EFFECTIVE ADSORPTION OF TETRACYCLINE WITH Co₃O₄/Fe₃O₄ BIMETALLIC NANOPARTICLES

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ABSTRACT

In the present study cobalt oxide/iron oxide bimetallic nanoparticles (Co₃O₄/Fe₃O₄ NPs) were synthesized by chemical co-precipitation method. The synthesized Co₃O₄/Fe₃O₄ NPs were characterized by SEM and XRD analysis. The synthesized nanoparticles were used as an adsorbent for the removal of a kind of antibiotic as Tetracycline (TC) from aqueous solutions. According to characterization results, small plate-like structures and agglomerated irregular spherical nanosized particles (101.85 ± 15.04 nm) were formed. The XRD data confirmed the structure of synthesized adsorbent was Co₃O₄/Fe₃O₄. The optimum tetracycline adsorption conditions were determined as the initial pH of solution 9.0, temperature 55°C, and adsorbent concentration 3.0 g/L. A linear increase was observed in equilibrium uptakes of TC with the increasing the initial antibiotic concentrations. The experimental equilibrium data was modelled with Langmuir and Freundlich isotherm models. The experimental equilibrium data was the best agreement to the Langmuir isotherm model. The maximum monolayer coverage capacity of Co₃O₄/Fe₃O₄ NPs for TC adsorption was found to be 149.26 mg/g at 55°C optimum temperature. The experimental kinetic adsorption data were defined as the best agreement with the pseudo-second-order kinetic model. Weber Morris mass transfer modelling results showed that both the film (boundary layer) and intra-particle diffusion were effective in the adsorption process. The thermodynamic studies suggested that the adsorption process was endothermic, spontaneous and the positive ΔS value indicated increased disorder at the solid-solution interface during the adsorption. Moreover, the synthesized adsorbent showed high adsorption efficiencies at the end of seven sequence usages.

Keywords: Adsorption, Bimetallic Nanoparticles, Cobalt Oxide, Iron Oxide, Tetracycline Removal
1. INTRODUCTION

Antibiotics, a kind of significant pharmaceutical ingredient, have been used for many decades as both human and veterinary medicines (Cao et al., 2018). Tetracycline (TC, C22H24N2O8) is the second most widely used antibiotics family in the world. TCs are often used in human therapy and livestock industry due to their broad-spectrum antimicrobial activity against a variety of pathogens (Ergün et al., 2013; Bao et al., 2013).

However, nowadays, the presence of antibiotics in the environment and their potential threat to human health and aquatic ecology has led to great concerns. Because antibiotics taken by humans and animals are not completely absorbed in the body. It has been suggested that about 90% of an administrated dose of antibiotic may be excreted through urine and feces (Turku et al., 2007). In addition, the removal of these drug residues reaching sewage treatment plants cannot be fully achieved due to their resistance to biological degradation. Therefore, antibiotic residues can easily mix with surface and ground waters. They also pose a risk for ecological and aquatic environments due to their toxic effects and long half-life (Zhao et al., 2011; Gilder, 2016).

It has been reported that the antibiotics concentrations in untreated domestic wastewater range between 100 ng/L and 6 μg/L, while the concentrations in pharmaceutical and hospital wastewater can reach up to 100–500 mg/L (Cao et al., 2018).

Therefore, the treatment of wastewater containing antibiotic residues with high organic load is one of the important environmental problems. So, it is necessary to develop inexpensive and efficient treatment methods for this purpose.

The oxidation methods, membrane filtration, reverse osmosis, ultrafiltration, Fenton process, and adsorption are applied as alternative treatment methods for the removal of antibiotics from wastewaters. Adsorption is commonly believed the easiest and cheapest one among these techniques.

Graphene oxide (Gao et al., 2012), carbon nanotubes (Ji et al., 2010), silica (Turku et al., 2007), kaolinite (Li et al., 2010), goethite (Zhao et al., 2011), clay mineral illite (Chang et al., 2012), montmorillonite (Parolo et al., 2008); biosorbents such as maize stalks (Balarak et al., 2016); Pachydicyton coriaceum and Sargassum hemiphyllum (Li et al., 2015); activated carbon (Martins et al., 2015), chitosan (Kang et al., 2010); composite materials such as Fe3O4/Al2O3-Chitosan/graphene oxide nanocomposite (Huang et al., 2017), Heteropolyacid–chitosan/TiO2 composites (Yu et al., 2014); nanomaterials such as Co-doped UiO-66 nanoparticle (Cao et al., 2018) and Fe/Ni bimetallic nanoparticles (Dong et al., 2018), and cobalt ferrite nanoparticles (Zhao et al., 2014) were used as adsorbents for the removal of TC.

The aim of this work synthesis and characterization of bimetallic Co3O4/Fe3O4 NPs and investigate the adsorption of TC on Co3O4/Fe3O4 NPs. In this study, the experimental parameters that affect the adsorption of TC on Co3O4/Fe3O4 NPs such as initial pH of the solution, adsorbent concentration, initial TC concentration, and temperature were optimized to obtain maximum TC removal yield and also, the reusability of adsorbent was tested. The thermodynamic, equilibrium, kinetic, and mass transfer modeling studies were also carried out to evaluate the adsorption process.

2. MATERIALS AND METHODS

2.1. Materials

All of the chemicals were of analytical grade and they were used without further purification. For the synthesis of Co3O4/Fe3O4 bimetallic nanoparticles, Fe(NO3)3·9H2O and Co(NO3)2·6H2O were supplied from Acros. Tetracycline hydrochloride (C21H24N2O8.HCl) was purchased from Sigma Aldrich. The chemical structure of TC antibiotics was presented in Fig. 1.

A stock solution of 250 mg/L of Tetracycline (TC) was first prepared and then the desired antibiotic concentrations were prepared by appropriate dilutions from the stock solution. The initial pHs of the solutions was adjusted with 0.1 N hydrochloric acid and/or 0.1 N sodium hydroxide.

Fig. 1. The structure of tetracycline, the framed regions represents the structural moieties associated with the three acidic dissociation constants (pKa).

2.2. Synthesis and Characterization of Co3O4/Fe3O4 NPs

The synthesis of Co3O4/Fe3O4 bimetallic nanoparticles (Co3O4/Fe3O4 NPs) was carried out by the chemical co-precipitation method. In the experiments, 25 mL of 0.1 M Fe(NO3)3·9H2O and 25 mL of 0.2 M Co(NO3)2·6H2O solution were mixed at room temperature for 15 min. Then 1.0 M sodium hydroxide solution was slowly added to the prepared solution. This mixture constantly stirred until the pH of 11.0 was reached. The changing of the color of the salt solution to intense black indicated the formation of Co3O4/Fe3O4 NPs. The obtained final mixture was kept under vigorous stirring for 3 h at 90°C. The formed nanoparticles were separated by centrifugation and then collected nanoparticles were washed several times with deionized water and dried in an oven at 105°C overnight.

The morphology of the Co3O4/Fe3O4 NPs was analyzed by Scanning Electron Microscope (SEM) analysis with Zeiss/Supra 55 SEM and the crystal structure was determined by X-ray Powder Diffraction (XRD) analysis, using nickel-filtered Cu Kα radiation in a Philips XPer MD apparatus operated at 40 kV and 30 mA, in the 20 range of 10°–90°.

2.3. Adsorption Studies

The batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks containing 100 mL of TC
antibiotic solution. 0.1 g of adsorbent, except for adsorbent concentration experiments, was contacted with 100 mL of TC solution at known initial antibiotic concentration and initial pH of solutions. Then the flasks were agitated at a constant temperature and shaking rate. Samples were taken before mixing the Co₃O₄/Fe₃O₄ NPs and TC solution and at pre-determined time intervals for the unadsorbed antibiotic concentration in the solution. Samples were centrifuged and the supernatant liquid was analyzed by UV-vis spectrophotometer at the wavelength of 360 nm.

The adsorbed amount of TC \( q_e \) (mg/g) and the percentage of adsorption \( \text{Adsorption (\%)} \) at equilibrium were calculated with Eqs. (1) and (2) as presented follows:

\[
q_e \ (\text{mg/g}) = \frac{C_0 - C_e}{m} \cdot V
\]

\[
\text{Adsorption (\%)} = \left( \frac{C_0 - C_e}{C_0} \right) \cdot 100
\]

Where \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of TC solution, respectively; and \( m \) (g) is the mass of adsorbent, and \( V \) (L) is the volume of the liquid phase.

3. RESULTS AND DISCUSSIONS

3.1. The Characterization of Co₃O₄/Fe₃O₄ NPs

The morphology of Co₃O₄/Fe₃O₄ NPs before and after adsorption was determined by SEM analysis and SEM images obtained at different magnifications were presented in Fig. 2. (a – d). SEM images of the synthesized Co₃O₄/Fe₃O₄ NPs (Fig. 2 (a, b)) showed that highly clustered surfaces, and agglomerated irregular spherical particles were formed. The SEM images obtained after the adsorption process showed that the morphology of Co₃O₄/Fe₃O₄ NPs changed a bit slightly; the clustered surfaces were disappeared, and the nanosized, spherical, and agglomerated particles became more apparent.

The mean particle size of the synthesized Co₃O₄/Fe₃O₄ NPs was calculated by using the modified form of the Williamson–Hall method, as presented following Eq. (3):

\[
\beta \cos(\theta) = k\lambda/D + 4\varepsilon \sin(\theta)
\]

Where \( \lambda \) is the wavelength of X-Ray (0.1541 nm), ‘\( \beta \)’ is FWHM (full width at half maximum), ‘\( \theta \)’ is the diffraction angle, \( \varepsilon \) is the strain, \( k \) is shape factor (0.9) and ‘\( D \)’ is mean particle diameter size.

The strain and particle size are calculated from the slope and y-intercept (k\( \lambda \)/D) of Williamson–Hall plot, i.e. the plot of between 4\( \sin(\theta) \) and \( \beta \cos(\theta) \). The slope of the graph gives strain and the intercept on the \( \beta \cos(\theta) \) axis gives the mean particle size corresponding to zero strain (Mote et al., 2012). The mean particle size of Co₃O₄/Fe₃O₄ NPs was calculated to be 57.75 nm by using the Williamson–Hall method.

Fig. 2. SEM images obtained at different magnifications before a) 50 KX, b)1000 KX; after c) 100 KX, d) 200 KX.
The mean particle size of the spherical particles was determined as 101.85 ± 15.04 nm by using the Image J program utilizing randomly selected particles from SEM images after the adsorption process.

The larger mean particle size of the Co$_3$O$_4$/Fe$_3$O$_4$ NPs was obtained from the SEM images than that obtained from XRD data. The reason for this result may be due to the fact that the SEM images indicate the size of polycrystalline particles which show the tendency to agglomerate due to their high surface energy.

The XRD pattern of synthesized Co$_3$O$_4$/Fe$_3$O$_4$ NPs was presented in Fig. 3.

Fig.3. XRD diagram of synthesized Co$_3$O$_4$/Fe$_3$O$_4$ NPs

The peaks at 2θ = 30.91°, 36.46°, and 58.83° correspond to Fe$_3$O$_4$ and the peaks at 2θ = 19.02°, and 44.59°, and 64.46° showed the Co$_3$O$_4$ phase (Manigandan et al., 2013).

3.2. Effects of Environmental Conditions on the Adsorption

3.2.1. Effect of initial pH

The initial pH is one of the most important parameters affecting the adsorption of TC on the active adsorbent surface. The interaction between the TC molecules and the adsorbent is mainly dependent on the TC species and variation of the surface loading of the adsorbent.

The isoelectric point (pH$_{IEP}$) of Co$_3$O$_4$/Fe$_3$O$_4$ NPs was determined by solid addition method at different pH (3.0 - 12) values (Uzunoğlu et al., 2016). The variation of the isoelectric point with pH was presented in Fig. 4.

Fig.4. The isoelectric point of Co$_3$O$_4$/Fe$_3$O$_4$ NPs

TC molecules are very sensitive to the initial pH of the solution due to their protonation status. As shown in Fig. 4, the isoelectric point at which the surface electrical charge of Co$_3$O$_4$/Fe$_3$O$_4$ NPs changes from negative to positive value was found to be pH 8.47.

Accordingly, the surface of Co$_3$O$_4$/Fe$_3$O$_4$ NPs was charged negatively below pH 8.47 and positively charged above this pH value. However, the structure of TC contains many polar and ionizable groups, including amino, carboxyl, phenol, alcohol, and ketone. The TC molecules can be present in three forms, cationic (pH<3.3), zwitterionic (3.3<pH<7.7) and anionic (pH>7.7) in aqueous solutions at different pH values (Roca Jalil et al., 2018). In this case, there is an electrostatic interaction depending on the initial pH values in the adsorption of TC on Co$_3$O$_4$/Fe$_3$O$_4$ NPs surface. The effect of initial pH on the adsorption of TC to Co$_3$O$_4$/Fe$_3$O$_4$ NPs was given in Fig. 5.

As shown in Figure 5, the highest adsorption capacity was obtained at the initial pH: 9.0. At pH: 9.0, the TC molecules are in anionic form, while the adsorbent surface is positively charged. Therefore, the amount of TC absorbed is the highest due to the increased electrostatic attraction between the TC molecules and the adsorbent surface at pH: 9.0.

Fig.5. Effect of initial pH on the adsorption of TC (Co=50 mg/L; Xo=1.0 g/L; T=25 °C; t= 420 min)

3.2.2. Effect of initial TC concentration

The effect of initial antibiotic concentration on adsorption was depicted in Fig. 6. As can be seen from Fig. 6, the adsorption capacities increased linearly (q=0.3047*C$_o$, $R^2=0.999$) in the studied TC concentrations as a result of the increase in the driving force (∆C) to get over mass transfer resistances of the pollutant between the aqueous and solid phases.

3.2.3. Effect of adsorbent concentration

The adsorbent concentration effect on the equilibrium uptake was presented in Fig.7. According to Fig. 7, a
decrease was observed in adsorption capacity by increasing the adsorbent concentration from 0.5 g/L to 3.0 g/L. However, the adsorption percentages increased by increasing the adsorbent concentration values. Therefore, although the highest adsorption capacity for tetracycline antibiotic was obtained at 0.5 g/L of adsorbent concentration, the optimum adsorbent concentration was determined as 3.0 g/L, since the highest removal yield was obtained at this adsorbent concentration value.

3.2.4. Effect of temperature

The effect of temperature was presented in Fig. 8. According to Fig. 8, the increase in temperature has a positive effect on the adsorption of TC. The obtained adsorption capacities were increased with the increase in temperature from 25°C to 65°C. This result indicated that the studied adsorption process was endothermic nature.

Also, it was observed that when the temperature was increased from 55°C to 65°C, a slight change was obtained on adsorption capacity. So, the adsorption capacities approximately became constantly after 55°C. Therefore, the optimum temperature value for TC adsorption was determined to be 55°C.

3.3. Thermodynamic Parameters

The temperature effect was also confirmed with thermodynamic studies by calculating the entropy change (ΔS), enthalpy change (ΔH), and Gibbs energy change (ΔG). ΔH and ΔS were calculated from the slope and intercept of the linear plot of ln Kc versus 1/T according to Van’t Hoff equation (Eq. 4), while ΔG was calculated according to Eq. 5.

\[
\ln K_c = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R}\right) \cdot \frac{1}{T} \quad (4)
\]

\[
\Delta G = -RT \ln K_c = \Delta H - T\Delta S \quad (5)
\]

In this study, the linear form of Van’t Hoff equation for the adsorption of TC onto CoO/FeO NPs was found as ln Kc = -8502.2 x T^-1 + 28.569 with the regression coefficient 0.993 (data not shown) and the thermodynamic parameters were calculated and presented in Table 1. According to Table 1, the calculated ΔG values had negative indicating that adsorption was spontaneous. The positive value of ΔS suggested that randomness of the adsorbed TC species at the solid-solution interface during adsorption and the studied adsorption systems were endothermic (ΔH>0).

| T (°C) | Kc | ΔH (kJ/mol) | ΔS (kJ/mol.K) | ΔG (kJ/mol) |
|-------|----|-------------|----------------|-------------|
| 298   | 1.1132 | -0.265     |                |             |
| 318   | 5.6439 | -4.575      |                |             |
| 328   | 12.824 | 70.68       | 0.237          | -6.957      |
| 338   | 34.555 | -9.955      |                |             |

Table 1. Thermodynamic parameters of adsorption
3.4. The reusability of adsorbent

The operation cost is one of the important issues that need to be carefully considered. Therefore, operation cost can be significantly reduced owing to adsorbent reusability in practical applications. The reusability of the adsorbent was evaluated through seven recycled tests. The results regarding the TC adsorption efficiency for seven cycles of the adsorbent were given in Fig. 9. Between each cycle of use, the adsorbent was separated from the solution with Whatman #1 filter paper, washed several times with deionized water and then applied for the next experiment without any modifications. After each recycling test, the adsorption percentage of TC was determined. As seen in Fig. 9, the adsorption % of TC declined slightly from 99.43% in the first cycle to 88.42% after seven cycles of adsorption for 10 mg/L of TC solution. This result showed that the adsorbent can be recycled and reused for at least seven successive cycles without any significant loss of its efficiency.

3.5. Equilibrium, Kinetic, and Mass Transfer Modelling

3.5.1. Equilibrium modelling

The well-known linearized forms of the Langmuir and Freundlich isotherm models were used to describe the adsorption equilibrium. The linearized forms of Langmuir and Freundlich isotherm models were given in Eqs. (6) and (7):

Langmuir: \[ \frac{1}{q_e} = \frac{1}{Q° b} \cdot \frac{1}{C_e} + \frac{1}{Q°} \]  

Freundlich: \[ \ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \]  

Langmuir isotherm model based on the assumption of maximum adsorption corresponds to a saturated monolayer of adsorbed molecules on the adsorbent surface with constant energy. Freundlich isotherm model suggests non-ideal sorption that involves heterogeneous surface energy systems (Malik, 2004).

The isotherm constants with regression coefficients \( R^2 \) were presented in Table 2. Also, the experimental and predicted isotherms for adsorption at 55°C was given in Fig. 10.

According to Table 2 and Fig. 10, the Langmuir isotherm model was better fitted to experimental equilibrium data. This result showed that the adsorption occurred at specific homogeneous sites within the adsorbent forming monolayer coverage of TC at the surface of Co3O4/Fe3O4 NPs. The maximum monolayer coverage capacity of Co3O4/Fe3O4 NPs was determined as 149.26 mg/g at 55°C which is the optimum temperature. Moreover, as seen in Table 2, the maximum monolayer coverage capacity values of the adsorbent for TC increased by increasing temperature may be due to the endothermic nature of the studied adsorption process. The comparison of \( Q° \) values of various types of adsorbents for TC adsorption was presented in Table 3.

Accordingly, it was seen that the adsorption capacity of Co3O4/Fe3O4 NPs was comparable with other adsorbents reported in earlier studies.

Table 2. The constants of the adsorption isotherm models with regression coefficients (pH=9.0; \( X_o=3.0 \) g/L; \( t=420 \) min)

| T (°C) | Langmuir isotherm model | Freundlich isotherm model |
|------|--------------------------|---------------------------|
|      | \( Q° \) (mg/g) | b (L/mg) | R² | \( K_F \) (mg/g)/(L/mg)1/n | 1/n | R² |
| 25   | 21.053 | 0.03536 | 0.999 | 1.0114 | 0.6988 | 0.995 |
| 35   | 55.249 | 0.01745 | 0.998 | 1.0443 | 0.8627 | 0.991 |
| 45   | 135.135 | 0.01380 | 0.997 | 1.9397 | 0.8699 | 0.979 |
| 55   | 149.254 | 0.01020 | 0.999 | 1.4745 | 1.0089 | 0.994 |
3.5.2. Kinetic modeling

The adsorption kinetics was elucidated by correlating the adsorption kinetic data using the linear forms of the Lagergén’s pseudo-first-order and the pseudo-second-order kinetic models. The linearized forms of pseudo-first-order and the pseudo-second-order kinetic models were given in Eqs. (8) and (9), respectively (Mall et al., 2007):

Pseudo first order: \( \log (q_e - q_t) = \log (q_e) - \frac{k_1 t}{2.303} \) (8)

Pseudo second order: \( \frac{t}{q_t} = \left( \frac{1}{q^2_{e} k_2} \right) + \frac{t}{q_e} \) (9)

For the adsorption of TC onto Co\textsubscript{3}O\textsubscript{4}/Fe\textsubscript{3}O\textsubscript{4} NPs, the parameters of the pseudo-first-order and pseudo-second-order kinetic models with regression coefficients were presented in Table 4. From Table 4, higher values of \( R^2 \) and the consistency between experimental and calculated uptake values showed a better agreement of the pseudo-second-order kinetics.

3.5.3. Effect of mass transfer

Weber-Morris model was used to determine the boundary layer and intra-particle diffusion mechanism between TC and adsorbent. Weber-Morris intraparticle diffusion model is expressed by the following Eq.(10):

\( q_t = K_i t^{0.5} + I \) (10)

In Weber-Morris equation; I is the intercept related to the boundary layer effect and \( K_i \) is the intraparticle diffusion rate constant which can be evaluated from the slope of the linear plots of \( q_t \) versus \( t^{0.5} \). According to this model, if the only intraparticle diffusion is the rate-controlling step in the adsorption process, the plot of uptake \( (q_t) \) versus the \( t^{0.5} \) should be linear and these lines pass through the origin. On the other side, the Weber-Morris plot can be linear and also has an intercept value if the adsorption system follows both intraparticle and film diffusion (Wu et al., 2009). The model parameters and regression coefficients were summarized in Table 4. Based on the results, it was observed a multilinear plot (figure not shown) indicated that both intraparticle and film diffusion were effective on the adsorption. Moreover, according to Table 4; it was seen that the internal (\( K_i \)) and external diffusion constants (I) gradually increased with increasing initial contaminant concentration.

Table 4. Kinetic and intra-particle mass transfer model parameters (pH=9.0, \( X_0=3g/L, t=420 \) min)

| Co (mg/L) | \( q_{e,\text{exp}} \) (mg/g) | \( Pseudo-first-order \) | \( Pseudo-second-order \) | Weber-Morris Model |
|-----------|---------------------------|--------------------------|-----------------------------|-------------------|
|           |                           | \( k_1 \) (min\textsuperscript{-1}) | \( q_{e,\text{cal}} \) (mg/g) | \( R^2 \) | \( k_2 \) (g/mg.min) | \( q_{e,\text{cal}} \) (mg/g) | \( R^2 \) | \( K_i \) (mg/g.min\textsuperscript{-0.5}) | I | \( R^2 \) |
| 5         | 2.503                     | 0.003685                 | 2.3637                      | 0.936          | 0.002233 | 2.749 | 0.970 | 0.0332 | 0.8925 | 0.995 |
| 10        | 3.163                     | 0.004376                 | 2.2014                      | 0.960          | 0.004520 | 3.300 | 0.995 | 0.1009 | 0.9907 | 0.982 |
| 25        | 7.879                     | 0.008521                 | 7.3198                      | 0.954          | 0.002852 | 8.453 | 0.991 | 0.3489 | 1.1454 | 0.990 |
| 50        | 15.086                    | 0.005758                 | 13.3967                     | 0.919          | 0.00071  | 17.065 | 0.972 | 0.563  | 1.9738 | 0.998 |
4. CONCLUSION

In this study, CoOx/FeOx NPs were synthesized by the co-precipitation method for the removal of TC which is a kind of antibiotic from the aqueous solutions. The characterization studies of CoOx/FeOx NPs were carried out by SEM and XRD analysis. According to XRD results, the peaks were obtained correspond to FeOx and CoOx.

The adsorption was highly dependent on initial pH, adsorbent concentration, initial TC concentration, and temperature. The kinetics of TC adsorption on CoOx/FeOx NPs followed the pseudo-second-order model. The equilibrium data fitted well in the Langmuir model of adsorption, showing monolayer coverage of TC molecules at the outer surface of CoOx/FeOx NPs. The maximum monolayer coverage capacity of CoOx/FeOx NPs for TC adsorption determined to be 149.26 mg/g. Both intraparticle and film diffusion effects were determined on the adsorption process. Moreover, the adsorbent showed reusability at least seven sequence usages without loss of adsorbent property. The TC adsorption onto CoOx/FeOx NPs was found to be feasible and spontaneous from thermodynamic studies.

Consequently, these results provided the synthesis of an efficient adsorbent for the effective removal of antibiotic contaminants like tetracycline in wastewater.

NOMENCLATURE

\( b \) : A constant related to the affinity of the binding sites (L/mg)
\( C_e \) : Unadsorbed Cr(VI) metal ion concentration at equilibrium (mg/L)
\( C_0 \) : Initial Cr(VI) metal ion concentration (mg/L)
\( K_F \) : Freundlich constant indicating adsorption capacity ((mg/g)/(L/mg))\(^{1/n}\)
\( k_i \) : Intraparticle diffusion rate constant (mg/g.min\(^{0.5}\))
\( k_1 \) : Pseudo first order kinetic rate constant (1/min)
\( k_2 \) : Pseudo second order kinetic rate constant (g/mg.min)
\( q_e \) : Adsorbed amount per unit mass of adsorbent (mg/g)
\( q_{e,cal} \) : Calculated adsorbed amount per unit mass of adsorbent from pseudo first order kinetic model (mg/g)
\( q_{e,cal} \) : Calculated adsorbed amount per unit mass of adsorbent from pseudo second order kinetic model (mg/g)
\( q_{e,exp} \) : Experimental adsorbed amount per unit mass of adsorbent (mg/g)
\( q_0 \) : Adsorbed amount per unit mass of adsorbent at any time (mg/g)
\( Q_{m} \) : Maximum monolayer coverage capacity of adsorbent (mg/g)
\( 1/n \) : Freundlich constant indicating adsorption intensity

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