Kinetics, Thermodynamics and Isotherm studies on Adsorption of Eriochrome Black-T from aqueous solution using Rutile TiO$_2$

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Abstract. In this study, rutile phase of TiO$_2$ particles have been synthesized by co-precipitation method and is used as an adsorbent for removal of toxic azo dye Eriochrome black-T (EBT) from aqueous solution. The rutile phase of TiO$_2$ was confirmed by the X-ray powder diffraction pattern. Effect of initial dye concentration, adsorbent dose, pH, agitation speed and temperature on the adsorption process of EBT was examined. Removal of EBT was increased by increasing in adsorbent dose and decrease in initial dye concentration and pH. The optimum conditions resulted were: 25 ppm initial dye concentration, 20 mg adsorbent dose and pH of 2. Using Langmuir, Freundlich and Temkin isotherm models, equilibrium data was determined. The Freundlich model showed the best fit for uptake of the EBT dye, which evident that the process of adsorption of EBT dye onto TiO$_2$ particles was heterogeneous. The kinetic data were analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion equation. The pseudo-second order showed the best fit for the kinetic studies (R$^2$ = 0.999), which ascertains that the adsorption process was of chemisorptions type. The intraparticle diffusion model indicated a linear relationship (R$^2$ = 0.99) suggesting the pore diffusion to be a limiting step in the overall adsorption process.

1. Introduction

There is a growing wastewater effluents amount which is being directly resulted during dyes production process as well as in consequences of their usages in many textile, printing and leather industries up to considerable limit [1]. Generally, dyes are of synthetic origin with complex aromatic molecular structures and as such found to be very stable which substantially becomes less biodegradable in nature [2]. Dyes are basically in coloured, ionizing and aromatic organic compound which shows an affinity towards the substrate to which it is being applied. It is generally applied as a aqueous or oil base solution and requires a mordant to improve the fastness on the material on which it is applied. Dyes have various functional variations like acidic, basic, disperse, azo, metal complex, anthraquinone based and others. These organic dyes are highly toxic in nature and therefore, the effluent bearing these dyes must be disposed to the environment after making adequate treatment. Nevertheless, the wastewaters bearing these dyes also obstruct light penetration, decrease the photosynthesis in aquatic plants and raises the COD which create many problems for aquatic life. Dyes can cause allergic dermatitis, skin irritation, cancer and mutations. In global scenario, annually there are more than thousand varieties of commercial dyes and pigments and over 735 tons of synthetic dyes are produced. From the literatures it was found that at about 10–15% of the dyes are lost in the effluent during the dyeing processes [3]. The main problems associated with coloured effluents are that there is the lowering of light penetration, photosynthesis and damage to aesthetic nature of the water surface [4]. Many organic dyestuffs are harmful to human lives, animals and microorganisms. In recent days it has been made mandatory to remove these waste dyes before its release into natural water bodies.
Several physical, chemical, and biological methods have been adopted such as, adsorption, electrochemical treatment, coagulation, precipitation, solvent extraction, membrane filtration and advanced oxidation process while removing dyes and other contaminants from numerous wastewater source [5,6,7]. Few of these processes are effective when the concentration of dye in the effluent is small/trace. Some of them produce large quantity of sludge causing disposal problems, thus causes on increasing the operational costs. However, in recent years the adsorption techniques for wastewater treatment have been widely accepted and practised by the researchers, owing to their efficiency and stability in comparison to biological methods [8-11].

Though, ample of studies are reported, the application of metal oxide particles in waste water treatment is scare in context of the removal of dyes and hence become an interesting area of research [12-19]. Now-a-days several research studies have been reported considering metal oxide particle as a suitable adsorbent. Transitional metal oxide particles have been chosen extensively due to their excellent performances as advanced materials in areas of environment, energy, and adsorption. These metal oxides have various geometrical structures which in turn lead to different chemical and electronic properties. Out of large number of metal oxides present in nature; some of the metal oxides are most useful in accordance with their applications to day to day life in science and technology. Physicochemical properties of metal oxides have special relevance in chemistry and it is mostly related to the industrial use of oxides such as sensors, ceramics, adsorbents and catalysts.

Among many metal oxides, titanium dioxide particles (TiO$_2$) have shown a greater potential for the adsorption of toxic dyes due to its surface physical and chemical property. Their crystal structure may vary depending on the arrangement of TiO$_2$ atoms. Moreover, it acts as a promising semiconductor which is extensively involved in removal of several toxic organic contaminations through both adsorption and photo catalytic process due to the stability of its chemical structure, biocompatibility, strong oxidizing power, non-toxicity and low cost of the metal precursors. In this study, TiO$_2$ particles have been used for removal of Eriochrome black-T (EBT) which is majorly used for dyeing silk, wool, nylon multifibers etc inspite of other chemical demand. However, this dye is hazardous as such and its degradation products like Naphtaquinone are still more carcinogenic nature. A literature survey showed that only few papers have raised the removal of EBT [20-26]. Therefore, TiO$_2$ was adopted as an efficient and low-cost adsorbent for removing this azo dye from aqueous solution in this study. The effect of initial dye concentration, adsorbent dose and pH on the removal efficiency and adsorption capacity has been investigated. Experimental sorption data were also applied to Langmuir, Freundlich and Temkin fitting models. Kinetic studies were carried out by using pseudo-first order, pseudo-second order and intraparticle diffusion equations.

2. Experimental

2.1. Synthesis of TiO$_2$

The co-precipitation method was employed to synthesize TiO$_2$. In a typical reaction 100 ml of distilled water was taken in a conical flask and it was manually cooled to 4°C using ice around the flask with continuous stirring (400rpm). Then 3ml of TiCl$_4$ was added drop wise and the reaction was carried out while covering the flask with aluminium foil for 1 hour under constant agitation mode. Later the solution was allowed for aging of 7 days and suspension formed was centrifuged, filtered and dried in an oven at 60°C over night. Subsequently, the powder obtained was further calcined at 300°C for 1 hour.

2.2. Adsorption experimental procedure

The adsorption of EBT onto TiO$_2$ phase was carried out in batch experiments mode where 100 ml Erlenmeyer flasks containing 50 ml of solutions was taken and to it the desired dose of TiO$_2$ was charged and placed in a magnetic stirrer. The adsorption efficiency of TiO$_2$ was examined in the
function of initial concentration of EBT dye, adsorbent, pH, agitation speed and temperature. To study the adsorption equilibrium, the adsorbent was equilibrated with a definite amount at 55°C temperature for definite time periods. The adsorbent was removed by simple filtration at the end of the predetermined time intervals. The filtrate was analyzed for the residual (i.e. unadsorbed EBT) using double beam UV-Vis spectrophotometer (Shimadzu, UV-1800, Japan) at 530 nm. The amount of EBT dye adsorbed by TiO$_2$ at equilibrium $q_e$ (mmol g$^{-1}$), and $q_t$ (mmol g$^{-1}$) at time $t$ were obtained according to equation (1) and (2) respectively, as follows:

$$q_e = \frac{(C_0 - C_e)V}{m}$$  

(1)

$$q_t = \frac{(C_0 - C_t)V}{m}$$  

(2)

In addition, the percentage of EBT dye adsorbed from aqueous solution with the TiO$_2$ was calculated using Eq. (3):

$$\%M = \frac{(C_0 - C_t)}{C_0} \times 100$$  

(3)

Where $C_0$ and $C_e$ (mol.L$^{-1}$) are initial and equilibrium concentration of EBT dye in aqueous phase, respectively, $C_t$ (mol.L$^{-1}$) is the concentration of EBT at time $t$; V (mL) is the volume of the solution and $m$ (g) is the mass of EBT.

3. Results and discussion

3.1. X-ray diffraction of TiO$_2$

The X-ray diffraction (XRD) pattern of the synthesized TiO$_2$ particles is shown in figure 1. The experimental XRD pattern agrees with the JCPDS card No. 76-1940. The peaks at 20 values 27.4$^0$ (110), 36.1$^0$ (101), 54.3$^0$ (211) and 41.2$^0$ (111) confirm the TiO$_2$ rutile structure. The spectra show the absence of spurious diffractions indicating the crystallographic purity. The intensity of the XRD peaks of the sample reflects that the formed TiO$_2$ particles are crystalline nature and broad diffraction peaks indicate very small size crystallite.

![Figure 1. XRD pattern of TiO$_2$ particles.](image)

3.2. Adsorption studies:

3.2.1. Effect of initial dye concentration:
The initial dye concentration variation study shows the capacity of adsorbents in adsorption process. Fig. 2(a) shows the rate of adsorption to be very rapid initially, and the adsorption equilibrium was achieved within 300 min. It was further observed that the % removal of EBT was decreased due to increase in dye concentration. As observed in Fig. 2(a), when the initial concentration of dye was increased from 5 to 45 ppm, the adsorption efficiency of TiO$_2$ particles decreased from 96.47% to 77.45%, respectively. Initial concentration provides an important driving force which helps to overcome all mass transfer resistances to the dye between the aqueous and solid phases. The reason of decrease in adsorption efficiency with initial concentration of dye is may be due to the dye agglomeration and the reduction of the thermal mobility of the adsorbed aggregates. Hence, a lower initial concentration of dye may enhance the adsorption process. Accordingly, initial EBT dye concentration of 25 ppm is chosen as the suitable concentration range for subsequent experimental studies [27].

3.2.2. Effect of adsorbent dose:
The loading efficiency of an adsorbent can be maximized by varying the adsorbent dose and hence the adsorption of EBT onto the TiO$_2$ as a function of sorbent dose was studied. The effect of adsorbent dose of TiO$_2$ particles on the adsorption of EBT dye was conducted over a range of 10 mg to 50 mg. As elucidated in Fig. 2(b), the efficiency of EBT adsorption was increased from 79.24 % to 97.85% when the adsorbent dose increases from 10 mg to 50 mg. The efficiency of adsorption increases with the adsorbent dose was due to increase in surface area and the availability of more adsorption active sites. Further by increase in the adsorbent dose beyond of 50 mg, the adsorption efficiency gradually decreases due to overlapping of adsorption sites as a result of overcrowding of adsorbent [28].

3.2.3. Effect of pH:
During the adsorption reaction, the effect of pH plays an important role on the active sites of the surface of the metal oxide. Effect of pH on EBT adsorption onto the TiO$_2$ particles was carried out at 25 ppm of initial dye concentration, 20 mg mass of adsorbent at 328K temperature at a stirring rate 400 rpm up to 300 min. Fig 2(c) displays the effect of pH on the removal of EBT from which, it can be observed that the maximum removal efficiency of dye was at pH 2.0. The effect of pH for the removal of EBT dyes from aqueous solution at varying solution pH 2.0 to 4.0. From the results, the removal percentage of EBT found to follow increasing trend (up to 94%) while decreasing the solution pH to 2.0 and then gradually decreases when the pH was increased to 4.0. Two possible mechanism of EBT adsorption onto TiO$_2$ may be considered (i) charged sites decreases and (ii) negatively charged sites increases. A negatively charged surface does not favour the adsorption of dye anions due to electrostatic repulsion. The presence of sulphonate groups (–SO$_3$) in EBT proves it is an anionic dye and form negative charge in aqueous solution. At lower pH range, as the H$^+$ ion concentration increases and in other way on increase in acidity of the solution lead to favour the adsorption process on due to again strong electrostatic attraction of oppositely charged ion as proton and EBT dye and consequence of which strong adsorption of EBT on to the metal oxide surface was resulted [29].

3.2.4. Effect of agitation speed:
Effect of agitation speed is one of the important factors which play the key role to control over the solid-liquid mass transfer mechanism while affecting the external boundary film as well as the distribution of the solute in the bulk solution. To ensure that the adsorption of EBT onto TiO$_2$ experiments were carried out by varying the agitation speed within 200-800 rpm at varied contact time (0 to 300 min) using 20 mg of samples, pH 2.0, temperature 328 K and 25 ppm concentration the dye solution. As shown in Fig. 2(d) the percentage of EBT adsorption was maximized at 400 rpm of
agitation speed at all the studied EBT concentration ranges and beyond which it decreases due to low mass transfer of adsorbate to the internal surface of TiO$_2$ particle. Therefore, further experiments were carried out keeping the agitation speed at 400 rpm.

![Graphs showing effect of initial dye concentration, adsorbent dose, pH, and agitation speed on adsorption of EBT on TiO$_2$.](image)

**Figure 2.** (a) Effect of initial dye concentration (b) Effect of adsorbent dose (c) Effect of pH (d) Effect of agitation speed, on adsorption of EBT on TiO$_2$ (conditions: 20mg of TiO$_2$, 25ppm of dye solution, pH 2, agitation speed 400 rpm).

3.2.5. *Effect of temperature:*

The nature of adsorption process like endothermic or exothermic can be ascertained by thermodynamic study. Therefore, the efficiency of adsorption of EBT on TiO$_2$ was investigated at the temperature range of 288-328 K where other parameters were kept fixed; the adsorbent mass 20 mg, agitation speed 400 rpm, EBT dye concentration 25 ppm and pH 2.0. The plot of percentage of adsorption vs. time at different temperatures was shown in Fig.3, from which it was observed that with increase in temperature of the solution the adsorption capacity of EBT increased. The equilibrium constant $K_c$ resulted from this study for adsorption was calculated using the equation (4).

$$K_c = \frac{C_a e}{C_e}$$  \hspace{1cm} (4)
Where \( C_{ae} \) and \( C_e \) are the concentrations of EBT in adsorbent phase (g/L) and in solution (g/L) at equilibrium, respectively. From the temperature variation plot the values of \( \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \) can be calculated by the following thermodynamic relationships in Eqns. (5), (6) and (7).

\[
\begin{align*}
\Delta G^0 &= -RT \ln K_c \\
\Delta G^0 &= \Delta H^0 - T \Delta S^0 \\
\log K_c &= \frac{\Delta S^0}{2303} - \frac{\Delta H^0}{2303RT}
\end{align*}
\]  

Where \( \Delta G^0 \) is the standard free energy, \( \Delta H^0 \) and \( \Delta S^0 \) are the enthalpy and entropy change of adsorption process. The plot of the \( \log K_c \) as a function of \( 1/T \), based on the Vant Hoff relationship in accordance to Eq.(7), showed straight lines was presented in Fig.4 (b).

![Figure 3](image3.png)

**Figure 3.** Effect of temperature on adsorption of EBT (conditions: 20mg of TiO\(_2\), 25ppm of dye solution, pH 2, agitation speed 400rpm).

![Figure 4](image4.png)

**Figure 4.** Effect of temperature on adsorption of EBT (a) Equilibrium constants for EBT on TiO\(_2\) as function of temperature (b) Van’t Hoff plot for exchange of EBT with TiO\(_2\).

The thermodynamics constants determined from the experimental study appear to be consistent and independent of initial dye concentration of the solution. The values of \( \Delta H^0 \) and \( \Delta S^0 \) were calculated
from the slope and intercept, respectively. The negative value of $\Delta G^\circ$ (-12.19, -13.67, -15.15, -16.63, -18.11 for temp. 288K, 298K, 308K, 318K and 328K for TiO$_2$ respectively) indicated the feasibility of the adsorption process and the spontaneous interaction of dye ion with active sites of the adsorbent. The negative value of $\Delta H^\circ$ (-30.43 kJmol$^{-1}$) of TiO$_2$ corresponds to an exothermic nature of the adsorption process. The positive values of $\Delta S^\circ$ (0.148Jmol$^{-1}$K$^{-1}$) reveals the increased randomness of the dye and adsorbent interface during adsorption process.

4. Kinetic study

The adsorption kinetics of EBT onto titanium dioxide particles are evaluated following to the pseudo first-order and pseudo second-order models. To understand the transient behavior of adsorption and its potential rate controlling step which accomplished the mass transport and chemical reaction processes, adsorption kinetics was investigated following three kinetic models i.e. pseudo-first-order, pseudo-second-order and intraparticle diffusion models as given in equations (8), (9) and (10), respectively. EBT dye adsorption onto TiO$_2$ phase can easily be explained by two distinct mechanisms: (a) An initial rapid binding of dye molecules on the adsorbent surface, and (b) Relatively slow intraparticle diffusion. The first-order, the pseudo second-order, and intraparticle or film diffusion models were applied to fit the resulted data from kinetic study experiments.

The pseudo-first order equation, which is based on solid capacity, is shown in Eq. (8):

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

Where $q_e$ is the equilibrium adsorption capacity (mg/g), $q_t$ is the adsorption capacity at time t (mg/g) and $k_1$ is the pseudo-first order rate constant (min$^{-1}$) [30].

The pseudo-second order model is represented by Eq. (9)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

Where $k_2$ is the rate constant of pseudo-second order adsorption (g/mg min) [31].

The intraparticle diffusion model indicates that the rate limiting step is the transport of the solute from the bulk of solution into adsorbent pores through an intraparticle process [32] and the corresponding equation is as given in Eq. (10):

$$q_t = X_i + K_p t^{1/2}$$

Where $k_p$ is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and $X_i$ is the thickness of the boundary layer.

To ascertain the characteristics of adsorption behaviour the pseudo first and pseudo second order kinetic model was applied to fit the experimental data obtained from adsorption experiments and shown in Fig. 5(a) and (b). The correlation coefficient values for pseudo-first order, pseudo-second order and intraparticle diffusion are of $R^2 = 0.989$, $R^2 = 0.999$ and $R^2 = 0.994$, respectively. In addition, it was found that the calculated equilibrium adsorption capacity ($q_e$) for pseudo-first-order kinetic model (TiO$_2$ = 1.076) was significantly lower than the pseudo-second order kinetics calculated value of $q_e$ (TiO$_2$ = 9.434). Thus, it was presumed that the pseudo-second-order model provides better correlation of sorption fit than the pseudo-first-order model for TiO$_2$ ensuring that the rate limiting step may be of chemisorption type [33].
**Figure 5.** (a) Pseudo-first-order kinetics and (b) Pseudo-second-order kinetics for adsorption of EBT by TiO$_2$ (conditions: 20mg of TiO$_2$, 25ppm of dye solution, pH 2, agitation speed 400rpm).

![Graph](image_url)

**Figure 6.** Fitting result of intra particle diffusion model for adsorption of EBT by TiO$_2$ (conditions: 20mg of TiO$_2$, 25ppm of dye solution, pH 2, agitation speed 400 rpm).

However, it should be noted that the intraparticle diffusion model (in Fig.6) also demonstrated a high R$^2$ value of 0.994, which indicates that pore diffusion also affects the rate of EBT adsorption. However, since the y-intercept ($X_i$) is not equal to zero, it implies that this mechanism does not solely limit the overall adsorption process. The rate-limiting step may be a combination of chemisorptions and intraparticle diffusion [33].

5. **Adsorption isotherms studies**

To comprehend the adsorption potential between adsorbent and adsorbate, the isotherm models such as Langmuir, Freundlich and Temkin need to be investigated. To fit the data for adsorption isotherm study, the experiments are conducted while varying initial EBT concentration (25 ppm) at 328 K and pH 2.0 and the other parameters were: mass of adsorbent 20 mg, agitation speed 400 rpm and solution volume of 50 ml kept constant. As shown in Fig. 2(a), it was seen that the amount of EBT dye adsorbed per unit mass material increased with time and reached the plateau value when the active sites of the adsorbent were saturated. The equilibrium adsorption data of different initial dye concentrations were analyzed according to Langmuir, Freundlich and Temkin isotherm models [34-35] as given in equations (11), (12) and (13), respectively.

$$
\frac{C_s}{q_e} = \frac{1}{bq_m} + C_e \left( \frac{1}{q_m} \right)
$$

(11)

$$
\log q_e = \log k_F + \frac{1}{n} \log C_e
$$

(12)

$$
q_e = k_1 \ln k_2 + k_1 \ln C_e
$$

(13)

Where $q_e$ (mg/g) is the amount of dye adsorbed at the equilibrium, $C_e$ (ppm) is the concentration of solution at the equilibrium state of the system, b is the Langmuir constant (L/mg), and $q_m$ is the maximum adsorption capacity, $k_F$ is the Freundlich constant (L/mg), $c_e$ is concentration of the dye at equilibrium (mg L$^{-1}$), $k_1$ (RT/b) is related to the heat of adsorption, and $k_2$ is the equilibrium binding constant (L.mg$^{-1}$).

The essential characteristics of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, $R_L$, defined by equation (14)

$$
R_L = \frac{1}{1 + bC_0}
$$

(14)
Where “b” is the Langmuir constant and \(C_0\) is the highest initial dye concentration. From this \(R_L\) we can determine the process of adsorption isotherm. The adsorption isotherm is irreversible if \(R_L = 0\), the isotherm is favorable if \(0 < R_L < 1\), linear if \(R_L = 1\) or unfavorable if \(R_L > 1\). From the Fig.6, it is clear that the Langmuir isotherm model is not well fitted, which suggests the surface of the particle is not homogeneous in nature.

**Figure 7.** Plot of Langmuir isotherm for adsorption of EBT by TiO\(_2\) (conditions: 20mg of TiO\(_2\), 25ppm of dye solution, pH 2, agitation speed 400 rpm)

The adsorption data were further interpreted while fitting with Freundlich isotherm model and the plot of \(\log q_e\) vs. \(\log C_e\) also showed straight lines as can be seen in Fig.8 is for TiO\(_2\). It is known that the value of \(K_F\) indicates adsorption capacity and \(1/n\) is the adsorption intensity and both of these values can be derived from the slope of the above plots. The values of \(R^2\), \(K_F\) and \(1/n\) are obtained from the slope and intercept of the straight line. According to the adsorption data, the Freundlich isotherm model showed well fitting \(R^2 = 0.999\). The surface heterogeneity of an adsorbent is represented by using \(1/n\) value, in which the adsorption is considered favorable and heterogeneous when the value of \(1/n\) lies between 0 and 1, the adsorption is homogenous in which there is no interaction among the adsorbed species when \(1/n = 1\) and the adsorption is unfavorable when \(1/n > 1.46\). In this case, the value of \(1/n\) is 0.996; this value implies only 90 % of active adsorption having equal energy level, indicating that there is a possibility of multilayer adsorption of EBT on the heterogeneous sites of TiO\(_2\).
**Figure 8.** Plot of Freundlich isotherm for adsorption of EBT by TiO$_2$ (conditions: 20mg of TiO$_2$, 25ppm of dye solution, pH 2, agitation speed 400rpm).

![Graph of Freundlich isotherm]

**Figure 9.** Plot of Temkin isotherm for adsorption of EBT by TiO$_2$ (conditions: 20mg of TiO$_2$, 25ppm of dye solution, pH 2, agitation speed 400rpm)

The derivation of Tempkin isotherm ensures that the fall in the heat of adsorption is linear rather than logarithmic as implied in the Freundlich equation. The heat of adsorption of all of the molecules in the layer would decrease linearly with coverage due to adsorbent/adsorbate interaction. The linear form of the Tempkin isotherm can be expressed as equation (13). A plot of $q_e$ versus ln$c_e$ was shown in Fig.9 and the values of constants $k_1$ and $k_2$ and the correlation coefficients for Tempkin was calculated. From the results, it was observed that the correlation coefficient ($R^2$) did not fit well with the experimental data. Therefore, the adsorption process is depending upon the chemical structures of the dye and also the absorbents. While comparing the results with Langmuir, Freundlich, Tempkin isotherm model, it was also seen that the $R^2$ value is close to unity in case of Freundlich isotherm’s model and Tempkin of TiO$_2$ indicating about the adsorption mechanism which is governed by chemisorptions process and the finding of the present study is well agreement with the reported literatures [27,36,37] where the several synthetic materials has been used to adsorb dye ions from aqueous solution.

### 6. Conclusion

In this study, the removal of EBT from its aqueous solutions was investigated. TiO$_2$ was synthesized by co-precipitation method. The X-Ray diffraction pattern showed that the structure of TiO$_2$ particles was rutile structure. The optimum conditions of various adsorption parameters obtained were 25 ppm initial dye concentration, 20 mg adsorbent dose, pH 2.0 and 328K temperature. Adsorption isotherm results showed best fit with Freundlich ($R^2$=0.999) and Tempkin ($R^2$=0.999) model. Kinetics result revealed adsorption of EBT is pseudo-second-order and chemisorptions type. Thermodynamic parameters such as change in Gibbs free energy ($\Delta G^\circ$), adsorption enthalpy ($\Delta H^\circ$) and adsorption entropy ($\Delta S^\circ$) were determined which showed the relevance on favoring the adsorption process. The negative value of $\Delta H^\circ$ (-30.43 kJmol$^{-1}$) indicates an exothermic nature of adsorption & positive value of $\Delta S^\circ$ (+ 0.148 Jmol$^{-1}$K$^{-1}$) indicates the increased randomness of dye during adsorption. The above results reveal the usages of rutile TiO$_2$ particles, to be effective absorbent for the purification of contaminated water as well as process aqueous solution.
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