Adsorption Isotherm, Kinetic And Equilibrium Studies On The Removal Of Basic Dye Eosin Yellow From Aqueous Solution By The Use Of Polyaniline And Its Composites

Subhendu B. Roy and Gaurav Lohar

Department of Chemical Engineering, Assam Engineering College, Guwahati-781013, Assam, India

ABSTRACT

In this study, polyaniline (PANI), composite of polyaniline with banana peel and composite of polyaniline with mushroom have been synthesized by chemical oxidation polymerization. This is a cost effective and simple method of preparing PANI and composites of PANI. The PANI and its composites were characterized by UV/Vis and IR analysis. These composite materials have been effectively used in adsorption of anionic dye from aqueous medium. It has been observed that these are good materials for adsorption of anionic dye. Detail equilibrium and kinetic studies have been reported here by taking Eosin Yellow as anionic dye. The experimental data for Eosin yellow adsorption was best fitted in Langmuir adsorption model. Adsorption of Eosin yellow follows 2nd order kinetic model.

Keywords: Adsorption, Polyaniline, PANI-banana peel and PANI-mushroom composite.

Introduction:
Since the discovery of conducting polymer, it has attracted the researchers and Technologists due to the promising properties like catalytic properties and magnetic susceptibility [1], microwave absorption properties [2], electrical and optical properties [3]. Conducting polymers have a wide range of applications such as in electronic, mechanical and (bio) chemical microsystems [4], biosensors [5,6], fuel cell [7], dye-sensitized solar cells (DSSCs) [8] etc. Polyaniline (PANI) is one of the most extensively used and studied conducting polymers. The major practical advantages of polyaniline are its high environmental and thermal stability [9], high electrical conductivity,
easy synthesis from aniline by simple chemical or electrochemical methods and the simple doping/dedoping of the material by acid/base treatment\(^{[10]}\) have made it one of the most promising members of conducting polymer family. The main limitation in the application of this material arrives due to its insolvibility in all organic solvents in the doped form which explains its limited processability due to a rigid backbone\(^{[11, 12]}\). With the introduction of alkyl and aryl substituents it becomes soluble in N-methylpyrrolidone, dimethylformamide, tetrahydrofuran etc. in undoped form. Therefore the composite materials of PANI with other organic or inorganic materials have attracted the researchers as a potential class of materials for a wide range of applications\(^{[12]}\). Also the doping of the material with inorganic acids improve features, such as electrochemical, mechanical or thermal behavior, or novel properties not observed for the isolated components\(^{[13, 14]}\).

Organic dyes are major components of the effluents from industry like textile plants. The release of dyes into the environment constitutes only a small proportion of water pollution, but dyes are visible in small quantities due to their brilliance\(^{[15]}\). Their colors in aqueous solution can be looked on as one sort of visual pollution. They will reduce light penetration into water due to blanching of their colors, which will decrease the efficiency of photosynthesis and affect the growth of the organisms in the water. Some dyes are easily water-soluble, it is estimated that about twenty percent of dyes remains in the effluent during the production of these dyes. As a result, efficient removal and recycling of these dyes in aqueous solution has drawn significant concerns\(^{[16]}\). The synthetic dyes are inherently prepared as stable and non-degradable molecules, the conventional treatment methods are not suitable for their removal from aqueous phase\(^{[16]}\). However, over the years, the possibility of techniques such as oxidative degradation\(^{[17]}\), electrocoagulation\(^{[18]}\), membrane based separation process\(^{[19]}\), and biochemical degradation\(^{[20]}\) have been exploited, but these methods possess drawbacks due to their inapplicability to large scale units along with both energy and chemical intensiveness. Nevertheless, adsorption is shown to be potentially powerful method for dye removal from aqueous phase because of its easy operation, inexpensive, insensitivity to toxic substances, ability to treat concentrated forms of the dyes, and the possibility of re-using the spent adsorbent via regeneration\(^{[21]}\). Subsequently, a variety of activated carbon based adsorbents derived from various materials, many other low cost or waste materials such as coconut coir, olive stone, orange peel, banana pith, rice husk and corn cob etc. for removal of dye have been investigated for their efficacy and efficiency for the removal of dyes\(^{[22]}\). However, the large volume of the wastewater with high dye concentration has been compelling for development of some non-toxic low cost efficient adsorbent with the possibility of regeneration for reuse. Unfortunately, activated carbons and low cost organic adsorbents are difficult to separate from the solution and have been discarded with the process sludge after use in water and wastewater treatment, resulting in secondary pollution\(^{[23]}\). PANI Emeraldine salt is reported as a useful adsorbent material for removal of anionic dyes\(^{[24, 25]}\).

In this study, we prepared PANI emeraldine salt (ES), PANI-banana peel and PANI-mushroom emeraldine salt (ES) by modification of method developed by Chattopadhyayeta\(^{[26]}\) and dispersion method\(^{[27-30]}\) respectively. It has been observed that even a
small amount of PANI composite can tremendously enhance the adsorption capacity. We have investigated detailed kinetic behavior of adsorption by these materials.

2. Experimental section:
2.1. Materials:
Whatman-40 filter paper was used for all the experiments. Aniline and Ammonium persulfate (APS) were bought from Thermo Fisher Scientific India Pvt. Ltd and used as received. Hydrochloric acid (HCl) was bought from S. D. Fine Chemicals Ltd. and used as received. The dye eosin yellow was purchased from Merck, India and used as received. Distilled water was used for all the experiments.

2.2. Preparation of PANI, PANI-banana peel and PANI-mushroom composite:
A solution of aniline and ammonium persulphate (APS) is prepared by dissolving 5g of aniline in 150 ml of 0.1M HCl and 12.25g of APS in 50 ml of 0.1M HCl respectively. A quantity of 50ml of APS solution was poured drop wise into the anilinium chloride solution over a period of 6 hours and the solution was continuous stirred by magnetic stirrer during the operation. The solution is then filtered through filter paper. The green color of the precipitate on the filter paper indicates the formation of PANI emeraldine salt. The green PANI (ES) was washed several time with distill water followed by drying in air at room temperature and finally in hot air oven at temperature not more than 60°C. In a similar way 1:1 PANI-banana peel and PANI-mushroom composites were synthesized. In all cases the weight were taken and these were 5g in all cases.

\[
\begin{align*}
4n \cdot \text{NH}_2 & + 5n \cdot (\text{NH}_4)_2\text{S}_2\text{O}_8 \\
\text{NH} \cdot \text{HSO}_4 & \quad \text{NH} \cdot \text{HSO}_4 \\
\quad & + 3n \cdot \text{H}_2\text{SO}_4 + 5n \cdot (\text{NH}_4)_2\text{SO}_4
\end{align*}
\]

Scheme 1: The oxidation of aniline with APS yields PANI hydrogen sulfate. Sulfuric acid and ammonium sulfate are by-products.

2.3. Dye used for Adsorption Experiment:
We have used the following dye for adsorption experiments:
2.4. Adsorption experiment:
In this study, all the adsorption experiments have been performed in a beaker. Stock solution of eosin yellow (500 ppm) was prepared in distilled water. The experimental solutions with desired dye concentration were obtained by successive dilution of this stock solution with distilled water. For adsorption experiments, 30mg of PANI (ES), PANI-banana peel and PANI-mushroom composites were added to 100 ml of eosin yellow dye solution having concentration level of 50 ppm. These solutions were stirred by magnetic stirrer and the adsorption had been studied for 2 h duration. Then the concentrations of the dye were determined by UV/visible absorption spectrometer (UV-1800 Shimadzu Spectrophotometer) at different intervals of time (0, 2, 5, 10, 20, 30, 60 and 120 min respectively). The dye concentrations were calibrated with Beer-Lambert law at $\lambda_{\text{max}}$ values of 517nm Eosin yellow.

3. Results and Discussions:

3.1. FTIR Analysis:
The IR spectra of the pure PANI and PANI-banana peel and PANI-mushroom Composite are shown in Fig. 2. The main characteristic peaks of the pure PANI are assigned as follows: 1473.62 and 1571.99 cm$^{-1}$ are attributed to C-C stretching of the benzoid and quinoid rings, respectively, for the HCl doped PANI. The characteristic absorption band around 1244.09 cm$^{-1}$, which is related to the C-N stretching in bipolaron structure, can be observed$^{[31]}$. These results indicate that the pure PANI is highly doped and exists in conducting emeraldine salt form. The peak at 1296.16 cm$^{-1}$ corresponding to C-N stretching of secondary amine in polymer main chain can be clearly seen. The existence of absorption band at 1109.07 cm$^{-1}$ has been interpreted as origination from plane bending vibration of C-H, which is formed in the structure of B-N+H-Cl, Q-N+H-Cl and N-Q-N during the protonation of HCl doped PANI$^{[32]}$.
Figure 2: FTIR analysis of pure polyaniline, PANI-banana peel and PANI-mushroom composite.

For PANI-banana peel and PANI-mushroom composite, its IR spectrum is almost identical to that of the pure PANI. But all bands shift slightly, which indicates that some interaction exists between PANI-banana peel and PANI-mushroom.

3.2. UV/Vis Analysis:

Figure 3: Defuse reflectance UV/Vis Spectra of PANI (ES) before and after Eosin Yellow adsorption.

The UV-visible absorption spectra of the PANI (ES) before and after adsorption of the eosin yellow dye was recorded by U-4100 Hitachi Spectrophotometer (Figure 4). The
UV-visible absorption spectrum of the PANI (ES) indicates that emeraldine salt is formed with its characteristic absorption peak at around 700 and 400 nm. The formation of electrical conducting PANI (ES) on the filter paper was characterized by appearance of the peak at 700 nm. Again the spectra of PANI (ES) show additional peak at 517 nm after adsorption of Eosin yellow. It is the characteristic peak of Eosin yellow. Thus, UV-visible spectra confirm PANI and adsorption of Eosin yellow on PANI (ES). The UV-visible spectra of PANI-banana peel and PANI-mushroom composite are same as PANI (ES) before and after adsorption that is why these are not shown in fig.3.

3.3. Adsorption Study
3.3.1. Adsorption of eosin yellow dye using PANI, PANI-banana peel, PANI-mushroom composite:

![Figure 4: Concentration profile of Eosin Yellow on PANI, PANI-banana peel and PANI-mushroom composite.](image)

Adsorption experiments were performed with PANI, PANI-banana peel and PANI-mushroom as adsorbent materials for anionic dye and the results have been compared with that of PANI, PANI-banana peel and PANI-mushroom (figure-4). Eosin yellow was taken as model dye for comparison. It was observed that with the increase in time the concentration of dye in the solution decreases due to effective adsorption. Among the adsorbents PANI-mushroom composite was found to show maximum adsorption. PANI-mushroom composite adsorbed 100% of the dye from the aqueous solution, whereas pure PANI and PANI-banana peel composite adsorbed 97 and 98% respectively. The detailed adsorption kinetics of eosin yellow dye using adsorbent as PANI-
mushroom composite will be carried out due to its best adsorbing character among the three adsorbents.

3.3.2. Effect of initial concentration of dye using PANI/mushroom as adsorbent: To study the adsorption phenomenon, further experiments were conducted with different initial concentrations of Eosin yellow in the presence of PANI-mushroom composite. Figure-5 shows the concentration profiles of Eosin yellow (ranging from 60-90 ppm initial concentration) at different time intervals. It was observed that the adsorption of the dye increases with initial concentration.

![Figure 5: Concentration profile of Eosin Yellow for Different Initial Concentration.](image)

At higher concentration, large number of dye molecules completely occupies the binding sites of the adsorbent materials which were not possible in the case of low dye concentration.

3.3.3. Effect of adsorbent dosage: The adsorption experiments have been performed to ascertain the effect of variation of amount of adsorbent on the uptake of the dye. Figure-6 shows the variation of concentration of Eosin yellow and with time for different amount of adsorbent at constant initial concentration 90 ppm. It was observed that the adsorption of dye increases with increase in the amount of adsorbent. The number of binding sites on the adsorbent surfaces increases with the amount of adsorbent materials. Thus greater number of dye molecules can bind if the amount of adsorbent is more.
Subhendu B. Roy and Gaurav Lohar

3.4. Adsorption Isotherms
The most studied adsorption isotherm models are Langmuir, Freundlich, and Temkin isothermal models. It is necessary to carry out adsorption isotherm studies to apply the adsorption technique for practical purposes. A relationship can be established between \( q_e \), the amount of adsorption of the adsorbate per unit weight of the adsorbent (mg/g) and \( C_e \), the equilibrium concentration of the adsorbate (mg/L).

3.4.1 Langmuir Adsorption Isotherm:
Langmuir Isotherm model is applicable for many adsorption processes. This model predicts the monolayer adsorption onto the adsorbent surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface and no further adsorption thereafter. It represents chemisorption on a set of well-defined localized adsorption sites, where no adsorption takes place after saturation \(^{[34, 35]}\). The Langmuir model is expressed as

\[
q_e = \frac{b Q_o C_e}{1 + b C_e}
\]

(1)

A linear form of this expression is

\[
\frac{C_e}{q_e} = \frac{1}{b Q_o} + \frac{C_e}{Q_o}
\]

(2)
Figure 7: The variation of Ce/qe with Ce.

The constant Q₀ and b are called Langmuir Constants where Q₀ represents the adsorption capacity in mg/g and b represents the adsorption constant in L/mg. Values of Q₀ and b are calculated from the slope and intercept of the plot of Ce/qe versus Ce. Figure 7 shows the amount adsorbed, qₑ as a function of the equilibrium concentration, Cₑ of the dye Eosin yellow and Methylene blue. The equilibrium uptake was calculated by using the equation

\[ qₑ = \frac{(C₀-Cₑ)V}{W} \]  

(3)

Where C₀ is the initial concentration of the dye solution, Cₑ is the equilibrium concentration of the dye solution; V is the volume of the solution and W is the mass of the adsorbent.

Table 1: Parameters obtained from correlation of Langmuir adsorption isotherm for Eosin Y on PANI-mushroom composite.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>Langmuir Isotherm Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>R²</td>
</tr>
<tr>
<td>PANI-mushroom</td>
<td>Eosin yellow</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Since the value of regression coefficient (R²) is 0.99 that is very closer to 1 the adsorption model is best fitted in Langmuir Isotherm model.

3.5 Kinetics studies:
Several kinetic models have been applied to examine the controlling mechanism of dye adsorption from aqueous solution. In this study pseudo-first-order and pseudo-second–order were applied.
Pseudo-first-order kinetic model

Lagerrgen’s first order rate equation is the earliest known to describe the adsorption rate based on adsorption capacity. The linear form of Lagergren’s first order rate equation is as follows \[^{[36]}\] :

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]  \(\text{(4)}\)

Where \(q_e\) and \(q_t\) are the amounts of dye adsorbed (mg g\(^{-1}\)) at equilibrium and at time \(t\) (min), respectively, \(k_1\) is the Pseudo-first order rate constant (min\(^{-1}\)).

**Figure 8:** (a) Pseudo first order kinetic plot for the adsorption of Eosin Y (different initial concentration) onto PANI-mushroom composite.

**Figure 8:** (b) Pseudo first order kinetic plot for the adsorption of Eosin Y onto PANI-mushroom composite (different adsorbent dose).
Adsorption Isotherm, Kinetic And Equilibrium Studies

Table 2: Pseudo-first-order values

<table>
<thead>
<tr>
<th>Initial concentration(C_0) ppm</th>
<th>Adsorbent dosage (mg)</th>
<th>Experimental q_e (mg g⁻¹)</th>
<th>Calculated K_1 (min⁻¹)</th>
<th>q_e (mg g⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>20</td>
<td>300</td>
<td>0.0678</td>
<td>41.765</td>
<td>0.57358</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>384</td>
<td>0.0255</td>
<td>232.83</td>
<td>0.7526</td>
</tr>
<tr>
<td>90</td>
<td>20</td>
<td>419.9</td>
<td>0.0589</td>
<td>335.3976</td>
<td>0.97325</td>
</tr>
<tr>
<td>90</td>
<td>40</td>
<td>216.25</td>
<td>0.097</td>
<td>26.0543</td>
<td>0.34514</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>149.41</td>
<td>0.1136</td>
<td>10.5959</td>
<td>0.31048</td>
</tr>
</tbody>
</table>

Pseudo-second-order kinetic model.
Ho [37] proposed a second order model for the sorption of divalent metal ions onto peat particles based on the adsorption capacity of the adsorbents with the goal of differentiating the kinetics of a second-order rate expression based on the adsorbent concentration from models which are based on the solute concentration and represent a pseudo-second-order rate expression.

The linearized form of the pseudo-second-order model as given by Ho [37] is

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

Where k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order, q_e and q_t are the amounts of dye adsorbed (mg g⁻¹) at equilibrium and at time t (min), respectively.

Figure 9: (a) Pseudo second order kinetic plot for the adsorption of Eosin Y (different initial concentration) onto PANI-mushroom composite.
Figure 9: (b) Pseudo second order kinetic plot for the adsorption of Eosin Y onto PANI-mushroom composite (different adsorbent dose).

Table 3: Pseudo-second-order values

<table>
<thead>
<tr>
<th>Initial concentration( (C_0) ) ppm</th>
<th>Adsorbent dosage (mg)</th>
<th>( q_e ) (mg/g)</th>
<th>Calculated</th>
<th>( K_2 ) (g mg(^{-1}) min(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>20</td>
<td>300.3</td>
<td></td>
<td>0.0127</td>
<td>0.99998</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>387.6</td>
<td></td>
<td>4.56x10(^{-4})</td>
<td>0.9872</td>
</tr>
<tr>
<td>90</td>
<td>20</td>
<td>434.78</td>
<td></td>
<td>4.6567x10(^{-4})</td>
<td>0.99523</td>
</tr>
<tr>
<td>90</td>
<td>40</td>
<td>216.45</td>
<td></td>
<td>0.0263</td>
<td>0.99999</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>149.48</td>
<td></td>
<td>0.064</td>
<td>0.99999</td>
</tr>
</tbody>
</table>

The straight line plots of log \((q_e-q_t)\) against time for the pseudo-first order reaction, and \(t/q_t\) against time for the pseudo-second-order reaction of the adsorption of Eosin Y onto PANI/mushroom composite are shown in Figs. 8 (a), (b) and 9(a), (b). The calculated value of \( k_1 \), \( k_2 \) and \( q_e \) and their corresponding regression coefficient values \( (R^2) \) are presented in Table 2 and 3 respectively. The correlation coefficients are closer to unity for pseudo-second-order kinetics than for pseudo first order kinetics. This suggests that the adsorption system can be better represented by the pseudo-second order model.

4. Conclusion:
In this work, polyaniline (PANI), composite of polyaniline with banana peel and Composite of polyaniline with mushroom have been synthesized on the surface of the filter paper by chemical oxidation of aniline. It has been observed that PANI (ES),
composite of polyaniline with banana peel and composite of polyaniline with mushroom act as good and cost effective adsorbent materials for eosin yellow. These materials have several advantages such as increased adsorption capacity, ease removal of adsorbent after adsorption etc. Thus, these materials may act as promising adsorbent materials for different charged species in solution.

5. Acknowledgement.
We thank the Department of Chemical Engineering, AEC, Guwahati, India, for their uninterrupted support and invaluable guidance.

6. References:
12. Jaymand, Mehdi. "Recent progress in chemical modification of polyaniline."


36. Lagergren, S., KungligaSuenskaVetenskapsakademiens.,Handlingar, 24 (1898) 1.
