



## **Adsorption Nature of Tartrazine Dye onto Synthesized Melamine-Formaldehyde-Tartaric Acid (MF-T) Resin (Kinetic, Isotherm and Thermodynamic Studies)**

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**Abstract:** The Melamine-Formaldehyde-Tartaric acid (MF-T) porous polymeric resin was synthesized in this work and examined as adsorbent for organic pollutants. Adsorption rate and isotherm of tartrazine, as an organic pollutant, onto MF-T from a synthetic wastewater was studied applying batch method. Initial concentration, contact time and temperature were considered as the variables of the adsorption experiments. Linear forms of pseudo-first and pseudo-second order kinetic models were applied using experimental adsorption-rate data. More than 60% of tartrazine was removed in the first 10 minutes and pseudo second-order model was found to well represent the adsorption kinetics with average capacity of about 23 mg/g over the studied temperature span. Linear forms of Langmuir and Freundlich isotherm models were applied using experimental adsorption-equilibrium data. In general, Freundlich model is selected to represent the adsorption isotherm. It was found that adsorption mechanism is temperature sensitive but retain spontaneous over the studied temperature span. Thermodynamic study revealed that physical mechanism contributes at low temperature range (15-30°C) and a dual mechanism of physical and chemical natures is postulated at the higher temperature range (30-45°C). The chemical part is suggested to be endothermic amide bonding of tartrazine with resin reactive functional groups.

**Keywords:** Polymeric resin, Chemical, Physical, Adsorption, Wastewater, Dyes.

### **1. Introduction**

Leather, carpet, textile, paper, printing and foodstuff industrial activities produce wastewaters that contain a considerable concentration of different coloring synthetic dyes. These dyes are poorly biodegradable under normal environmental conditions and their decay because of sunlight and oxidizing agents is limited due to presence of aromaticity in their chemical structures [1,2].

They often have toxic and carcinogenic effects to humans and these effects are increasingly probable due to accumulation of such materials in water bodies such as lakes, rivers, seas and ground water reservoirs. Industrializing countries suffers from such problem due to notably recognized increase in activities releasing dyes with no parallel legislation and technical progress that handle this subject.

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It is important to remove these types of dyes before discharge of contaminated-effluents. Adsorption is a popular and effective separation methodology for the removal of many pollutants (including dyes) from wastewater. Practically, activated carbon is the most commonly used adsorbent in industrial wastewater treatment systems. However, many synthetic adsorbents have been produced for such application and many are porous polymeric resins. Synthetic porous polymeric resins are well dedicated for such application due to the capability to control its physical properties such as porosity and hydrophilicity during preparation as a chemical tailoring concept.

In the present work, the MF-T polymeric porous resin was synthesized under acidic condition by anchoring tartaric acid through amide bond to melamine during the melamine–formaldehyde gelling reaction [3,4]. According to its chemical structure, this resin is chelating and can be used to remove some heavy metal ions from wastewater. Two similar chelating resins (melamine–formaldehyde-NTA and melamine–formaldehyde-DTPA) have been prepared and their removal ability towards Co(II), Cu(II), Cd(II) and Zn(II) as inorganic pollutants from wastewater was studied [4,5]. MF-NTA and MF-DTPA resins have successfully verified these ions removal [3,4]. These resins (MF-NTA, MF-DTPA and MF-T) can also be classified as macroporous adsorbent and accordingly capable of removing organic pollutants because of its porous matrix texture [6]. Using this type of resin to remove organic pollutants may encourage its application for water treatment as a universal adsorbent (i.e, to remove inorganic and organic pollutants). To examine its ability to remove organic compounds, tartrazine was selected, for present study because it is a good representative for contaminating organic dyes. Tartrazine is synthetic yellow azo-dye (has a maximum absorbance in an aqueous solution at 426 nm) and is food, drink and drug coloring agent. There is high chance to contaminate water by this dye because of its high water-solubility (solubility  $\approx$  110 g/l).

## 2. Experimental

### 2.1. Theory

#### 2.1.1. MF-T resin preparation

The matrix of melamine–formaldehyde resin (MF) is produced by methylolation of melamine under acidic condition at elevated temperature (90 to 150°C). under these conditions,  $-\text{NH}_2$  groups of melamine react with formaldehyde to give methylol groups ( $-\text{NH}-\text{CH}_2\text{OH}$ ). Methylol groups, then, condense to form methylene and ethylene-ether bridges between melamine molecules and this process give the main platform of the matrix [3-5,7-10]. During matrix formation by bridging and with the presence of tartaric acid [on molar basis; tartaric acid : Melamine = 1/3], carboxylic groups ( $-\text{COOH}$ ) of tartaric acid react with an amine groups ( $\text{NH}_2-$ ) of melamine forming amide covalent bond. This process anchors tartaric acid to the MF matrix forming the porous polymeric MF-T [11,12]. This procedure was previously followed for the preparation of melamine–formaldehyde-NTA and melamine–formaldehyde-DTPA where anchoring of NTA and DTPA to MF matrix was confirmed to be achieved through amide bond [3,4]. The produced solid MF-T has the needed rigidity to withstand grinding (during preparation of resin grains) and hydraulic stress (during adsorption process). If tartaric acid not added, fluffy-pasty MF is produced which is not suitable for adsorption applications. The suggested reaction of resin formation and final resin formula is shown in Scheme 1 [4].

### 2.1.2. MF-T resin characterization

The percentage of water content, intrinsically held by the resin, can be determined by the following equation [3]:

$$W\% = (W_w - W_d) \times 100 / W_w \quad (1)$$

where  $W_w$  and  $W_d$  are the wet and dry weights of the resin, respectively. The intrinsic water content reflects the degree of hydrophilic character of produced resin. The surface area of the resin was calculated using the following equation [3,13]:

$$A_s = G \times N_{Av} \times \phi \times 10^{-20} / (M \times M_w) \quad (2)$$

where  $A_s$  ( $\text{m}^2/\text{g}$ ) is the resin surface area,  $G$  (g) the amount of adsorbed methylene blue,  $N_{Av}$  ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ) is the Avogadro's number,  $\phi$  ( $197.2 \text{ \AA}^2$ ) the methylene blue molecular cross section,  $M_w$  the molecular weight of methylene blue ( $373.9 \text{ g mol}^{-1}$ ) and  $M$  is the mass of adsorbent (g). As a rough estimate of surface area was needed (and no detailed data about surface area categories was required), this method was followed because of simplicity.

### 2.1.3. Tartrazine adsorption onto MF-T

Isotherm study of an adsorption system gives the capacity or a related parameter of an adsorbent towards certain adsorbate. Also, it is helpful giving an idea about the energy homogeneity of adsorbent surface and the nature of interaction between the solute and the adsorbent.

Freundlich and Langmuir adsorption models were used in this work by applying their linear forms. The linear form of Freundlich model is as follows [14,15]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3)$$

where  $q_e$  is the adsorbed amount at equilibrium and  $C_e$  is the concentration at equilibrium. Freundlich parameters,  $K_F$  and  $n$ , are related to the adsorption capacity and intensity respectively. Freundlich model considers energy-heterogeneous surface of adsorbent and suggests a multilayer adsorption process. The linear form of Langmuir model is as follows [14,15]:

$$1/q_e = 1/Q_o + 1/bQ_o C_e \quad (4)$$

where  $q_e$  and  $C_e$  have the same definitions as for Freundlich model. The term  $Q_o$  is the adsorption capacity (mg/g) and term  $b$  is related to energy of adsorption (1/mg). Langmuir model considers energy-homogeneous surface of the adsorbent and monolayer adsorption process.

Kinetic study gives the rate of adsorption of solute onto adsorbent surface. In this work, pseudo-first and pseudo-second order kinetic models were applied. The integral forms of pseudo-first and pseudo-second order have the following linear equations [16]:

$$\text{Pseudo-first order:} \quad \log(q_e - q_t) = \log q_e - (k_1 / 2.303) t \quad (5)$$

$$\text{Pseudo-second order:} \quad t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

where  $q_e$  and  $q_t$  (mg/g) are the solute amounts adsorbed at equilibrium and time  $t$  respectively. The parameters  $k_1$  (1/min) and  $k_2$  (g/mg.min) are the adsorption rate constants. The experimental adsorption capacity ( $q_{exp}$ ) at equilibrium was calculated using the following equation:

$$q_{exp} \text{ (mg/g)} = (C_i - C_e) \times V / M \quad (7)$$

where  $C_i$  is the initial concentration (mg/l),  $V$  (l) is solution volume and  $M$  (g) is the mass of the adsorbent. The values estimated from the kinetic models were compared to those calculated by this equation.

For thermodynamic study, the adsorption equilibrium stability constant can be determined applying the following formula:  $K_c = (C_i - C_e) / C_e$  [17,18]. The Gibbs free energy of the adsorption process ( $\Delta G_{ads}$ ) can be calculated using the Van't Hoff equation:

$$\Delta G_{ads} = -RT \ln K_c \quad (8)$$

Enthalpy ( $\Delta H_{ads}$ ) and entropy ( $\Delta S_{ads}$ ) of adsorption can be determined from the slope and intercept of plot of  $\ln K_c$  versus  $1/T$  according to the following equation:

$$\ln K_c = (\Delta S_{ads}/R) - (\Delta H_{ads}/RT) \quad (9)$$

## 2.2. Materials and Procedures

### 2.2.1. Chemicals and instruments

Analytical grade of melamine 99% (Aldrich), formaldehyde 38% (BDH), tartaric acid 99% (Sigma) were used in this work. Tartrazine (form El-Nasr chemicals, local company) was used in its commercial form and no extra purification was performed. Deionised water was used for MF-T resin synthesis and for the preparation of tartrazine and methylene blue solutions. The following instruments were used in this study: Shimadzo spectrophotometer (UV-120-02) for measuring tartrazine concentration in solutions, Hanna instrument pH-meter (H18519), Lab. Companion SI-300R shaker and Perkin–Elmer FT-IR spectrometer.

### 2.2.2. Preparation of the MF-T resin

One important advantage of preparing MF-T is simplicity as it is a one-pot process. To a vial (50 ml) containing 25 ml of acidified water (pH 1.1), melamine (6.3 g) and tartaric acid (2.5 g) were added and agitated until forming dense suspension. Then, formaldehyde (10 ml) was added to the suspension and the vial was tightly closed. The vial was again agitated until homogenous white thick slurry was formed. The vial was then placed in a preheated oven at 120°C. Shortly after 5 minutes, a clear colorless slightly viscous gel is produced. After another 15 minutes, the gel solidified into white monolithic MF-T resin. The resin was left for an extra 30 min for more curing (melamine bridging) at same temperature. Then, the vial was removed from the oven and left about 24 hours on bench (at room temperature) for more hardening. The resin sample was picked from the vial and ground. The formed grains were washed several times each by agitation with 500 ml of hot (~95°C) deionised water for an hour until pH became about neutral. After washing, the resin grains were left to cool. The excess water was removed by centrifugation leaving grains with intrinsic water only. Resin grains were then sieved and each fraction was kept in a tightly closed vial.

### 2.2.3. MF-T resin characterization (water content, surface area and IR analysis)

**Intrinsic water content:** MF-T resin grains (355–710  $\mu\text{m}$ ) were soaked in deionised water for 48 hours to ensure water content equilibrium. Excess water was removed by centrifugation for 45 minutes at 1000 rpm and then weighed. The same sample was dried at 50°C for 72 h and reweighed. The difference between the two weights gives the intrinsic water content. This process was performed three times to get an average. The percentage of intrinsically held water in the resin was determined applying the following equation (1)

**Surface area:** The bulk surface area of MF-T resin was determined by adsorbing methylene blue dye of known initial concentration. It is suggested that monolayer adsorption of this dye occurs on solid adsorbents [21]. Diluents solutions of methylene blue were prepared from initial stock solution of concentration 0.0178 g/l and a calibration curve was determined using spectrophotometer, at  $\lambda = 660 \text{ nm}$ , by measuring diluents-absorbance. To calculate MF-T resin surface area, 0.1 g of MF-T was immersed in 25 ml of methylene blue of concentration 0.0178 g/l. The treatment continued until there was no more decrease in absorbance. The amount of methylene blue adsorbed was calculated according to difference in concentration between the initial and equilibrium values and then surface area was determined by applying equation (2)

**IR analysis:** The spectra of dried samples of MF-T, MF-T-C (resin bearing tartrazine due to adsorption at 15°C) and MF-T-W (resin bearing tartrazine due to adsorption at 45°C) were recorded in the range 400–4000  $\text{cm}^{-1}$  using KBr disc method.

### 2.2.4. Tartrazine adsorption characterization

A stock solution of 100 ppm of tartrazine was prepared by dissolving 0.1 g in 1000 ml of deionised water. Other working solutions were prepared from this stock solution by appropriate dilutions. All adsorption experiments in this work were carried out applying batch method with some conditions kept fixed: tartrazine solution volume (50 ml in 200 ml conical flask), sample agitation rate (100 rpm), pH of tartrazine solution ( $6.7 \pm 0.02$ ), amount of resin in hydrated form (0.2 g) and its grain size (355–710  $\mu\text{m}$ ).

Kinetic study was performed at three different temperatures, 15, 30 and 45°C and each sample has tartrazine initial-concentration of 50 ppm. Every 10 minutes for a total period of 90 minutes, a liquor sample of 3 ml were withdrawn from sample flask with a micropipette and absorbance was recorded and the liquor volume returned back to the sample flask to avoid change in initial concentration for the next record.

Adsorption isotherm was performed at 30°C using five initial concentrations of tartrazine: 30, 40, 50, 60, and 70 ppm. Liquor samples were withdrawn at equilibrium which previously was determined to occur within less than 2 hours and absorbance was recorded. For the thermodynamic study, the adsorption equilibrium (initial concentration: 50 ppm) was investigated for temperatures of 15, 22.5, 30, 37.5 and 45°C.

## 3. Results and Discussion

### 3.1. General

The produced MF-T resin is rigid and its grains are white. By adsorbing tartrazine at any temperature, its color changed into yellowish and this may imply physical adsorption as the sole mechanism.

### 3.2. Characterization of MF-T Resin

The intrinsic water content of resin was found to be notably high (about 53.89 mmol/g, i.e.  $W\% \approx 96.8$ ). This obviously is due to the strong hydrophilic character resin surface [19]. The hydrophilic character is basically due to presence of non-reacted carboxylic (of tartaric acid), amide and non-reacted amino (of melamine) groups present in matrix structure. This high hydrophilicity facilitates solution fast-migration inside pores and hence rapid adsorption of a pollutant [20].

The 0.2 g of hydrated-resin used in adsorption experiments contains only about 0.0064 g resin active mass. This indicates the high porosity of the prepared MF-T. According to equation (2), surface area of the resin was found to be only about 11.6 m<sup>2</sup>/g. It can be concluded that macropores dominate the MF-T-matrix structure which are highly dedicated for the removal of large organic molecules from wastewater [21,22].

### 3.3. Kinetics of Adsorption Process

Experimental data for tartrazine-removal rate by MF-T at temperatures 15, 30 and 45°C are shown in Fig. 1. About 60% of tartrazine was removed during the first 10 minutes for the studied different temperatures. Hydrophilic character is the basic reason of such behavior. Removal at 15°C has the highest rate for the whole period. Accordingly, even at low temperature, adsorption process did not face diffusion-resistance because of macroporosity of resin. Experimental data from Fig. 1 was employed for the investigation of adsorption kinetics applying pseudo-first and pseudo-second order models. Linear regression was applied to get the plots of the two models as shown in Fig. 2 and Fig. 3. From the plots, parameters of each kinetic model, correlation factors,  $r$ , and standard errors,  $SE$ , were determined by applying regression tool of Microsoft Excel program and are given in Table 1. The two models, for each data set (with respect to temperature condition), showed that all correlation factors are significant (the probability that variables are uncorrelated was found to be  $< 5\%$ ) [23]. To recommend a model to best represent these data sets, capacity at equilibrium ( $q_e$ ), correlation factors ( $r$ ), and standard errors ( $SE$ ), were considered.

From table, it can be observed that each capacity value derived from pseudo-second-order model ( $q_e$ ) better represents the corresponding experimental capacity ( $q_{exp}$ ) than those derived from pseudo-first-order model. Also, the values of correlation factors ( $r$ ) and standard errors ( $SE$ ) assign pseudo-second-order model to represent the kinetics of tartrazine removal by MF-T for considered specified temperatures. As adsorption rate follows pseudo-second order model, a sort of chemical interaction involving sharing of electrons between tartrazine and functional groups of the resin can be suggested according to Ho *et al* [24,25,26]. However, a discussion about model-parameters ( $k_2$ ) and ( $h = k_2 q_e^2$ , which defined as initial adsorption rate), may imply some different conclusion. Rate constant ( $k_2$ ) significantly increased as temperature increased. This indicates that process shows a chemical behavior solely. But in parallel to rate constant increase, the capacity ( $q_e$ ) on the contrary significantly decreased. For an endothermic chemisorption process, this can not easily happen especially when isotherm suggests monolayer coverage as discussed in section 3.4. It can be suggested that some sort of exothermic physical interaction, even with comparatively small percentage, is responsible for adsorption of certain amount of tartrazine. And that is why as temperature increases, the capacity ( $q_e$ ) decreases due to desorption of physically adsorbed part. This means that desorption occurs for higher temperature causing noticed decrease in capacity ( $q_e$ ). As will be given in section 3.4., some sort of heterogeneity is suggested for MF-T surface towards tartrazine and physical interaction has a potential probability in this case.



These results suggest that pseudo-second-order model can represent physical adsorption as well as a chemical adsorption. Accordingly, chemical and physical interactions involving electrons sharing and/or exchange and/or intensive working van der Waals forces between adsorbate (tartrazine in this study) and adsorbent surface (MF-T in this study) can be suggested.

### 3.4. Adsorption Isotherm

Figure 4 shows the equilibrium capacity of tartrazine removal ( $q_e$ ) against equilibrium concentration of tartrazine ( $C_e$ ) at 30°C. The isotherm curve shows regular increase of  $q_e$  and curve is concave to the concentration axis which indicates initial rapid increase in adsorption process curve. This indication is in agreement with outputs of kinetic study. This plot is of type I according to Brunauer's classification which belongs to Langmuir model [27,28].

Figures 5 and 6 present the linear plots of the data of adsorption isotherm according to Freundlich and Langmuir models respectively. From these plots, the parameters of each model, correlation factors and standard errors were determined by linear regression applying Microsoft Excel program and are presented in Table 2.

Traditionally, Freundlich and Langmuir models are always applied to investigate the adsorption isotherm of an adsorption isotherm. Such investigation is important to find out the degree of heterogeneity of adsorbent surface towards the specified solute and to find out if the adsorption is monolayer. For the present adsorption system, the two models showed significant correlation [23]. Langmuir model have lower standard error and correlation factor than those shown by Freundlich model. This discussion concludes that some sort of energy non-homogeneity is predicted for resin surface and a certain dual mechanism may be responsible for adsorption. It can be suggested that chemical interaction occurs between tartrazine and resin-groups and the contribution of this reaction in the whole process increases with temperature as kinetic section (3.3.) suggests. This chemical interaction can cause monolayer coverage of MF-T surface by tartrazine. Physical interaction is also suggested to contribute as temperature decreases and in this case monolayer coverage is not solely considered.

This idea can be supported by discussion given about adsorption-kinetic. The Langmuir model gives maximum capacity of 15.38 mg/g which is markedly lower than equilibrium value given by kinetic study at the same temperature (i.e less by 30%,  $q_e \approx 22$  mg/g). Accordingly, although Freundlich model shows higher *SE*, it can be concluded that this model is better to accept the represented tartrazine adsorption on MF-T.

### 3.5. Thermodynamic Behavior

Figure 7 shows the plots of  $\ln K_c$  against  $1/T$  for tartrazine adsorption onto MF-T. It can be concluded from the figure that adsorption behavior changes with temperature. Two ranges can be identified: 15 to 30°C and 30 to 45°C. Exact mid-point between the two ranges may not be specified at 30°C, but it is likely to be close [3].

Table 3 gives the values of enthalpy and entropy changes upon adsorption. For the range 15 – 30°C,  $\Delta H_{ads}$  is negative which means an exothermic adsorption process. Its comparatively small value (5.73 kJ mol<sup>-1</sup>) can indicate that physical-adsorption mechanism dominate this range with minor contribution of chemical-adsorption mechanism, if present. For range 30 – 45°C,  $\Delta H_{ads}$  is positive with a very low value (1.17 kJ mol<sup>-1</sup>). The positivity may indicate a complicated physical/chemical adsorption mechanism with overall endothermic behavior. It can be hypothesized an endothermic chemical interaction which consumes energy emerged

from the accompanying exothermic physical interaction and consumes another excess amount from the surrounding. In this specific case, it can be suggested that energy-contribution of endothermic chemical part slightly overweighs the contribution of exothermic physical part even if its percentage-contribution may be less.

The postulated chemical interaction can be estimated by regarding the chemical structure of tartrazine and the active groups present on the resin surface. Tartrazine molecule includes two sulphonate groups ( $-\text{SO}_3\text{Na}$ ) which can react with linking amine groups ( $-\text{NH}-$ ) due to gentle heating ( $30 - 45^\circ\text{C}$ ) producing sulphonamide. This reaction release NaOH as a side product. This postulated reaction was supported by simple auxiliary experiment in which pH value of a sample was determined before and after tartrazine-adsorption at  $45^\circ\text{C}$ . A measurable increase of about  $0.1 (\pm 0.02)$  was detected and can be explained by the release of NaOH. The increase-value is small due to the small amount of resin used in this experiment.

IR analysis may help understanding the adsorption behavior by considering the IR spectra of MF-T (no adsorbed tartrazine), MF-T-C (tartrazine adsorbed at  $15^\circ\text{C}$ ) and MF-T-W (tartrazine adsorbed at  $45^\circ\text{C}$ ) as shown in Fig. 8. The spectra of MF-T, MF-T-C are almost identical and this means domination of physical adsorption (note: tartrazine does not clearly attribute in the second spectrum due its very low mass percentage in the sample). On the contrary, the comparison of IR spectra of MF-T and MF-T-W gives marked differences especially at  $1752.2 \text{ cm}^{-1}$  (carbonyls of carboxylic group and amide group of matrix-pendent tartrazine). This peak slightly masked by  $1552.9 \text{ cm}^{-1}$  band, spectrum (C), (however, has a recognizable shoulder) due to shift of  $\text{C}=\text{O}$  lower value which masked by  $1552.9 \text{ cm}^{-1}$  band. Depending on this discussion, sulphonate reaction with amine producing sulphonamide is the most probable one.

The azo group, and its environment, which is responsible for the color of tartrazine did not involve in the reaction and that is why the color did not change with this chemical adsorption as mentioned in section 3.1.

For  $15 - 30^\circ\text{C}$  range,  $\Delta S_{\text{ads}}$  is positive and indicates increase in disorder during adsorption of tartrazine from solution to the adsorbent surface. Adsorption of tartrazine molecule itself on MF-T causes more order, but during adsorption hydrating water spheres (tartrazine is highly hydrated due to presence of negatively two sulphonate groups and a carboxylate group) is librated and become mobile in aqueous phase which increase disorder [4]. For  $30 - 45^\circ\text{C}$  range,  $\Delta S_{\text{ads}}$  is also positive obeying same mechanism. However, its value is less in this case due to less water-molecules librated as tartrazine is already less hydrated for this range.

Generally,  $\Delta G_{\text{ads}}$  values are negative confirming the spontaneous nature of this adsorption process in the studied temperature span, Table 4. The absolute value increases with temperature which indicates favoring higher temperatures, i.e more contribution of chemical adsorption mechanism with temperature increase [30].

#### 4. Conclusions

In acidified aqueous medium, melamine–formaldehyde–tartaric acid porous resin (MF-T) was successfully synthesized by anchoring tartaric acid to melamine–formaldehyde matrix. The resin is macroporous with surface area of about  $11.6 \text{ m}^2/\text{g}$  and intrinsic water content of  $96.8\%$  with a hydrophilic surface. The adsorption rate of tartrazine exceeds  $60\%$  within the first 10 minutes for the different temperatures and pseudo-second-order model is assigned to represent the kinetics of tartrazine removal by MF-T. Due to detailed discussion about pseudo-second-



order model parameters and correlation this with outputs of isotherm and thermodynamic studies, chemical and physical interactions between tartrazine and resin are postulated and temperature is the controlling factor to predominate one mechanism over the other. It is important to clarify that, according to the discussions given above, pseudo-second-order model can reflect the nature of adsorption processes which comprises interactions involving electrons sharing and/or exchange and/or intensive working van der waals forces between adsorbate and adsorbent surface. Freundlich model is selected to describe the adsorption process due to concluded energy non-homogeneity of MF-T surface towards tartrazine. Thermodynamic clearly elucidate that tartrazine adsorption onto MF-T is temperature dependent where physical-adsorption dominate lower temperature range (15 – 30°C) and physical/chemical-adsorption is strongly suggested for the higher temperature range (30 – 45°C). Adsorption process is spontaneous in the studied temperature span.

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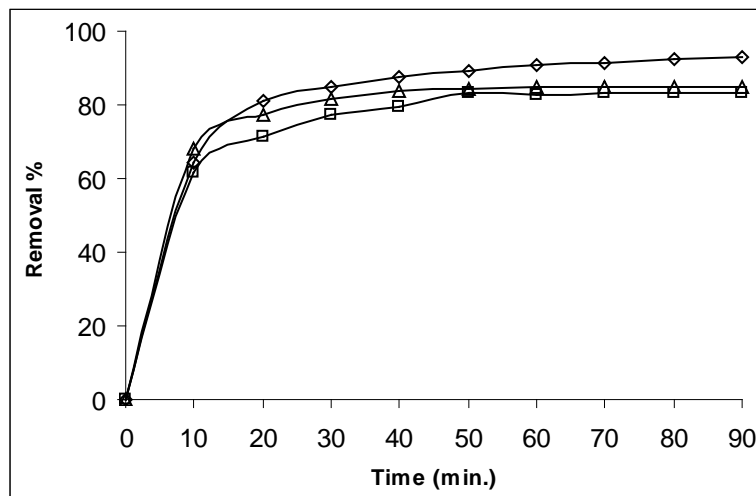
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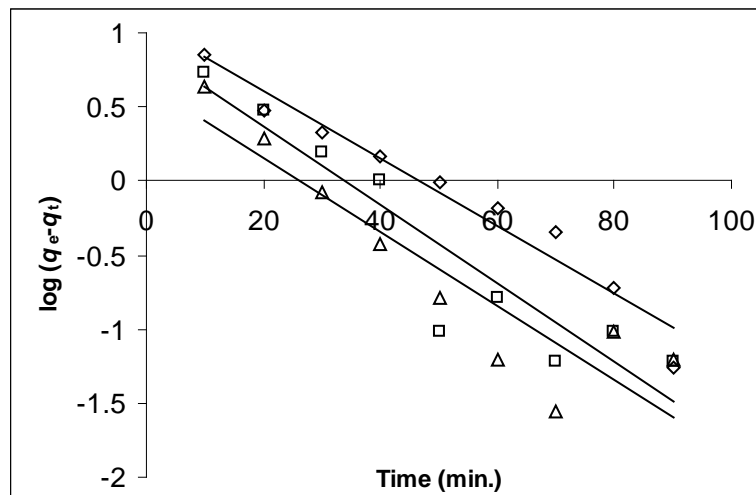
**Table 1 Kinetics data fitting of TZ -removal according to PFO and PSO models**

Temp. (°C)	$C_i$ (ppm)	$q_{exp}$ (mg/g)	Pseudo first order				Pseudo second order			
			$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R$	$SE$	$k_2$ ( $\frac{\text{g/mg}\cdot\text{min}}{h}$ ) ( $\text{mg/g min}$ )	$q_e$ (mg/g)	$r$	$SE$
15	50	23.3	0.0527	11.69	0.9547	0.1614	$8.7 \times 10^{-3}$ 5.216	24.45	0.9999	0.0129
30		20.9	0.0610	7.88	0.8750	0.2999	$1.2 \times 10^{-2}$ 5.565	21.93	0.9995	0.0298
45		21.3	0.0576	4.53	0.8402	0.3554	$2.0 \times 10^{-2}$ 9.443	21.95	0.9998	0.0211

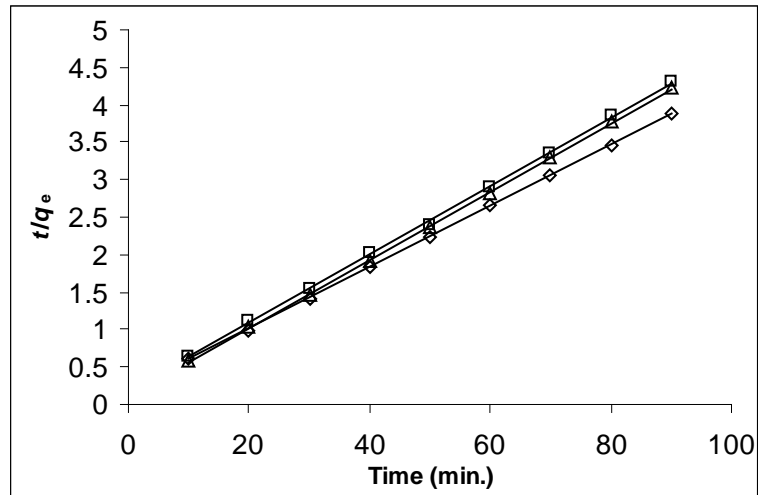




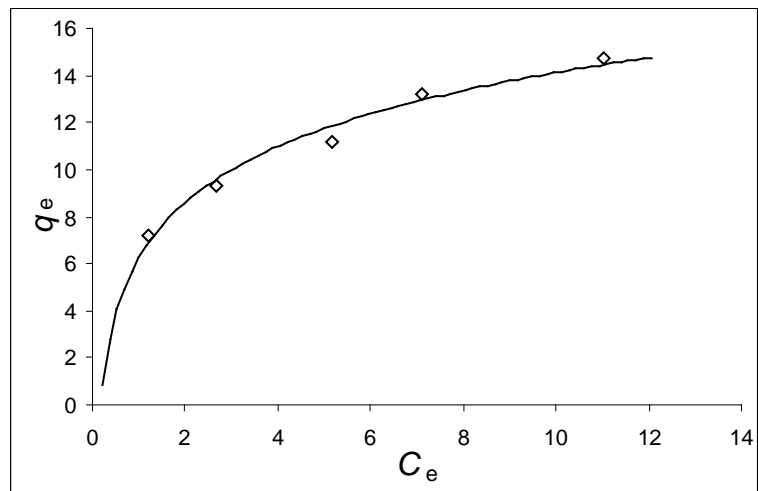
**Fig. 1** TZ removal rate by MF-T at T =15 (◇), 30 (□) and 45 °C (Δ) and initial concentration 50 ppm.



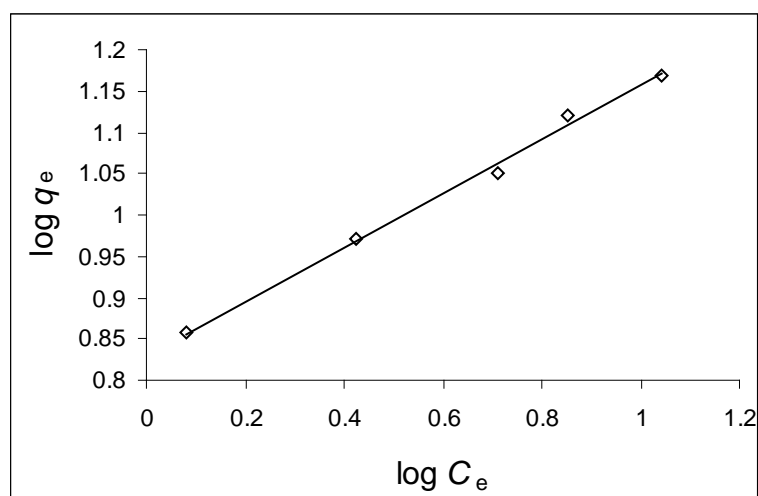
**Fig. 2** PFO plots for TZ adsorption onto MF-T at T =15 (◇), 30 (□) and 45 °C (Δ) and initial concentration 50 ppm.



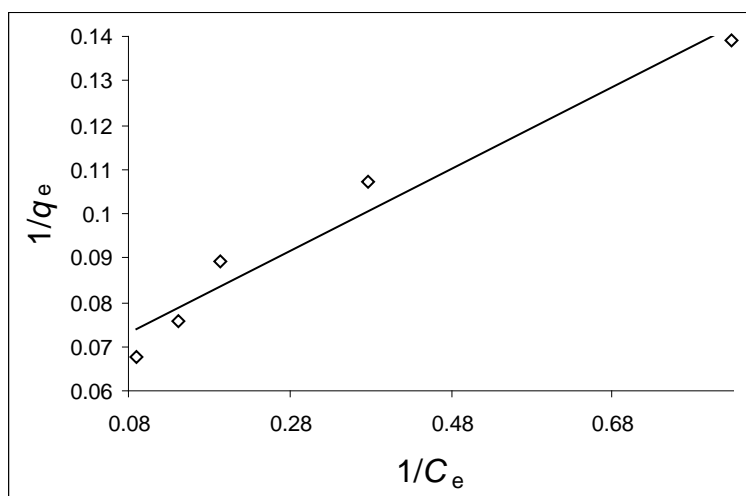
**Fig. 3.** PSO plots for TZ adsorption onto MF-T at  $T = 15$  (◇),  $30$  (□) and  $45$  °C (△) and initial concentration 50 ppm.



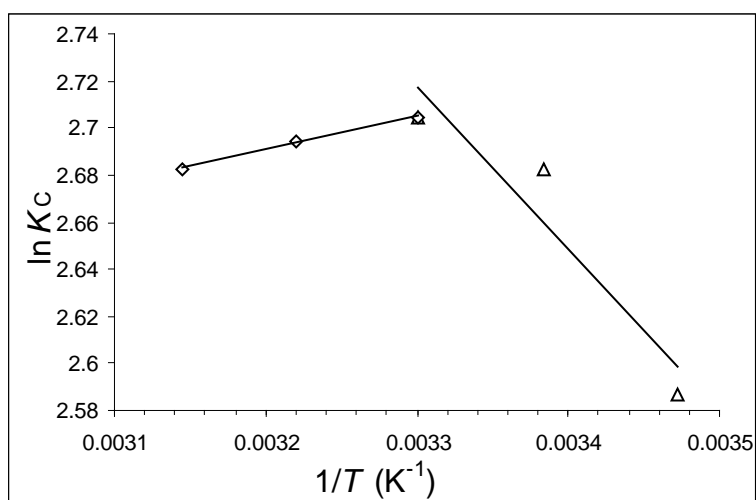
**Fig. 4** Adsorption isotherm (at  $30$  °C) of tartrazine onto MF-T with initial concentrations: 30, 40, 50, 60 and 70 ppm.



**Fig. 5** Freundlich adsorption isotherm of tartrazine onto MF-T (at  $30$  °C).



**Fig. 6** Langmuir adsorption isotherm of tartrazine onto MF-T (at 30 °C).



**Fig. 7** Plots of  $\ln K_c$  against  $1/T$  for TZ adsorption onto MF-T.



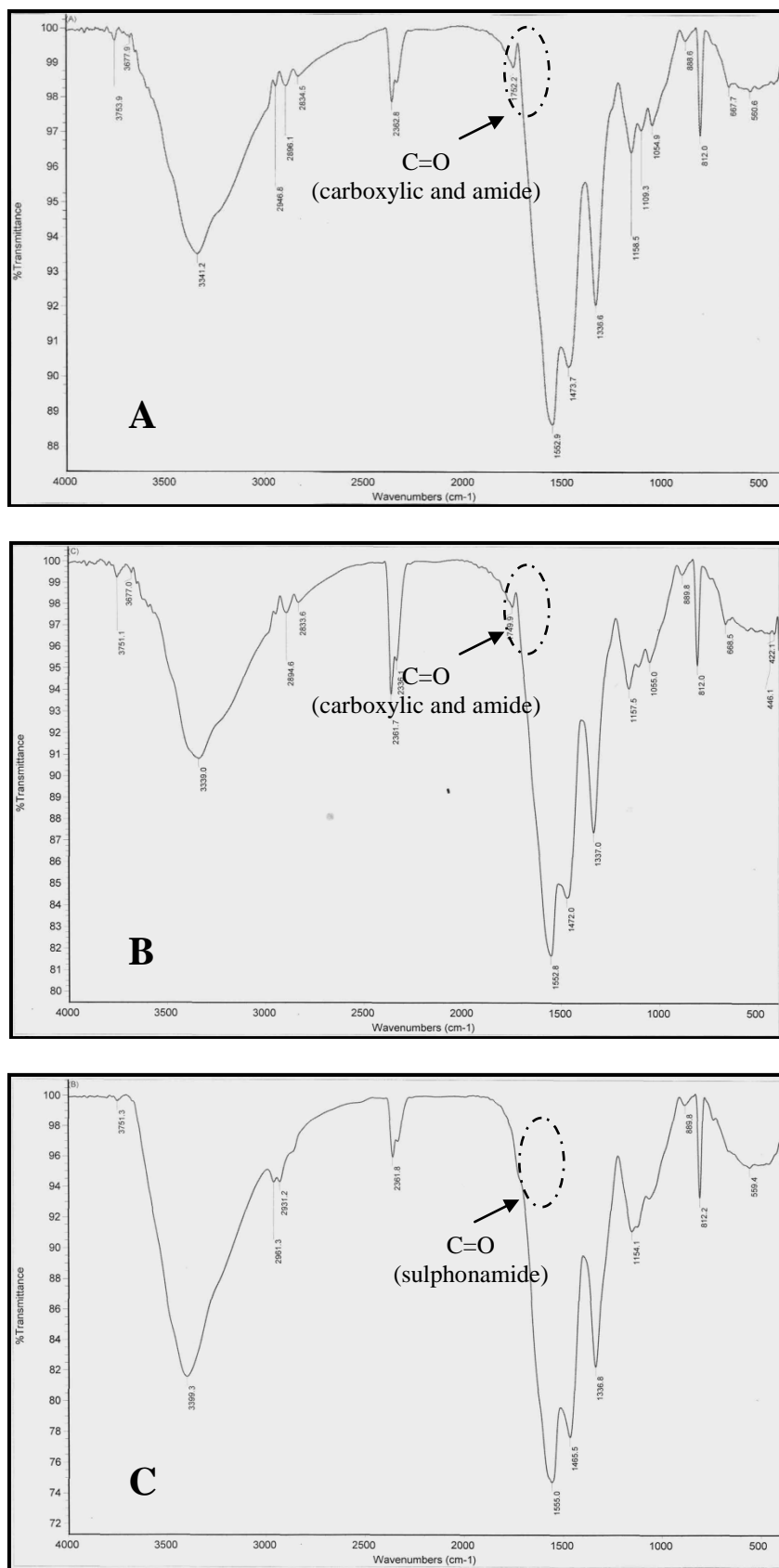


Fig. 8 IR spectra of (A) MF-T, (B) MF-T-C and (C) MF-T-W resins.