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Adsorption Studies of Methylene Blue on TiO_2 Nanoparticles: Experimental and Mathematical Modeling

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Abstract. TiO_2 nanoparticles are well known for their photocatalytic activities of converting dyes present in the industrial effluent, into carbon dioxide and water. The photocatalytic process comprises of two steps: adsorption and the reaction. Adsorption of dye on TiO_2 nanoparticles, being the first and important step is explored experimentally to study the equilibrium and kinetics in dark. Choosing methylene blue as a model dye, adsorption studies of it were carried out on commercially procured P-25 TiO_2 nanoparticles (~21 nm). A pseudo-first order reaction equation is found to be matches well with the experimental data suggesting that adsorption of methylene blue on TiO_2 nanoparticles is a surface controlled reaction step.

Keywords: Adsorption, methylene blue, TiO_2 nanoparticles

1. Introduction

Wastewater from textile industries contains different types of dyes and their mixtures. Disposal of them in the water bodies without proper treatment is a threat to the environment. Removal of dyes from the effluents is a major problem. Various physical and chemical methods like adsorption, precipitation, coagulation, flocculation, membrane technologies etc. [1]-[5] are either high in cost or produces toxic secondary waste [5], [6]. Some of these toxic contaminants are very reactive and are issue worldwide due to increase in environmental awareness and legislations. This has lead to the rapid research in the field of semiconductor photocatalysis which has shown a great potential as an environment friendly, no generation of secondary contaminants and a low cost waste-water treatment technology [6], [7].

Among the many semiconductor catalysts, titanium dioxide (TiO_2) has shown a great potential for the degradation of organic pollutant [8], [9]. As both the reduction and oxidation sites are available on TiO_2 surface, a light having the energy, equal or greater than the band gap of TiO_2 nanoparticles falls on its surface, series of oxidative- reductive reactions occurs. This in turn degrade the organic moieties and convert them into carbon-dioxide and water [9]. TiO_2, being non-porous in nature is not a good adsorbent, but adsorption of organic moieties which are to be treated on the TiO_2 surface is the vital step in photocatalytic degradation of dyes and organic pollutant [10].

The aim of this work was to study the adsorption capacity of the commercially available TiO_2 nanoparticles for the methylene blue dye (MB), as an organic model pollutant from the textile industry. Preliminary adsorption study of this system is already reported in literature [11], [12]. Here, we had reported detailed studies on adsorption. All the experiments were performed in the dark, so that the change in the concentration of dye is attributed only because of adsorption.

2. Experimental

2.1. Materials

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The commercial dye methylene blue was purchased from Merck India. It is a cationic dye with C.I. number 52015 and λ_{max} at 664 nm. The chemical structure of methylene blue is shown in figure 1. The TiO_2 nanoparticles were supplied by Degussa (P25-TiO_2). The water used in the experiments was double distilled and deionized.

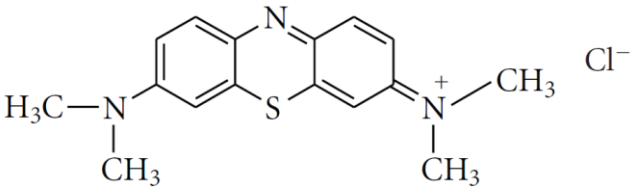

Fig. 1: Chemical structure of MB

2.2. Equilibrium studies

Six solutions with volume (V) of 20 ml of aqueous methylene blue solution each of known concentration (C_0) were prepared. Same mass (M) of TiO_2 nanoparticles were added to all the samples. The suspensions were kept for 24 hours in the dark and shaken occasionally. The MB samples were collected after 24 hours and were centrifuged at 13500 rpm for 15 minutes. Absorbance was measured using UV-Vis spectrophotometer. Corresponding concentration was obtained using calibration chart. The obtained value of concentration is the equilibrium concentration C_e. Amount of methylene blue adsorbed per unit mass of TiO_2 nanoparticles (q_e) was calculated using equation 1.

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{1}$$

2.3. Kinetics

Five solutions of volume 20 ml each of MB with initial known initial concentration of C_0 were taken in different beakers. These were numbered as 1, 2, 3 and so on. The solutions were kept on continuous stirring on Multi-Station Magnetic Stirrer. 0.05gm of TiO_2 nanoparticles were added to each. After 10 minutes, 5 ml sample was drawn from beaker 1 and centrifuged. Similarly, samples were taken from other beakers after every 10 minutes till 40 minutes. The samples were similarly analyzed as mentioned in section 2.2 by UV-Vis spectrophotometer after centrifugation.

3. Results and Discussion

3.1. Equilibrium studies

In the equilibrium studies of MB dye on TiO_2 nanoparticles, concentration of dye at equilibrium was analyzed experimentally after 24 hours. The mass of TiO_2 nanoparticles was same for every run, i.e. 0.05 gm. Subsequently q_e was calculated from equation 1. All the values obtained are mention in table 1.

Table 1: Experimental and calculated values of equilibrium studies

Sl.No	C_0(mg/l)	C_e (mg/l)	q_e(mg/gm)
1.	4.98	4.58	0.168
2.	9.5	8.8	0.28
3.	15.2	13.5	0.68
4.	25.1	22.5	1.04
5.	30	26.63	1.348
6.	56.5	50	2.6

The graphical representation of q_e vs. C_e is shown in figure 2. It shows that the mass of dye adsorbed per unit mass of TiO_2 nanoparticles (q_e) varies linearly with the concentration of dye at equilibrium.

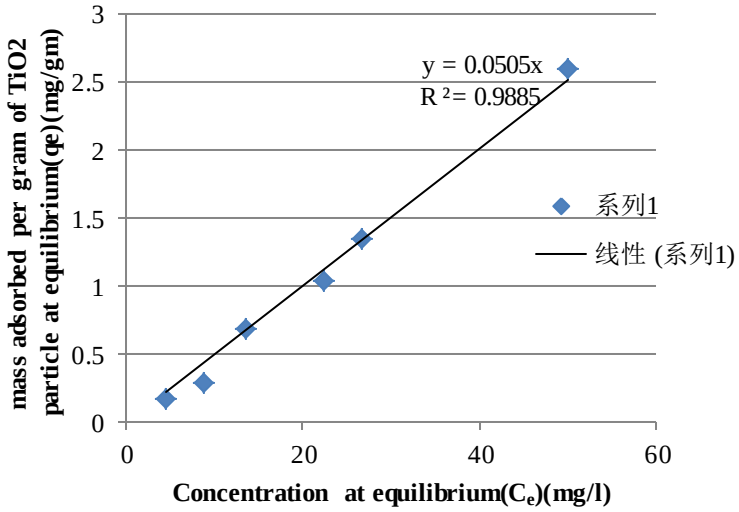

Fig. 2: Equilibrium Studies (q_e vs. C_e)

The equilibrium data may be correlated by $q_e = 0.05 \times C_e$. The equilibrium constant for the system being 0.05 l/gm.

3.2. Kinetics

From the kinetics studies of dye on TiO_2 nanoparticles in dark, figure 3 shows the change in the concentration of dye with time. It can be seen that the adsorption of dye on nanoparticles is small and it appears that 40 minutes of contact time is sufficient for the adsorption process. These studies were on similar lines as it was found in literature [11], [12].

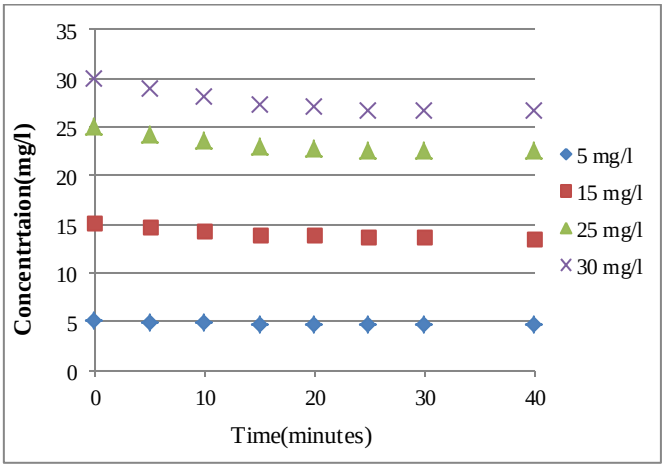

Fig. 3: Kinetic studies (Concentration vs. time)

4. Mathematical Modeling

Adsorption of MB on TiO_2 nanoparticles in dark is modeled considering adsorption as a reaction and MB and TiO_2 are acting as two different reactants. We are assuming that the adsorption is limited by surface reaction which is of 2nd order reaction and can be represented as:

$$-V\frac{dC}{dt} = k_2 C_{NP}.C.V \qquad (2)$$

Where, k_2 is a rate constant, C_{NP} is the concentration of TiO_2 nanoparticles, C is the concentration of dye and V is the total volume. Concentration of dye which is actually taking part in the reaction controlled mechanism is the (C_D-C_e) and as C_{NP} is in bulk the reaction 2. Equation 2 was further modified and solved as:

$$-V\frac{d(C_D-C_e)}{dt} = k_2(C_D - C_e).C_{NP}.V \quad (3)$$

The equation is further turned down in the pseudo first order reaction.

$$\frac{-d(C_D - C_e)}{dt} = \lambda(C_D - C_e) \quad (4)$$

$$\text{Where, } \lambda = k_2.C_{NP}$$

Solving equation 3 by integration with boundary conditions,

$t = 0;\ C_D = C_0$ (C_0 = Initial dye concentration)

$$(C_D - C_e) = (C_0 - C_e)\exp(-\lambda t) \quad (5)$$

$$-\ln\left(\frac{C_D - C_e}{C_0 - C_e}\right) = \lambda t \quad (5)$$

$$\frac{(C_0 - C_D)}{(C_0 - C_e)} = 1 - e^{-\lambda t} \quad (6)$$

After solving this, $-\ln\left(\frac{C_D-C_e}{C_0-C_e}\right)$ was plotted against time (Eqn. 4) to find out the value of λ of different experimental runs. The averaged value of λ is 0.00165 sec^{-1}. Experimental values were matched and compared with the theoretical value as in the form of equation 5.

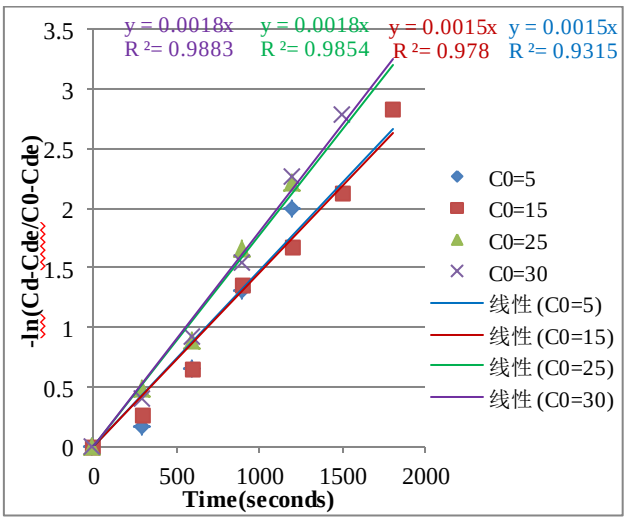

Fig. 4: Plot of $-ln\left(\frac{C_D-C_e}{C_0-C_e}\right)$ $vs.time$

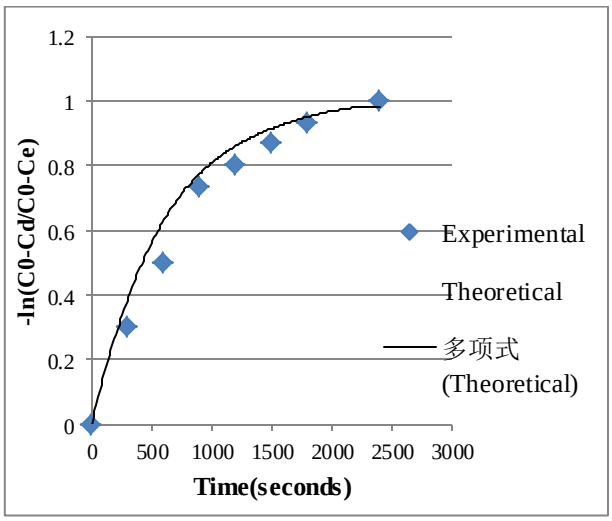

Fig. 5: Experimental vs. theoretical values of adsorption

As the experimental data points are in accordance with the theoretical line, it can be said that model developed assuming adsorption of dye on TiO_2 nanoparticles as pseudo first order reaction seems ok. From this model moles of dye adsorbed per unit area of nanoparticles can be calculated from the formula:

$\frac{\text{Volume}.(C_0-C_e)}{\text{Area of 1 particle}*\text{Number of particles}}$, which is 4.3×10^{-12} gm.mole/cm^2.

5. Conclusion

Adsorption studies, done prior to photochemical studies to estimate the adsorption capacity of TiO_2 nanoparticles reveals that the adsorption of dye on TiO_2 nanoparticles is very less. It usually takes 40-50 minutes of time to complete the adsorption process. The model developed by considering the process as a surface limiting one matches the experimental results which suggest that surface reaction is slower than the diffusion. Hence, the whole adsorption process is a surface reaction controlled process.

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