in \( B_i \) vs time plots in the entire concentration range, but the straight lines obtained do not pass through

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity mg/g</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola stalks</td>
<td>25.06</td>
<td>20</td>
</tr>
<tr>
<td>Beech wood sawdust</td>
<td>5.06</td>
<td>21</td>
</tr>
<tr>
<td>Spent brewery grains</td>
<td>30.5</td>
<td>22</td>
</tr>
<tr>
<td>Soil</td>
<td>3.47</td>
<td>23</td>
</tr>
<tr>
<td>Waste Brewery’s yeast</td>
<td>3.56</td>
<td>24</td>
</tr>
<tr>
<td>Untreated S. marginatum</td>
<td>35.62</td>
<td>25</td>
</tr>
<tr>
<td>Exfoliated graphitic nanoplatelets</td>
<td>85.172</td>
<td>Present study</td>
</tr>
</tbody>
</table>
origin, revealing thereby that the rate-determining process is film diffusion at this temperature for chosen adsorbent.

The $D_i$ values were also calculated for each adsorbent material at the three different temperatures (30, 45 and 60°C) using Eq. (6), and the values observed specify that $D_i$ increases within increasing temperature. This may be due to the increased mobility of ions and decreased retarding forces acting on diffusing ion. The energy of activation ($E_a$), entropy of activation ($\Delta S^e$), and pre-exponential constant ($D_o$) analogous to the Arrhenius frequency factor are evaluated indicating no significant change in the internal structure of xGnPs during the adsorption, as shown below:

$$D_i = D_o \exp \left[ - \frac{E_a}{RT} \right] \quad \cdots (6)$$

$$D_o = (2.72d^2 kT / h) \exp \left[ \frac{\Delta S^e}{R} \right] \quad \cdots (7)$$

where $d$ is the average distance between the successive exchange sites and is taken as 5 Å; and R, h and k are the gas, plank and Boltzmann constants respectively. The values of $E_a$, $D_o$, $D_{ci}$, $\Delta S^e$ and other parameters are given in the Table 4. The negative values of $\Delta S^e$ reflect that no significant change occurs in the internal structure of chosen adsorbent using the adsorption process.

**Conclusion**

The study shows that xGnPs is an effective adsorbent for the removal of AO7 from aqueous solution. The adsorption of AO7 is dependent on the initial concentration and agitation time. Equilibrium of AO7 adsorption reaches at 160 min.

The pseudo first- and second-order equations provide a best fit description for the sorption of AO7 onto xGnPs related to Elovich model, but the pseudo first-order correlation coefficient has better correlation value than pseudo second-order equation. Pseudo first-order equation is consider to be the most appropriate due to high correlation coefficient when compared to pseudo second-order equation, and adsorption takes place via film diffusion process. Langmuir and Freundlich adsorption isotherms correlate the equilibrium adsorption data. The adsorption of AO7 onto xGnPs is an exothermic reaction based on enthalpy change values.

**Acknowledgement**

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**References**


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**Table 4 — Values of energy of activation ($E_a$), entropy of activation ($\Delta S^e$), effective diffusion coefficient ($D_i$) and pre-exponential factor ($D_o$)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$D_o$, cm$^2$/s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>30° C</td>
<td>1.4687 × 10$^{-11}$</td>
</tr>
<tr>
<td>45° C</td>
<td>1.313 × 10$^{-11}$</td>
</tr>
<tr>
<td>60° C</td>
<td>1.093 × 10$^{-11}$</td>
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<tr>
<td>$E_a$, kJ/mol$^{-1}$</td>
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<tr>
<td>$\Delta S^e$, JK/mol$^{-1}$</td>
<td>-179.53</td>
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<tr>
<td>$D_o$, cm$^2$/s$^{-1}$</td>
<td>9.4932 × 10$^{-12}$</td>
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