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***Research Article***

# ADSORPTION OF AZO DYE METHYL ORANGE OVER ALUMINUM OXIDE NANO PARTICLES

***Ekta Khosla**
*Department of Chemistry, Hans Raj Mahila Maha Vidyalaya, Jalandhar 144001 (Punjab)*
**Author for Correspondence*

## ABSTRACT

The adsorption behavior of an azo dye Methyl orange (MO) on Aluminum oxide nano particles (ANP) generated by sol gel method has been performed to understand the physicochemical process involved and to explore the potential use of nano particles in textile effluent treatment and management. The results revealed that ANP can remove MO dye up 124.6 mg/g at 303 K. The adsorption process is found to be pH dependent and optimum pH obtained is 2.0. The equilibrium was established in 1h. Langmuir, Freundlich and Temkin Isotherm models were applied on the system. Scanning electron microscopic analysis reveals nanoporous morphology of the material. The results of FTIR spectroscopy reveal that the process is electrostatic complexation mechanism driven. XRD studies revealed nano crystalline structure of ANP. BET surface area measurement suggests high pore volume and surface area of adsorbent. The kinetic measurements suggest pseudo second order kinetic processes. The thermodynamic measurements suggest that all processes are endothermic accompanied with negative $\Delta G^o$ and positive $\Delta S^o$, $\Delta H^o$.

***Keywords**: Sol Gel Method, Nano Particles, Methyl Orange, Kinetics, Thermodynamics*

## INTRODUCTION

It is well recognized that the presence of dyes in aquatic environment can be most undesirable. Dyes are water soluble in nature and most suited in their action in aqueous medium. Textile waste water is one of the major environmental concerns now days due to increasing environmental concern. Many industries like plastics, pharmaceuticals, textiles, leather, cosmetics, paints and varnishes etc. use dyes to color their final products. Consequently, the waste water effluents are highly colored and the disposal of this waste in water bodies causes damage to aquatic flora and fauna. These dyes affect photosynthetic activities of aquatic flora due to reduced penetration of sun light. Most of the dyes are xenobiotic and non-biodegradable in nature. The conventional waste water treatment technologies depend upon removal of biological oxygen demand but reduction of BOD is ineffective against color removal. The combination of technologies like adsorption and dye degradation can provide the solution to the problem (Chatterjee *et al*., 2001). Although these processes are still in laboratory stage of development. Chemical oxidation of dyes is very successful for azo dyes as it can initiate the cleavage of azo bond. The problem of secondary pollution due to formation of oxidized amines and chlorine (in case of NaOCl) is suspected (Slokar *et al*., 1998). In recent times UV/$O_3$ has been used as treatment technology. This is applicable in gaseous state and almost all types of dyes can be removed successfully without formation of any sludge. The process is pH dependent and associated with high cost and also suffers from limitation of UV-light penetration (Gogate *et al*., 2004). Sonoelectrolysis is also evaluated for the azo dye removal. The electro oxidation of dye (50 ppm) in saline solution involving in situ generation of hypochlorite ion was enhanced using ultrasound (20 kHz, 22w) when carried out in a semi sealed cell which reduced the ultrasonic degassing (Lorimer *et al*., 2000). Adsorption is a conventional technology for dye removal with very high efficiency and simple process. Activated carbon is very efficient adsorbent and very efficient for cationic and anionic dyes. The adsorbent use of carbon in wastewater treatment is impractical due to competitive adsorption of other organic molecules along with dye molecules, the carbon as adsorbent can be thus used in end of treatment steps exclusively for color removal. The non-conventional adsorbents are in application due to their easy availability. Adsorption technology is non destructive technology involving phase change from aqueous phase to solid surface immobilization. Some techniques involving adsorption with catalytic degradation of dye seems to be more lucrative. Chen *et al*., (2008) removed aromatic compounds on single walled carbon nanotubes. The application of nanoparticles as adsorbents has come up as an interesting area of research because of their small particle size and high surface area. The active sites are also more and capable of interacting with pollutant species (Khaled *et al*., 1999). The application of ANP has been evaluated for the removal of hexavalent chromium from aqueous medium (Sharma *et al*., 2010). A previous study indicates that adsorption capacity remains unchanged after regeneration of nano sized adsorbent (Khosla *et al*., 2013). ANP are prepared by using sol-gel method. The material of high purity can be prepared by this method. In the present study ANP prepared by sol-gel method are used for adsorptive removal of azo dye MO from aqueous medium.

## MATERIALS AND METHODS

### *Preparation of Dye Solution*

Methyl Orange was procured from Thomas Baker Company and used without any purification. The structure of dye is given in Figure 1. Methyl orange (MO) or Orange-III is an anionic azo dye. Its IUPAC name is Sodium 4- [[4- (dimethylamino) phenyl] diazenyl] benzenesulfonate. It is orange colored powder soluble in warm water. Its C.I. number is 13025. It is used for dying variety of materials of nylon, silk and wool. This is also used as an indicator in acid base titrations. It is highly toxic and its ingestion may cause eye, skin, mucous membrane and upper respiratory tract irritation. This dye shows $\lambda_{max}$ at 427 nm. 1000 ppm (1000 $mgL^{-1}$) solutions was prepared by dissolving appropriate amount of dye in water and stored in dark colored bottle and diluted by adding suitable amount of distilled water to the stock solution as per requirement.

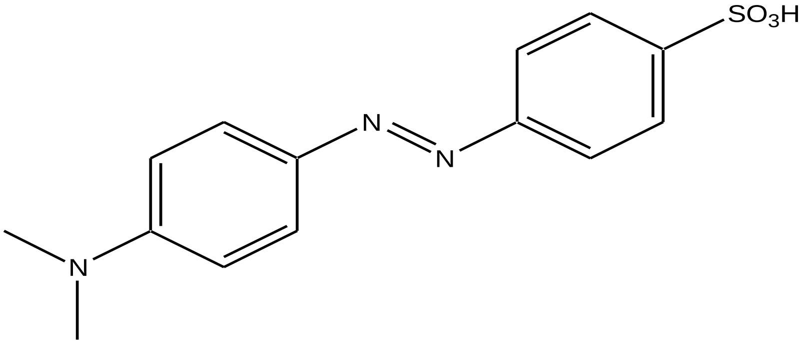

**Figure 1 Structure of Methyl Orange**

### *Preparation of Nano Particles*

Nano-$Al_2O_3$ particles (ANP) were synthesized by sol gel method (Sharma *et al*., 2010). For this purpose saturated solution of aluminium sulphate was precipitated with 6N ammonia solution till a gel is obtained. The gel was then calcined in a muffle furnace at 1073 K for 1h. The powder ANP was stored in a dessicator till further use.

### *Batch Experiments*

The series of experiments were conducted by placing 50 ml of dye solution in an Erlenmeyer flask and adding the required amount of adsorbent to that in an incubator shaker. The pH of different solutions was adjusted with 0.1 N HCl and 0.1 N NaOH. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration using UV visible spectrophotometer. From the absorbance data $q_e$ (mg $g^{-1}$) was determined using equation 1.

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

Where $C_0$ is initial dye concentration, $C_e$ is final dye concentration and V is volume of dye in liters and W is mass of adsorbent in g. Duplicate experiments were performed to get concordant results. The results showed variation in the range of ±5%. The kinetics of dye removal was studied using required dye concentration. The samples were withdrawn at regular intervals and residual concentration was analyzed after centrifugation using ultracentrifugation at 1000 rpm. The isotherms were studied by using 50 ml of dye solution within optimum range of concentration at 303 K, 313 K and 323 K. After the attainment of equilibrium, the residual dye concentration was analyzed spectrophotometrically. The dye concentration before and after adsorption was determined by using Shimadzu (2101 PC) spectrophotometer. A standard plot is drawn for known concentrations and the concentration of dyes was determined by converting the optical density to corresponding concentration. The dyes were analyzed at their respective $\lambda_{max}$. The $pH_{zpc}$ (pH zero point charge) was determined by the method reported earlier (Gogate *et al*., 2004). The pH of dye solutions and $pH_{zpc}$ were determined by using pH meter by Toshvin (TMP-85). The weighing was carried out on a digital weighing balance of accuracy up to 0.1 mg by citizen Co. BET surface area measurement is carried out by using micromeritics surface area analyzer. This also gave monolayer volume of $N_2$ and pore volume of the adsorbents. The FTIR of ANP was carried out with Perkin Elmer spectrophotometer in the range 400-4000 $cm^{-1}$ using perkin elmer spectrophotometer. The adsorbent is mixed with anhydrous KBr to make a pellet and 400 scans are carried out to give the average FTIR scan. The adsorbent samples were also characterized by powder X-ray diffractometry using an X'PERT PRO PANalytical with Cu-$K_\alpha$ radiation. SEM is carried out by using ZEOL scanning electron micrograph. TEM provided topographical, morphological, compositional and crystalline information of nano adsorbents. The images allow us to view samples on a molecular level, making it possible to analyze structure and texture. The data analysis was carried out by using correlation analysis employing least square method and sum of error square was calculated by SPSS-17 statistical software.

## RESULTS AND DISCUSSION

### *Characterization of the Adsorbent*

The Characteristics of ANP are given in Table 1. The SEM and TEM of ANP are shown in Figure 2 indicating morphology of ANP's. The X-ray diffraction analysis of the ANP was carried out and shown in Figure 3 revealed the nano structured ANP. FTIR spectra (Figure 4) revealed that O-H vibrations 3459 $cm^{-1}$ due to the water in the lattice and O-H bending vibrations appears at 1644 $cm^{-1}$. Weak bands are observed at 1386 $cm^{-1}$ due to Al-O bond vibrations.

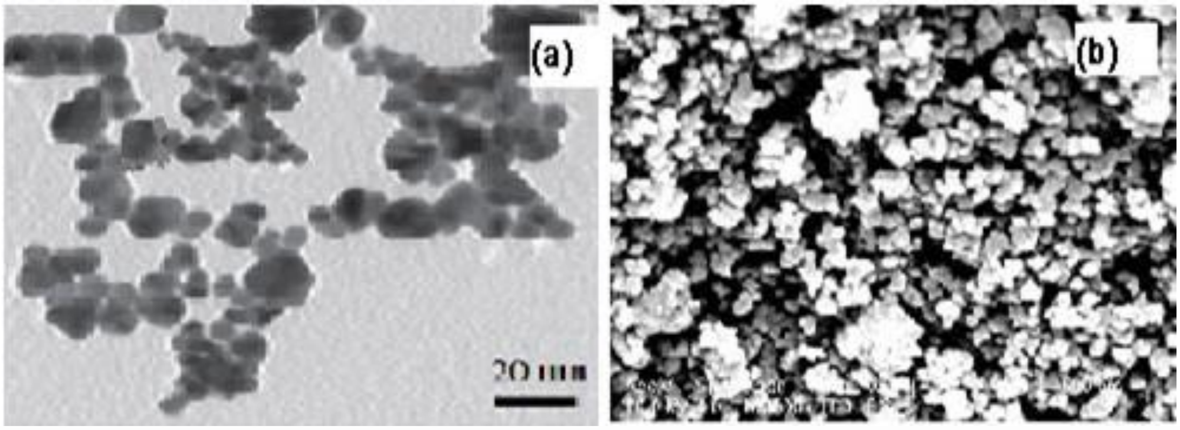

**Figure 2 (a) TEM of ANP (b) SEM of ANP**

The bands at 1071 $cm^{-1}$ and 846 $cm^{-1}$ appears due Al-O bonds. BET surface area analysis shows that surface area of ANP is 82.91 $m^2\ g^{-1}$ and the pore volume is 0.389 $cm^3\ g^{-1}$ the density of ANP was determined and found to be 0.976g $cm^{-3}$.

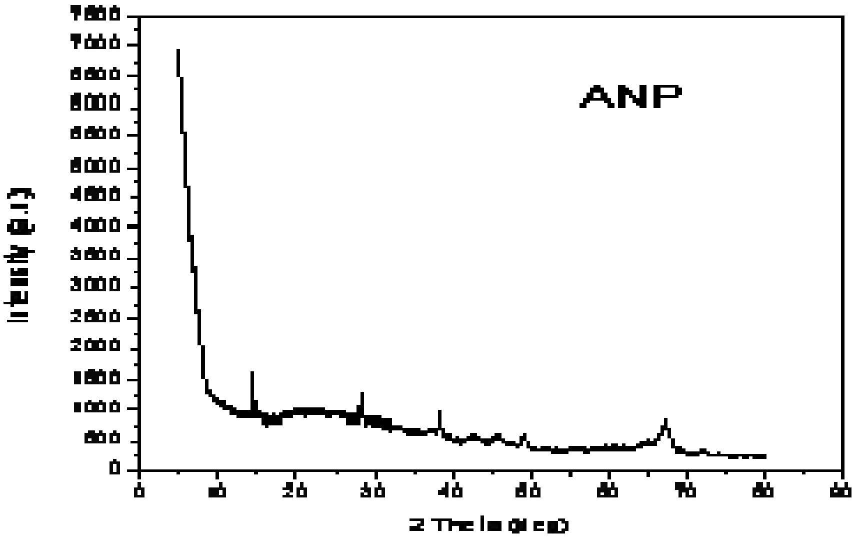

**Figure 3 XRD of ANP**

***Effect of Adsorbent Dose***

To investigate the effect of adsorbent dose on adsorption of dye on ANP and its surface derivatives, the experiments were conducted with adsorbent dose between 0.1 g - 12.5 g in 100 ml at 303 K and it was found that with an increase in the dose, the adsorption increases. This may be credited to the reason that at lower adsorbent dosage the number of dye molecules is comparatively higher as compared to availability of adsorption sites. It was observed that when adsorbent dose was doubled the percentage dye removal increased by a factor of 1.5. Almost optimum adsorption was observed at 0.1g per 100 ml.

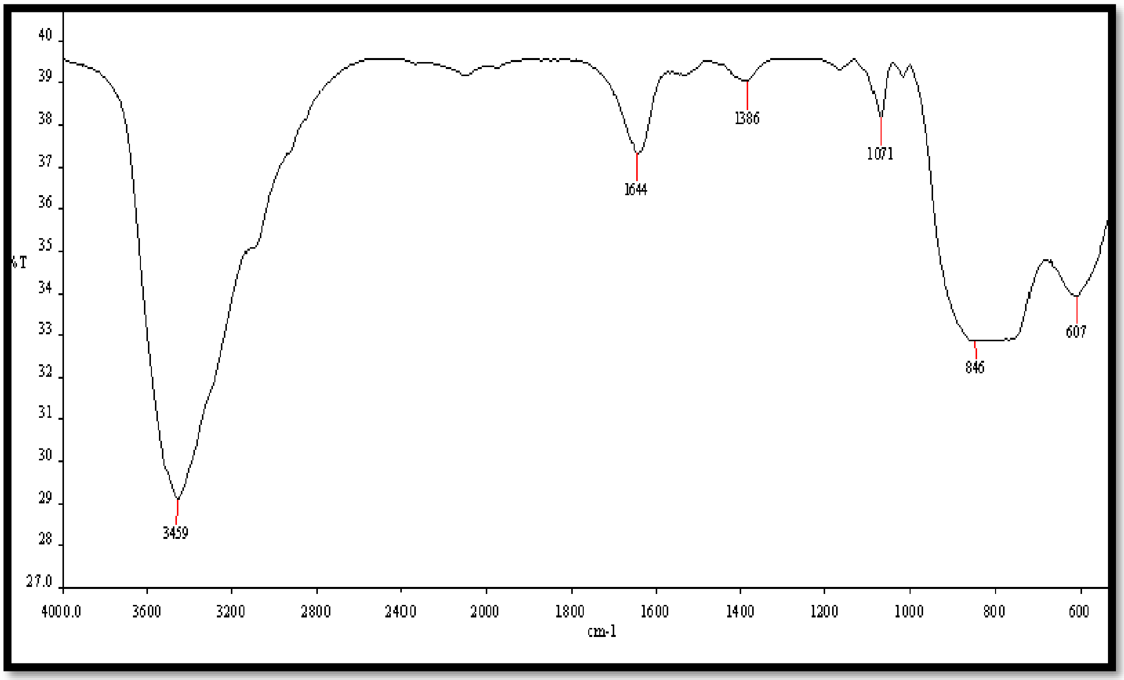

**Figure 4 FTIR of ANP**

**Table 1: Characteristics of ANP**

| | |
|---|---|
| **Surface area ($m^2g^{-1}$)** | **82.91** |
| **Bulk density (g $mL^{-1}$)** | **0.976** |
| **Zero point charge ($pH_{pzc}$)** | **8.0** |
| **Total surface acidity ( mmol $g^{-1}$)** | **0.253** |
| **Total surface basicity (mmol $g^{-1}$)** | **6.879** |

### *Effect of pH*

The dye adsorption is affected by solution pH and in the present study the effect of pH is studied in the range of 2-9 while initial concentration (100 mg $L^{-1}$), adsorbent dose (0.1 g/100 ml) and temperature (303 K) were kept constant. The effect of initial pH on the dye removal is shown in Figure 6. The adsorption capacity decreases when the pH increases. The maximum adsorption of MO occurs at pH 2. This may be ascribed to the reason that in the aqueous medium the functional groups such as hydroxyl groups develops on the surface which are protonated in acidic medium causing more electrostatic interactions between protonated ANP and anionic dye. The $pH_{zpc}$ measurement suggests that $pH_{zpc}$ for ANP is 8.0. Thus, beyond $pH_{zpc}$ negative charge develops on the surface so anionic dyes are best adsorbed below their $pH_{zpc}$. As the pH of the system increases the number of positively charged sites decreases hence the adsorption of anionic dye also decreases. A positively charged site on the adsorbent favors the adsorption of anionic dyes due to electrostatic attractions.

### *Effect of Contact Time*

The effect of contact time was investigated in the batch mode at dye concentration 100 mg $L^{-1}$. The results suggest that the adsorption capacity of dyes increases with increasing contact time. The rate of dye removal is high initially due to high concentration gradient and more availability of adsorption sites. The rapid transport of dye molecules from aqueous solution to the bulk makes the adsorption fast. The surface of ANP is charged and the net charge at the surface at a particular pH governs the adsorptive removal of dye from the solution.

### *Effect of Temperature*

The effect of temperature on adsorption of MO on was studied by carrying the temperature controlled equilibrium experiments. The equilibrium adsorption capacity increases as a function of temperature as revealed by adsorption isotherms. The results advocate that the adsorption capacity of ANP increases with the increase in temperature suggesting that all the adsorption processes are endothermic in nature. The increase in adsorption at higher temperature can be attributed to the fact that at higher temperature kinetic energy of dye and water molecules increases in aqueous medium and the dye binds preferably to the active sites having higher surface area. The positive effect of temperature also indicates chemisorptions (Tsai *et al.*, 2005) as a mode of binding of dye with ANP. Similar results have been found for the removal of basic dyes by other workers (Vazquez *et al.*,1997) suggesting that in this work behavior of ANP towards dyes remains same and binding energy of adsorbate and adsorbent varies as the slope of different curves is different.

### *Adsorption Isotherms*

The Freundlich, Langmuir, and Temkin isotherm models have been successfully applied to all of the above system at various temperatures 303 K, 313 K and 323 K and thermodynamic parameters calculated accordingly. For the equilibrium concentration of adsorbate ($C_e$) and amount of dye adsorbed at equilibrium ($q_e$), the following linear forms of Langmuir (equation 2), Freundlich (equation 3) and Temkin (equation 4) isotherms were studied. Langmuir adsorption model is well known two parameter model of adsorption. It has produced a good agreement with the experimental data suggesting the monolayer adsorption of MO on ANP.

In the Langmuir adsorption the primary binding forces are physical and it is assumed that adsorption capacity of all binding sites is equal and binding on one site does not affect another. $Q_o$ and $b$ are Langmuir constants in the following equation.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \qquad (2)$$

$Q_o$ (mg g$^{-1}$) and $b$ (L mg$^{-1}$) indicates maximum dye uptake and Langmuir equilibrium constant respectively. These isotherms characterize the equilibrium parameters of homogenous surfaces, monolayer adsorption and allocation of adsorption sites. This isotherm fitted well on data (Table 2) suggesting that the adsorption of MO on the active site does not affect the neighboring site. The values of $Q_o$ decrease with the increase of temperature due to increase in kinetic energy of dye molecules in aqueous medium. The essential characteristics of Langmuir isotherm can be calculated by using a dimensionless adsorption constant $R_L$ which can be defined as follows.

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

Where $C_0$ is initial dye concentration. In this experiment the value of $R_L$ was found in the range of 0.02-0.03 which lies between 0-1 suggesting favorable adsorption. The value of $R_L$ is very small suggesting that the size of adsorbent sites. Freundlich isotherm is the earliest known two parameter isotherm model based on the fact that exponentially decaying adsorption site energy distribution can be applied to non ideal sorption. $K_F$ and $n$ are Freundlich constants

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4)$$

The Freundlich parameters calculated for the adsorption of MO on ANP suggests that values of n ranges between 0.90 -1.0 since the values of 1/n for the process lies in the range 0 to 0.9. This indicates favorable adsorption. The value of $K_F$ indicates adsorption capacity in L g$^{-1}$ and $K_F$ increases with the increase of temperature suggesting stronger binding forces operating at higher temperature between ANP and MO. On the basis of statistical analysis it is clear that Freundlich isotherm fits superior on the process.

Temkin isotherm assumes that the fall in heat of adsorption of MO on ANP would decrease linearly for the ANP and MO interactions. The isotherm can be represented by following linear form.

$$qe = \frac{RT}{b_t}\ln(a_t C_e) \qquad (5)$$

Where $b_t$ is temkin constant related to the heat of sorption J mol$^{-1}$and $a_t$ is temkin isotherm constant (Lg$^{-1}$). The value of $a_t$ lies very close to 1.000 at all temperatures and $b_t$ decreases with the increase of temperature suggesting endothermic nature of the adsorption. Langmuir and Freundlich isotherms fitted the data better than temkin as this is clear from the statistical analysis of the data.

The changes in the reaction on ANP is expected during the process require the brief idea of the thermodynamic parameters which were also calculated from the above data using Equation 6-8.

$$\Delta G^0 = -RT \ln b \qquad (6)$$

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \bullet \frac{1}{T} \qquad (7)$$

Where $b$ is Langmuir equilibrium constant. The values $\Delta H^o$ and $\Delta S^o$ are determined from intercept and slope of equation 7. The values of thermodynamic parameters are given in Table 3.

**Table 2: Adsorption Isotherm and Statistical Comparison Values of Adsorption Isotherm**

| *Isotherm Model* | *Isotherm Parameters* | *303 K* | *313 K* | *323 K* |
|---|---|---|---|---|
| Freundlich | $K_F$ | 2.223 | 2.228 | 2.154 |
| | n | 0.900 | 1.100 | 1.115 |
| | R | 0.9901 | 0.9962 | 0.9957 |
| | Std Error | 0.00999 | 0.0317 | 0.0023 |
| | Std Deviation | 0.02447 | 0.07766 | 0.0023 |
| | t | -11.568 | -4.492 | 7.954 |
| Langmuir | $Q_0$ | 0.8766 | 0.7509 | 0.6086 |
| | b | 0.3155 | 0.9425 | 1.517 |
| | R | 0.99017 | 0.9516 | 0.9957 |
| | Std Error | 0.00395 | 0.0037 | 0.00353 |
| | Std Deviation | 0.0109 | 0.00906 | 0.00806 |
| | t | 1.265 | 2.945 | 6.332 |
| Temkin | $a_t$ | 0.999 | 0.997 | 0.995 |
| | $b_t$ | 191.728 | 182.712 | 168.135 |
| | R | 0.93377 | 0.9542 | 0.9884 |
| | Std Error | 4.5236 | 2.8296 | 5.0095 |
| | Std Deviation | 11.0805 | 6.9313 | 12.271 |
| | t | -8.646 | -13.527 | -9.111 |

The Gibbs free energy, $\Delta G°$ was found to be negative at all temperatures, indicating spontaneous process at all the temperatures while enthalpy $\Delta H°$, was positive suggesting endothermic and irreversible nature of the process. The positive value of entropy, $\Delta S°$ suggests favorable randomness factor though its value is small. This suggests that in spite of small particle size of adsorbent the reaction is energetically favorable. The thermodynamic parameters were calculated and are given in Table 3.

### *Kinetic Studies*

The rate of removal of MO indicates that the equilibrium was attained in 1h. Adsorption rate constant study was carried out with the famous Lagergran rate equation (equation 8).

$$\log\,(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (8)$$

The pseudo first order equation (Figure 8) was evaluated. The $K_1$ was found to be $2.121X10^{-2}$ $min^{-1}$. The suitable agreement was found between Pseudo first order data in statistical analysis, the correlation coefficient is high and standard error is low. The second order equation was also tested on the whole range of time. The plot is shown in Figure 5 indicating. The pseudo second order equation (equation 9)

$$\frac{t}{qt} = \frac{t}{k_2 q^2{}_e} + \frac{1}{q_e} t \qquad (9)$$

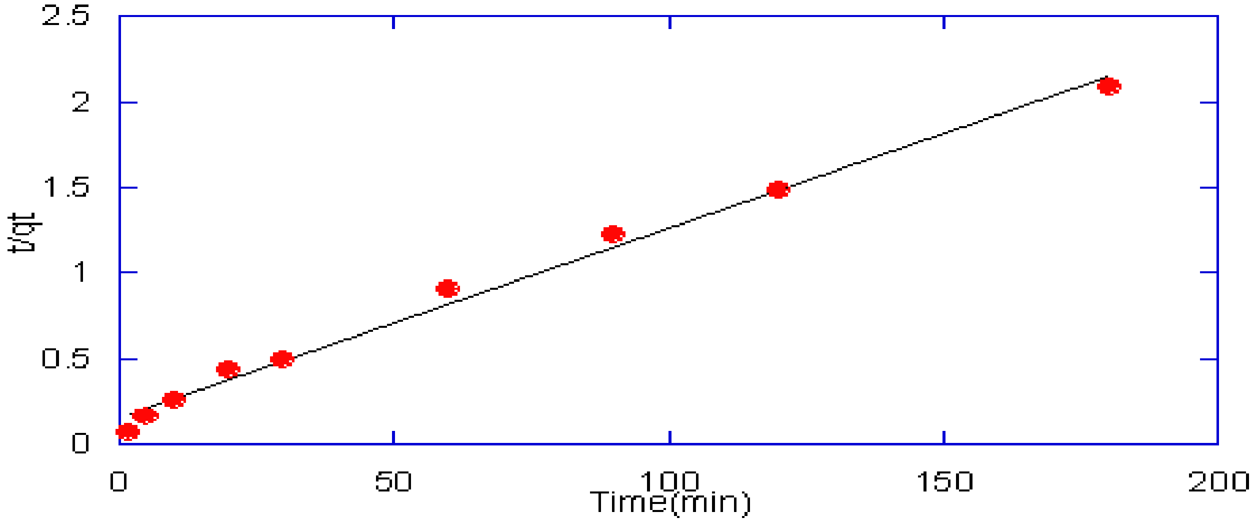

**Figure 5 Pseudo second order kinetics plot for desorption of MO on ANP, 100 ppm dye concentration, 303 K, pH=2**

The pseudo second order kinetic model fitted better than lagergren model. The correlation constant was higher than first order model. The rate constant $K_2$ was found to be $4.924X10^{-4}$ $mg.g^{-1}$ $min^{-1}$. Elovich kinetic model (equation10) was also applied on the data to evaluate the possibility of chemisorption.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (10)$$

The plot between qt vs lnt was a straight line. The regression coefficient was found to be 0.9855, a very small standard error was obtained. Several kinetic parameters are calculated for different models and represented in Table 4.

**Table 3: Thermodynamic parameters of adsorption of MO on ANP**

| ***Temperature*** | ***$\Delta G^o$*** | ***$\Delta H^o$*** | ***$\Delta S^o$*** |
|---|---|---|---|
| **(Kelvin)** | **(J mol-1)** | **(J mol-1)** | **(J k-1 mol-1)** |
| **303** | **-309.85** | | |
| **313** | **-3569.8** | **+167.98** | **+5.779** |
| **323** | **-6562.6** | | |

**Table 4: Comparison of Kinetic Constants for the Adsorption 0f Mo on Anp**

| Kinetic model | Kinetic constants | Values |
|---|---|---|
| Lagergren model | $k_1$ | 0.01032 $min^{-1}$ |
| | R | 0.9822 |
| | Std Error | 2.582 |
| | Std Deviation | 60747 |
| Pseudo second order | $k_2$ | $9.424X10\text{-}^{4}$ $mg.g^{-1}$ $min^{-1.}$ |
| | R | 0.9956 |
| | Std Error | 2.267 |
| | Std Deviation | 6.789 |
| Elovich model | α | 29.414 |
| | β | 0.07127 |
| | R | 0.9809 |
| | Std Error | 0.6779 |
| | Std Deviation | 2.329 |

### *Conclusion*

This study shows that MO can be successfully removed from the aqueous solution by adsorption on ANP and this can be an effective and valuable mean for controlling water pollution due to dyes. The following conclusions can be drawn from this study: The batch adsorption experiments show that the adsorption of the MO over ANP and its derivatives is dependent on pH, amount of adsorbent, concentration, contact time, and temperature, and 100% dye removal could be accomplished. The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration. The Freundlich, Langmuir and Temkin isotherms fitted the data well. The results of kinetic experiments show that the adsorption proceeds via pseudo second order kinetics over all adsorbents.

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