Kinetic and Isotherm Modelling of the Adsorption of Congo Red Dye onto NiFe$_2$O$_4$ and NiFe$_2$O$_4$ decorated Exfoliated Graphite

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Abstract. Adsorption using novel materials is a common and highly applicable process in remediation of hazardous dyes in wastewater. Herein, we attempted the synthesis of NiFe$_2$O$_4$ decorated-exfoliated graphite (EG@NiFe$_2$O$_4$), an inexpensive and environmental benign material, and analyzed the adsorption process of the as-synthesized adsorbent against Congo red dye. Kinetic of the adsorption was investigated using various models including first-pseudo kinetic, second-pseudo kinetic, Bangham model and Elovich model. Isotherm of the process was evaluated by Langmuir, Freundlich, Temkin and Dubinin − Radushkevich model. Lastly, thermodynamic parameters of the adsorption towards Congo red dye was calculated. Our findings indicated that kinetic and isotherm of the adsorption process of both adsorbents (EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$) could be well explained by the pseudo-second-order model ($R^2 > 0.99$) and Langmuir isotherm ($R^2 = $) respectively. In addition, kinetic parameters showed that EG@NiFe$_2$O$_4$ possesses greater adsorption capacity in comparison with NiFe$_2$O$_4$. Estimated thermodynamic parameters also indicated the spontaneous and endothermic adsorption ($\Delta G = $) of the EG@NiFe$_2$O$_4$ composite against Congo red dye.

1. Introduction
Prevalence of dyes presenting in industrial effluents has called for development of decontamination measures that are specific for dye treatment. Of which, adsorption using a wide range of materials such as activated carbon, anion exchange resin, active sludge, peat, steel plant slag and fly ash has been shown to be effective in removing dye in aqueous media [1-14]. Expanded graphite (EG), has recently gained attention as a promising adsorbent due to high sorption capacity against many contaminants [15-18]. Especially against dye, EG has shown excellent adsorption efficiency due to its low density and multi-porosity nature. However, after adsorption, EG is difficult to be recovered, limiting its applications. One approach that has been suggested to address this issue is to attach a magnetic component, such as NiFe$_2$O$_4$ into adsorbent to allow recovering of the adsorbent by a magnetic field [18-22]. Structurally, the inverse spinel structure of NiFe$_2$O$_4$ consists of ferric ions that are evenly distributed on the tetrahedral sites (A-sites) and on the octahedral sites (B-sites). Conventional applications of NiFe$_2$O$_4$ include microwave absorber and as material in high density magnetic recording media and magnetic refrigeration [21-22].

Herein, we combined EG and NiFe$_2$O$_4$ precursors to manufacture an EG@NiFe$_2$O$_4$ nanocomposite that is applicable in adsorption technologies. Various adsorption characteristics of the as-synthesized...
EG@NiFe$_2$O$_4$ were calculated. In addition, the fit of the adsorption process to pseudo-second-order rate model, as well as Freundlich and Langmuir isotherm models was evaluated.

2. Materials and methods

2.1 Synthesis of EG@NiFe$_2$O$_4$

EG@NiFe$_2$O$_4$ was synthesized by sol-gel method, which was initiated by dissolving NiCl$_2\cdot$6H$_2$O (1 mmol) and FeCl$_3\cdot$6H$_2$O (2 mmol) in 60 mL of water. The mixture was then heated under stirring to 90°C. Then, citric acid solution was added (molecular ratio of acid/molar Fe$^{3+}$ of 4: 1) and the mixture was allowed to react at 90°C for 1 h. Afterwards, EG was added (EG/NiFe$_2$O$_4$ ratio of 3:1) slowly and the mixture was gently stirred. The solution pH was approximately 7–8.

pH was then adjusted for the second time until the exfoliate was appeared on the reaction vessel surface, forming a gel solution. The afforded gel was dried at 80°C for 20 hours and then heated in a muffle kiln to separate the graphite layers again.

2.2 Adsorption experiments

Congo red (CR), a type of azo dye, was selected as the adsorbate in this study. The adsorption reaction system consists of 100 mL of CR and 0.05 g of as-synthesized EG@NiFe$_2$O$_4$ in a 250 mL beaker. The mixture was shaken at 200 rpm under room temperature. The equilibrium adsorption capacity, $q_e$ (mg/g) and removal efficiency were calculated as follows:

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

(2.1)

Removal (%) = \frac{C_0 - C_e}{C_0} \times 100\%$$

(2.2)

where $C$ is the CR concentration (mg/L). The subscript 0 and e denotes the initial and equilibrium concentration state of the system, respectively. $V$ is the CR volume and $m$ is the adsorbent weight.

2.3 Estimation of adsorption kinetics

Four kinetics including first-pseudo kinetic, second-pseudo kinetic, Bangham model and Elovich model were selected for analysis in this study. The kinetics represent the diffusion of adsorbate molecules into pores of the adsorbent. In each kinetic, multiple initial concentration values of CR were selected including 20, 30, 40, 50 and 60 mg/L. In each experiment, total adsorption time was 4 hours and solution samples were taken after certain intervals to measure for CR concentration using UV–vis spectrometry at 497 nm of wavelength.

2.4 Estimation of adsorption isotherms

Four adsorption isotherms including Freundlich, Langmuir, Dubinin and Temkin – Radushkevich model were considered. Each isotherm represents the relationship between total mass of solids adsorbed on the material surface and the equilibrium concentration at a certain temperature.

2.5 Estimation of thermodynamic parameters

The thermodynamic equation represents the relationship between temperature and reaction energies and describes the transformation of energies into other energy forms and their influence on the adsorption process. The Van't Hoff thermodynamic equation is expressed as follows:

$$\ln K_C = \left(\frac{\Delta H^o}{R} \right) \frac{1}{T} + \left(\frac{\Delta S^o}{R} \right)$$

(2.3)

where $\Delta H^o$ and $\Delta S^o$ are values of enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$), respectively. $R$ is the gas constant; $T$ is the absolute temperature and $K_C$ is thermodynamic equilibrium constant. Of which, $K_C$ is calculated as follows.

$$K_C = \frac{q_e}{C_e}$$

(2.4)
To gather data for calculation of $K_c$ and for estimation of $\Delta H^o$ and $\Delta S^o$, multiple adsorption experiments were carried out initially at 20 mg/L of CR concentration with 0.05 g of adsorbent at different temperatures of 283, 293, 303 and 313 K. The estimated $\Delta H^o$ and $\Delta S^o$ parameters were then used to calculate Gibb’s free energy ($\Delta G^o$) values corresponding to four temperature levels using the formula:

$$\Delta G^o = -RT\ln KC$$ (2.5)

3. Results and discussion

3.1 Adsorption kinetics

The adsorption kinetic study provides valuable information about the processes and mechanisms of adsorption reactions in the treatment of wastewater using nanomaterials. Figures 1 and 2 show data points and fittings of different kinetics models with experimental data. Model parameters are also summarized in Tables 1 and 2. Since the adsorption process could be influenced by the number of factors including structure of the adsorbent, estimation of multiple models is preferred. Among examined models, the pseudo-second order model reveals a higher coefficient of determination ($R^2 > 0.99$) than other models, suggesting better fit of experimental data. When compared with the pseudo-first order, the pseudo-second order model with $R^2$ is closer to unity and a higher $Q_{max}$ presented a better fit. The CR adsorption models on NiFe$_2$O$_4$ also share the same trend with EG@NiFe$_2$O$_4$ models. Therefore, the second order quadratic model, which describes the chemical adsorption, is more suitable to describe the current adsorption process.

On the other hand, Elovich model results of both materials showed that the CR adsorption rate ($\alpha$, mg/g.min) is much higher than the desorption rate CR ($\beta$, g / mg). However, the difference between $\alpha$ and $\beta$ in the Elovich result of EG@NiFe$_2$O$_4$ is more profound than in that of NiFe$_2$O$_4$, suggesting better adsorption capacity of EG@NiFe$_2$O$_4$. From the Bangham model, it can be seen that the correlation coefficient was ranged between 0.77549 and 0.97169, indicating the key role of pore diffusion in CR uptake onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$. Moreover, estimated parameters of the Bangham model indicated that pore diffusion is not the sole driver of adsorption rate, as evidenced by the linearity of Bangham plot. Multilinear profile was obtained for intraparticle diffusion model plot and this plot did not pass through the origin (Fig. 1(d), Fig. 2(d)), this suggests that boundary layer diffusion also occurred in the uptake of CR onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$.

![Figure 1. Kinetic models for adsorption of CR using EG@NiFe$_2$O$_4$ with a) Pseudo-first-order b) Pseudo-second-order; c) Elovich model; d) Bangham model](image1)

![Figure 2. Kinetic models for adsorption of CR using NiFe$_2$O$_4$ with a) Pseudo-first-order; b) Pseudo-second-order; c) Elovich model and d) Bangham model](image2)
\[ t = \frac{1}{Q_k} \rho \frac{1}{Q_0} + \frac{1}{Q_k} \frac{t}{Q_0} \]

\[ H = k_2Q_2^2 \]

\[ \log (\frac{k_2}{Q_2}) + \frac{t}{Q_2} = K_2 \]

\[ H = k_2Q_2^2 \]

Table 1. Kinetic model parameters for adsorption of CR using EG@NiFe₂O₄

| Models | Parameters | Concentrations (mg/L) |
|--------|------------|-----------------------|
|        |            | 20   | 30   | 40   | 50   | 60   |
| Pseudo-first-order (3.1) | k₁ | (min⁻¹)(mg/L)¹/₁₀ | 0.0166 | 0.0135 | 0.0091 | 0.0122 | 0.0117 |
|        | Q₁ (mg/g) |       | 8.95  | 13.44  | 25.53  | 15.69  | 22.11  |
|        | R²        |       | 0.8825 | 0.77969 | 0.92895 | 0.93234 | 0.90096 |
| Pseudo-second-order (3.2) | k₂ (g/(mg.min)) | | 0.0057 | 0.0030 | 0.0015 | 0.0031 | 0.0015 |
|        | Q₂ (mg/g) |       | 37.85  | 56.46  | 76.51  | 93.11  | 48.78  |
|        | H = k₂Q₂² |       | 8.19  | 9.67  | 8.71  | 26.94  | 3.62  |
|        | R²        |       | 0.99969 | 0.99929 | 0.99637 | 0.99957 | 0.99461 |
| Elovich (3.4) | β (g/mg) | | 0.2654 | 0.1411 | 0.1262 | 0.1949 | 0.1380 |
|        | α (mg/(g.min)) | | 484.44 | 117.72 | 432.23 | 469.73 | 22.35 |
|        | R²        |       | 0.74904 | 0.72331 | 0.97559 | 0.96056 | 0.91968 |
| Bangham (3.5) | kₕ (mL/(g/L)) | | 0.053  | 0.037  | 0.046  | 0.093  | 0.121  |
|        | αₚ | | 0.35017 | 0.38975 | 0.31013 | 0.1535 | 0.27096 |
|        | R²        |       | 0.86255 | 0.77549 | 0.95461 | 0.97169 | 0.87557 |

Table 2. Kinetics model parameters for adsorption of CR using NiFe₂O₄

| Models | Parameters | Concentrations (mg/L) |
|--------|------------|-----------------------|
|        |            | 20   | 30   | 40   | 50   | 60   |
| Pseudo-first-order (3.1) | k₁ | (min⁻¹)(mg/L)¹/₁₀ | 0.0196 | 0.0151 | 0.0195 | 0.0234 | 0.0236 |
|        | Q₁ (mg/g) |       | 14.74  | 19.06  | 18.57  | 23.67  | 32.40  |
|        | R²        |       | 0.95777 | 0.97645 | 0.93581 | 0.86259 | 0.6757 |
| Pseudo-second-order (3.2) | k₂ (g/(mg.min)) | | 0.0026 | 0.0019 | 0.0026 | 0.0025 | 0.0015 |
|        | Q₂ (mg/g) |       | 28.47  | 38.47  | 41.27  | 44.36  | 39.01  |
|        | H = k₂Q₂² |       | 2.15  | 2.85  | 4.48  | 4.89  | 2.29  |
|        | R²        |       | 0.99643 | 0.99572 | 0.99767 | 0.99814 | 0.98674 |
| Elovich (3.4) | β (g/mg) | | 0.2607 | 0.1952 | 0.1930 | 0.1659 | 0.2645 |
|        | α (mg/(g.min)) | | 31.48 | 41.69 | 86.32 | 50.98 | 360.54 |
|        | R²        |       | 0.97579 | 0.97017 | 0.93842 | 0.95447 | 0.92916 |
| Bangham (3.5) | kₕ (mL/(g/L)) | | 0.0303 | 0.0266 | 0.0252 | 0.0189 | 0.0174 |
|        | αₚ | | 0.28722 | 0.25533 | 0.20561 | 0.21529 | 0.14132 |
|        | R²        |       | 0.975  | 0.97319 | 0.95719 | 0.96749 | 0.94306 |
3.2 Adsorption isotherm

To elucidate the thermodynamics of CR adsorption onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$, the adsorption data was analyzed by using Freundlich, Langmuir, Temkin and D-R. Calculated parameters are listed in Table 3. By comparing $R^2$ values, it was shown that Langmuir model gave better higher fittings than Freundlich, Temkin and Dubinin-Radushkevich (D–R) models, implying CR adsorption onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ may follow the chemisorption process. The Langmuir isotherm suggests that only one layer of solute molecules is adsorbed onto a surface that have identical adsorption sites.

Table 3 gives results on Langmuir isotherm fittings with coefficient of determination ($R^2$) of 0.96025 and 0.99915 respectively corresponding to Langmuir isotherm of EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ adsorption. Considering that $K_L$ values are very important equilibrium parameters for estimating equilibrium constants (determination of thermodynamic parameters), the use of Langmuir linearized isotherms could lead to erroneous estimation of Gibb’s free energy change ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$), and entropy change ($\Delta S^\circ$) of adsorption [1]. Besides, the adsorption energy ($E$) obtained from Dubinin–Radushkevich (D–R) isotherm reached under 10 kJ/mol, suggesting that the uptake of CR onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ were by physisorption.

![Figure 3. Isotherm models of EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$ with a) Langmuir isotherm model; b) Freundlich isotherm model; c) Temkin isotherm model and d) Dubinin–Radushkevich isotherm model](image-url)
Table 3. Parameters of Freundlich, Langmuir, Dubinin–Radushkevich and Temkin isotherms for adsorption of dyes onto EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$

| Model       | Parameters          | EG@NiFe$_2$O$_4$ | NiFe$_2$O$_4$ |
|-------------|---------------------|------------------|---------------|
| Langmuir    | $k_L$ (L/mg)        | 0.79             | 0.28          |
|             | $\frac{1}{Q_e} = \left( \frac{1}{Q_m K_L} \right) C \left( 1 + K_L C \right)$ |                  |               |
|             | $Q_m$ (mg/g)        | 112.36           | 52.57         |
|             | $R_L = 1/(1+K_L C)$ | 0.0247           | 0.0667        |
|             | $R^2$               | 0.96025          | 0.99915       |
| Freundlich  | $k_F$ (mg/g)/(mg/L)$^{1/n}$ | 49.01            | 15.88         |
|             | $\ln Q_L = \ln K_F + \frac{1}{n} \ln C_L$ | 1/n               | 0.3930        |
|             | $R^2$               | 0.78863          | 0.82533       |
| Temkin (4.9):| $k_T$ (L/mg)       | 1.5730           | 3.2041        |
|             | $Q = B_t \ln K_T + B_t \ln C_T$ | 21.1962           | 8.9824        |
|             | $R^2$               | 0.81051          | 0.8742        |
| D-R         | $B$ (kJ/mol$^2$)    | 1.422            | 0.355         |
|             | $Q_m$ (mg/g)        | 84.18            | 43.41         |
|             | $E$ (J/mol)         | 592.97           | 375.29        |
|             | $R^2$               | 0.75905          | 0.98913       |

3.3 Thermodynamic parameters
To have a depth-knowledge about thermodynamic parameters of adsorption CR from solutions and mechanism of the adsorption process, an investigation was be carried out (Fig. 4). The thermodynamic parameters extracted from slope and intercept of ln $K_C$ vs 1/T and Gibb’s free energy are tabulated in Table 4. A positive enthalpy change ($\Delta H^o$) suggests that the reaction acquired heat from the system to promote self-reaction. The spontaneous adsorption process is confirmed by the negative values of Gibb’s free energies. On the other hand, higher absolute value of free energy is associated with elevated temperature and implies a more facilitated adsorption process. Apparently, the reaction seems to be most accelerated at the temperature of 313 K (40 ºC), which is selected as optimal temperature.

![Figure 4. Thermodynamic plot for CR removal by EG@NiFe$_2$O$_4$](image)
Table 4. Thermodynamic parameters of CR sorption process by EG@NiFe$_2$O$_4$

| Samples     | Temp (K) | $\Delta G^\circ$ (kJmol$^{-1}$) | $\Delta H^\circ$ (kJmol$^{-1}$) | $\Delta S^\circ$ (Jmol$^{-1}$K$^{-1}$) |
|-------------|----------|---------------------------------|---------------------------------|---------------------------------------|
| EG@NiFe$_2$O$_4$ | 283      | $-1.0510$                       | $62.487$                        | $224.52$                              |
| EG@NiFe$_2$O$_4$ | 293      | $-3.2961$                       |                                 |                                       |
| EG@NiFe$_2$O$_4$ | 303      | $-5.5413$                       |                                 |                                       |
| EG@NiFe$_2$O$_4$ | 313      | $-7.7864$                       |                                 |                                       |

4. Conclusions

This study has compared kinetics and isotherms of the adsorption process against CR dye using two adsorbent, EG@NiFe$_2$O$_4$ and NiFe$_2$O$_4$. The adsorption process kinetic seems to be well described using pseudo-second-order model. Kinetic parameters showed that EG@NiFe$_2$O$_4$ possesses higher adsorption capacity than NiFe$_2$O$_4$. Langmuir isotherm, which implies chemical adsorption, was also found to be more suitable to explain the adsorption data. Furthermore, calculated thermodynamic parameters suggested that the adsorption using EG@NiFe$_2$O$_4$ material towards CR was spontaneous and endothermic. Current findings support studies involving EG@NiFe$_2$O$_4$ to further enhance its removal capacity and the sol-gel method in fabricating EG decorated with magnetic ferrites.

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