Kinetic and equilibrium study of the removal of reactive dye using modified walnut shell
Shenmaishang Li, Zuoxiang Zeng and Weilan Xue

ABSTRACT

Modified walnut shell (EAWNS) was prepared by reaction with epichlorohydrin and alkaline solution of aspartic acid and used to remove reactive dye (Reactive Brilliant Blue (KN-R)) from aqueous media. The isotherms, kinetics and thermodynamics of KN-R adsorption onto EAWNS were studied at 298–318 K. The isotherm data of KN-R adsorption onto EAWNS agreed closely with the Langmuir model. The theoretical monolayer adsorption capacity for KN-R was 224.42 mg/g at 318 K. The result from the Dubinin–Radushkevich model showed that the KN-R adsorption onto EAWNS is chemisorption. The adsorption rate of KN-R onto EAWNS conformed to the pseudo-second-order model. The diffusion mechanism was investigated by the intraparticle diffusion model. The mass-transfer coefficient calculated by the surface mass-transfer coefficient model was in range of $2.95 \times 10^{-5}$ to $2.93 \times 10^{-4}$ cm/s. The thermodynamic results suggested that the adsorption of KN-R onto EAWNS is spontaneous and endothermic in nature. The design of a single-stage batch adsorption process based on EAWNS adsorbent was carried out. Furthermore, the recycled EAWNS maintains high adsorption capacity despite four cycles.

Key words | kinetics, reactive dye, regeneration, thermodynamics, walnut shell

INTRODUCTION

Annually, several million tons of dyes are produced and widely used in various industries, such as dyestuffs, textiles, paper, printing, plastics, leather, food, pharmaceutical, petrochemical and cosmetics industries (Zhang et al. 2013; Fabiano et al. 2016; Jacob et al. 2017). It is assumed that a loss of 1–2% in production and 1–10% loss in use are a fair estimate. For reactive dyes, this figure can be about 4% (Esther et al. 2004). Most of the dye loss enters the water medium, which could seriously affect the aquatic systems and humans, because many synthetic dyes are toxic (mutagenic and carcinogenic), allergenic and irritating to the skin and intestinal wall (Betina et al. 2009). Moreover, they are stable and very difficult to degrade in the water. Thus, it is necessary to remove most of the dyes to meet emission standards.

At present, several treatment technologies including membrane filtration (Ciardelli et al. 2000), biodegradation, chemical oxidation (Turgay et al. 2011), ozonation and flocculation (Guo et al. 2012) have been used in wastewater treatment. Among these technologies, adsorption offers an attractive option for treating dye wastewater, specifically the low-cost adsorbents. In recent years, the application of agricultural wastes as inexpensive adsorbents for wastewater treatment has aroused great interest. Walnut shell (WNS) is a significant agriculture residue because of its availability, abundance and low prices. Thus, this residual material could become an alternative absorbent for wastewater treatment. Especially, the adsorption capacity of WNS modified with some functional groups (i.e., carboxyl, amine and amide groups) could be significantly improved. Cao et al. (2014) proposed a modified method, in which a modified WNS was prepared after reaction with epichlorohydrin and diethylenetriamine. However, the first step of the above study is that WNS reacts with epichlorohydrin in sodium hydroxide (NaOH) solution. However, disadvantages are that epichlorohydrin would hydrolyze in aqueous solution to form glycerol and diethylenetriamine is relatively expensive. Therefore, it is necessary to develop new methods to modify WNS. In this paper, a new modified WNS (EAWNS) was synthesized by using solid sodium hydroxide and aspartic acid instead of sodium hydroxide solution and diethylenetriamine, respectively. EAWNS was characterized...
by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), point of zero charge analysis and N₂-BET analysis. The kinetics, isotherms and thermodynamics of Reactive Brilliant Blue (KN-R) adsorption onto EAWNS were studied at 298–318 K. The effect of pH on dye adsorption was investigated. The diffusion mechanism was investigated by the intraparticle diffusion and surface mass-transfer coefficient models. The reusability of EAWNS was evaluated after adsorption of dyes.

METHODS

Reagents and instruments

Aspartic acid (C₄H₇NO₄, >99%, CAS: 56-84-8) was obtained from Shanghai Yuanju Biotechnology Co., Ltd. KN-R (C₂₂H₁₆N₂Na₂O₁₁S₃, CAS: 2580-78-1) was supplied by Shanghai Macklin Biochemical Co., Ltd. Epichlorohydrin (>99%, CAS: 106-89-8), NaCl (99.5%, CAS: 7647-14-5), HCl (35 wt%, CAS: 7647-01-0) and NaOH (97%, CAS: 1310-73-2) were purchased from Shanghai Titan Scientific Co., Ltd. The chemicals involved were of analytical reagent grade and were used without any further purification. FTIR spectroscopy and SEM were performed using: a Nicolet MQGNA-IR 550 infrared spectrometer adopting KBr pellet and a JEOL JSM-6701F microscope (Japan), respectively. The pH at the point of zero charge (pH_pzc) of an adsorbent is an important feature that defines the pH at which the surface of adsorbent has net electrical neutrality. The pH_pzc of WNS and EAWNS was measured in 0.1 mol/L NaCl solution under pH ranging from 2.0 to 12.0, which was adjusted using 0.1 mol/L HCl or NaOH solution. The initial pH and final pH were accurately noted. The Brunauer-Emmett-Teller (BET) analysis used to measure the surface area from N₂ adsorption using a high-vacuum volumetric apparatus (mMK-TriStar 3000) at 77 K. The concentration of KN-R was analyzed using a UV-VIS spectrophotometer (UV-1800, Shimadzu, Japan).

EAWNS preparation

WNS, obtained from food processing plants, was washed with distilled water and dried completely. Dried WNS was crushed and particles with the desired mesh size (100–200 mesh) were collected. The aspartic acid disodium salt aqueous solution with a desired concentration was formulated by adding aspartic acid into NaOH solution. The modified process is described in detail as follows.

(1) About 10 g of WNS was immersed in 100 mL of NaOH solution (1 mol/L) at room temperature for 2 hours, and then filtered to obtain particles. (2) The filter particles and 0.30 g of solid sodium hydroxide were added to a 250-mL three-neck flask containing 100 mL of epichlorohydrin. The mixture was heated to 45–50 °C and stirred at this temperature for 2 hours, and then filtered to remove the liquid phase. (3) The remains were dispersed in 100 mL aspartic acid disodium salt aqueous solution (2 mol/L), and the reaction was performed at 60 °C for 4 hours. The mixture was successively filtered, washed with distilled water to neutral and dried to constant weight, and finally the sample of EAWNS was obtained. The reaction involved in this modified process is shown in Figure S1.

Adsorption experiments

Static equilibrium experiments were performed by adding 0.16 g of EAWNS to 250-mL stopped Erlenmeyer flasks containing 100 mL KN-R solution with different initial concentrations at 298–318 K. The flasks were placed in a thermostated water bath at a given temperature. At an initial concentration 550 mg/L, the effect of initial pH was studied over the range 1.0–11.0 at 298 K. The initial pH was attuned by addition of HCl and NaOH solution. The samples were withdrawn at equilibrium, and the residual dye concentrations were analyzed spectrophotometrically. The adsorption capacity at equilibrium, qₑ (mg/g), is calculated as

\[ qₑ = \frac{(C₀ - Cₑ)V}{w} \]  

where \( C₀ \) and \( Cₑ \) (mg/L) represent the initial and equilibrium concentrations of KN–R, respectively. \( V \) (L) is the solution volume; \( w \) (g) is the adsorbent weight.

The kinetic experiment of KN–R adsorption onto EAWNS was carried out by adding 0.16 g of EAWNS to KN–R solutions (100 mL) with initial concentration of 350 mg/L at 298–318 K. The samples were removed and analyzed at different time intervals. All the tests were repeated for three times. The adsorption capacity \( q_t \) (mg/g) at time \( t \), is calculated as:

\[ qₜ = \frac{(C₀ - Cₜ)V}{w} \]  

where \( Cₜ \) (mg/L) is the concentration of KN–R at time \( t \).

Adsorption capacity of WNS for KN–R was measured in the same way as the above experiment.
Regeneration

To recycle the used EAWNS for the further reactive dye adsorption, the KN–R-loaded EAWNS was regenerated by NaOH solution. The detailed process is described as follows. KN–R-loaded adsorbent was washed with distilled water and then dispersed in 0.5 mol/L NaOH solution for 24 hours, and then filtered, washed with distilled water, dried and used for the next cycle. The reusability of the reganerated EAWNS was subjected to a further four successive adsorption–desorption experiments. The recycled efficiency \( W_r \) for each cycle could be obtained as follows:

\[
W_r(\%) = \frac{q_n}{q_1} \times 100
\]

where \( q_n \) and \( q_1 \) (mg/g) represent the adsorption capacities for the \( n \)th and first cycles, respectively.

RESULTS AND DISCUSSION

Characterization of EAWNS

The FTIR spectra of WNS and EAWNS are illustrated in Figure 1, indicating the presence of various functional groups. The peak at 1,737 cm\(^{-1}\) attributed to C=O stretching vibrations and that at 1,157 cm\(^{-1}\) ascribed to the C–O stretching vibration indicate the presence of -COO- groups on the EAWNS (Liu et al. 2006; Yang & Qiu 2010). There is a new peak yielded at 1,643 cm\(^{-1}\) which could be attributed to the bend vibrations of N–H (Wang et al. 2010). These features indicate the aspartic acid is successfully introduced into the surface of EAWNS.

SEM images (Figure 2) show the surface morphology of WNS and EAWNS. From Figure 2, when WNS was modified to synthesize EAWNS, the structure of the material changed from tight to loose; that is, the surface area of adsorbent increases, indicating EAWNS is conducive to adsorption. Also, from the FTIR spectra (Figure 1), the molecular structure of EAWNS has been changed, which leads to the change of surface structure.

The results of \( \text{pH}_{\text{pzc}} \) and BET analysis are listed in Table 1. From Table 1, the \( \text{pH}_{\text{pzc}} \) of WNS and EAWNS are almost the same. Yet the value of surface area for EAWNS is twice that for WNS, which is consistent with the results of SEM.

Effect of pH on KN–R adsorption

The effect of pH on KN–R adsorption onto EAWNS is presented in Figure 3. As shown in Figure 3, the adsorption
capacity decreases with the pH increases; especially, it increases rapidly when pH decreases from 6.0 to 2.0, and changes a little when pH is less than 2.0. This phenomenon could be explained as follows: lower pH (pH < 6.0), that is, a higher concentration of positive charge H\(^+\) in the solution, will result in more amine protonation in KN\(–\)R, which will enhance adsorption of KN\(–\)R due to the electrostatic interaction between carboxyl groups of EAWNS and protonated amino groups (–NH\(3^+\)) of KN\(–\)R. It can be expressed by Equation (4)

\[
\text{EAWNS–COONa} + A–NH_2 + HCl \\
\rightarrow \text{EAWNS–COONH}_3^–A + \text{NaCl}
\] (4)

where A–NH\(2\) represents the reactive dye KN–R.

In contrast, as pH increases from 2.0 to 6.0, protonation would be weakened and the electrostatic attraction would be reduced, which lead to the reduction of adsorption capacity of the EAWNS. When the pH is above 6.0, the adsorption capacity maintained a low value. Therefore, the further experiments were carried out at pH 2.0.

### Adsorption isotherms

Adsorption equilibrium data are important in the adsorption system design, and are always fitted by the adsorption isotherm models (Qu et al. 2012). In this study, three isotherms: Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models are tested.

The Langmuir model (Langmuir 1918) is

\[
q_e = \frac{C_0 q_m K_L}{1 + C_0 K_L}
\] (5)

where \(q_m\) is the maximum monolayer adsorption capacity. \(K_L\) is the Langmuir parameter, which is related to the energy of adsorption.

The separation factor \((R_L)\) from the Langmuir model is defined as

\[
R_L = \frac{1}{1 + K_L C_0}
\] (6)

The Freundlich model (Freundlich 1906) is

\[
q_e = K_F C_e^{1/n}
\] (7)

where \(K_F\) is the Freundlich constant, which can be as an indicator of adsorption capacity, and \(1/n\) is the Freundlich parameter related to the adsorption intensity.

The D–R model (Dubinin 1960) assumes physical and chemical adsorption of molecules on the surface of porous solids, and is generally written as

\[
q_e = q_D e^{-K_D \varepsilon}
\] (8)

with

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\] (9)

\[
E = \frac{1}{\sqrt{2K_D}}
\] (10)

where \(q_D\) represents the maximum adsorption capacity, \(K_D\) is the coefficient related to the adsorption energy, \(\varepsilon\) is the Polanyi potential, \(R\) and \(T\) are the mean molar gas constant and temperature respectively, and \(E\) is the mean energy, which is utilized to evaluate the adsorption type. If \(E < 8.0\) kJ/mol, the adsorption process takes place physically; if \(8 < E < 16\) kJ/mol, the adsorption process proceeds chemically (Dubinin et al. 1947; Kiran et al. 2006).

The correlation coefficients \((R^2)\) along with the parameters for fitting equilibrium data (Figure 4) with the
above three models are listed in Table 2. From Table 2, the values of R² from the Langmuir model (R² > 0.99) are close to 1.0 and larger than the ones from the Freundlich model (R² < 0.98), indicating the Langmuir model provides a better fit for the experimental data than the Freundlich model. These results suggest the surface of EAWNS is homogeneous, and the maximum monolayer adsorption capacity for KN–R is 224.42 mg/g at 318 K. The values of RL at different temperatures are all in the range of 0 to 1 (0.701–0.105 at 298 K, 0.657–0.0876 at 308 K, and 0.651–0.0854 at 318 K), which reveals the adsorption of KN–R onto EAWNS is favorable. It also can be seen from Table 2 that the R² obtained from the D–R model is larger than 0.99, which indicates the experimental results fitted well with the D–R model. The values of E are found to be 10.64, 11.12 and 11.21 kJ/mol at 298, 308 and 318 K, respectively, and they are all between 8 and 16 kJ/mol, which shows that the KN–R adsorption onto EAWNS takes place chemically.

The maximum adsorption capacity for KN–R compared with various adsorbents is listed in Table 3. From Table 3, the adsorption capacity of EAWNS is larger than that of other adsorbents; in particular it is 18 times that of WNS, which indicates the EAWNS is more advantageous for adsorption. This phenomenon is attributed to the increase in the surface area of the adsorbent (SEM and BET) and the change in the surface structure (FTIR) by grafting aspartic acid.

**Kinetics**

To comprehend the mechanism of KN–R adsorption onto EAWNS, a kinetic investigation was conducted. The rate constant could be determined by the kinetic models, such as pseudo-first-order (Lagergren 1898), pseudo-second-order (Ho & McKay 1999) and Elovich (Peers 1965) models.

The pseudo-first-order model is expressed as

\[
q_t = q_e(1 - e^{-k_1t})
\]

where \( k_1 \) (min⁻¹) is the pseudo-first-order rate constant.

The pseudo-second-order model is expressed as

\[
q_t = \frac{k_2q_e^2t}{1 + k_2q_e^2t}
\]

where \( k_2 \) (g/(mg-min)) represents the pseudo-second-order rate constant.

The initial adsorption rate, \( h_0 \) (g/(mg-min)), at \( t \to 0 \) is calculated as

\[
h_0 = k_2q_e^2
\]

The time required to reach 50% of equilibrium adsorption capacity, \( t_{50} \) (min), is computed by the expression

\[
t_{50} = \frac{1}{k_2q_e}
\]
The Elovich model is written as

$$ q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t $$

where $a$ (mg/(g·min)) and $b$ (g/mg) are the initial adsorption rate and the desorption constant, respectively.

The effect of contact time on KN–R adsorption onto EAWNS at 298–318 K is depicted in Figure 5 and the data were correlated by the above three models. From Figure 5, the adsorption rate is fast within the first 90 min because of the higher concentration gradient and vacant adsorption active sites, and then slows down until the equilibrium is achieved. The experimental equilibrium adsorption capacity $q_{e,exp}$, the parameters and the correlation coefficients ($R^2$) of these three kinetic models are listed in Table 4. From Table 4, the values of $R^2$ of the pseudo-second-order model ($R^2 > 0.999$) are higher than those of the pseudo-first-order model ($R^2 < 0.72$), and the obtained equilibrium adsorption capacity $q_{e,cal}$ based on the pseudo-second-order model is close to $q_{e,exp}$, indicating the adsorption of KN–R obeys the pseudo-second-order model. The values of $h_0$ increase and the values of $t_{50}$ decrease with the temperature increase, suggesting the endothermic nature of the KN–R adsorption onto EAWNS. In addition, the $R^2$ of the Elovich model is not low ($R^2 > 0.98$), suggesting the chemisorption (chemical reaction) mechanism is probably rate-controlling in the process of KN–R adsorption onto EAWNS. These results match the conclusion from the D–R model.

### Adsorption mechanism

Generally, the adsorption process can be considered as four steps: (1) transport of adsorbate (dye) from bulk solution to the adsorbent surface (film diffusion); (2) the binding between dye and the adsorption sites onto the outer surface of EAWNS; (3) transport of dye in the pores of the EAWNS (intraparticle diffusion); (4) adsorption of dye on the adsorption sites on the inner surface of EAWNS. Steps (2) and (4) are fast; in order to determine the rate-controlling step, the intraparticle diffusion model (Weber & Morris 1965) is applied to fit the kinetic data shown in Figure 5.

The intraparticle diffusion model is written as

$$ q_t = k_{id} t^{0.5} + C $$

where $k_{id}$ (mg/(g·min$^{0.5}$)) represents the rate constant of intraparticle diffusion; $C$ is a coefficient which is proportional to the boundary layer thickness. If the plots of $q_t$ vs. $t^{0.5}$ are linear and pass through the origin ($C = 0$), then the rate-controlling step is due only to the intraparticle diffusion (Huang et al. 2009). Figure 6 shows the plots of $q_t$ vs. $t^{0.5}$ for intraparticle transport of KN–R adsorption onto EAWNS at different temperatures. From Figure 6, the plots of $q_t$ vs. $t^{0.5}$ include three linear portions with different slopes and the first linear portions do not pass through the origin, suggesting that the intraparticle diffusion is not the sole rate-controlling step, and there are three stages during the whole adsorption process. The first stage can be attributed to film diffusion; the second stage is attributed to intraparticle diffusion; the last stage is the equilibrium section.

The surface mass-transfer coefficient model raised by McKay (McKay et al. 1981) was also utilized to further illustrate mass transfer at the interfaces between the solution and
the surface of EAWNS. This model is expressed as
\[
\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right) = \ln\frac{mK}{1 + mK} - \frac{mK}{1 + mK} \beta_L S_S t
\]
where \(m (g/L)\) is the adsorbent mass per unit volume of adsorbate solution; \(K\) is the product of \(q_m\) and \(K_L\) in the Langmuir model; \(\beta_L (cm/s)\) is the surface mass-transfer coefficient; \(S_S (cm^{-1})\) is the outer surface of adsorbent per unit volume of particle slurry, and it can be calculated by Equation (19) which is based on the smooth spherical particle assumption
\[
S_S = \frac{6m}{d_p \rho_p (1 - \epsilon_p)}
\]
where \(d_p (cm)\) is the diameter of particle; \(\rho_p (g/cm^3)\) is the density of adsorbent; \(\epsilon_p\) is the porosity of adsorbent.

For the surface mass-transfer coefficient model, if the adsorption process is dominated by film diffusion, the plot of \(\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right)\) vs. \(t\) would be a straight line; if not, it is governed by intraparticle diffusion. The plots of \(\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right)\) vs. \(t\) at the KN–R concentration from 50 to 1,000 mg/L at 298 K are shown in Figure 7. From Figure 7(a), the value of \(\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right)\) is not a linear function of time for the overall adsorption process. However, Figure 7(b) presents the plots of \(\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right)\) vs. \(t\) at the initial period of adsorption (0–90 min), and it shows good linear relationship \((R^2 > 0.99)\) between \(\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK}\right)\) and \(t\). This shows the adsorption process is governed by the film diffusion merely at the initial period, which is consistent with the conclusion from the intraparticle diffusion model.

The values of \(\beta_L\) could be calculated from the slope of Figure 7(b), and are listed in Table 5. From Table 5, the values of \(\beta_L\) decrease as the KN–R concentration increases

<table>
<thead>
<tr>
<th>(C_0 (mg/L))</th>
<th>(\beta_L (cm/s))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>(2.93 \times 10^{-4})</td>
<td>0.9981</td>
</tr>
<tr>
<td>150</td>
<td>(1.64 \times 10^{-4})</td>
<td>0.9983</td>
</tr>
<tr>
<td>250</td>
<td>(1.39 \times 10^{-4})</td>
<td>0.9914</td>
</tr>
<tr>
<td>350</td>
<td>(9.28 \times 10^{-5})</td>
<td>0.9901</td>
</tr>
<tr>
<td>500</td>
<td>(7.12 \times 10^{-5})</td>
<td>0.9988</td>
</tr>
<tr>
<td>750</td>
<td>(4.54 \times 10^{-5})</td>
<td>0.9964</td>
</tr>
<tr>
<td>1000</td>
<td>(2.95 \times 10^{-5})</td>
<td>0.9957</td>
</tr>
</tbody>
</table>
(ranging from $2.93 \times 10^{-4}$ to $2.95 \times 10^{-5}$ cm/s). This phenomenon can be explained as follows: in the initial period of the adsorption process, a film is formed around the adsorbent (Figure S2) and the dye molecule will transport across the film to the surface of adsorbent. Assuming that the diffusion coefficient is constant at a given temperature, the mass transfer coefficient is inversely proportional to the thickness of the film. When the dye concentration increases, the thickness of film becomes larger (Figure S2), which leads to a decrease in the mass transfer coefficient. Meanwhile, it could be predicted that the surface mass-transfer coefficient could increase with increasing adsorption temperature (McKay et al. 1981; Song et al. 2013).

**Thermodynamics**

The orientation and feasibility of physicochemical adsorption could be estimated by thermodynamic parameters including Gibbs free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) associated with the adsorption of KN–R onto EAWNS, which can be obtained as follows:

$$K_c = \frac{C_{es}}{C_e}$$ (20)

$$\Delta G = -RT \ln K_c$$ (21)

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ (22)

where $K_c$ is the equilibrium partition constant. $C_{es}$ (mg/g) represents the equilibrium solid-phase concentration. The values of $\Delta H$ and $\Delta S$ can be obtained from the slope and intercept of the plot of $\ln K_c$ against $1/T$, and the thermodynamic parameters are listed in Table 6.

From Table 6, the negative value of $\Delta G$ reveals the process of KN–R adsorption onto EAWNS is spontaneous. The positive $\Delta H$ indicates the adsorption of KN–R on EAWNS is endothermic in nature. The positive value of $\Delta S$ suggests the KN–R adsorption onto EAWNS is entropy driven (Cheng et al. 2016).

**Table 6** Thermodynamic parameters of KN–R adsorption onto EAWNS

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/K/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-16.70</td>
<td>7.48</td>
<td>81.10</td>
</tr>
<tr>
<td>308</td>
<td>-17.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>-18.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Design for single-stage batch adsorption system**

The single-stage batch adsorption system could be designed using the isotherm parameters. Let concentration of KN–R be $C_0$ and $C_t$ at initial time and time $t$, the solution volume be $V$, KN–R loaded onto $W$ mass of EAWNS adsorbent will change from 0 to $q_t$, and the mass balance equation could be given as

$$V(C_0 - C_t) = W \cdot q_t$$ (23)

When the equilibrium is achieved, $C_t = C_e$, $q_t = q_e$. And the KN–R adsorption onto EAWNS obeys the Langmuir model. Therefore, Equation (23) can be written as

$$\frac{W}{V} = \frac{C_0 - C_t}{q_t} = \frac{C_0 - C_e}{C_e} = \frac{(C_0 - C_e)(1 + C_eK_L)}{C_eq_mK_L}$$ (24)

where $q_e = C_eq_mK_L/(1 + C_eK_L)$.

Therefore, when the initial concentration of KN–R is 50 mg/L and the temperature is 298 K, the amount of EAWNS adsorbent corresponding to different removal efficiency is shown in Figure 8. From Figure 8, the required mass of EAWNS increases from 5.45 to 57.71 g/L when the removal efficiency rises from 90% to 99%. Moreover, the growth rate of the required adsorbent mass increases with the increase of removal efficiency. Especially, when the removal efficiency is larger than 96%, the growth rate of the required adsorbent mass will increase dramatically. For example, when the removal efficiency increases from 96% to 97% and from 97% to 98%, the growth rate of the required adsorbent mass is 54.16% and 50.91%, respectively.

**Figure 8** The relationship between the amount of EAWNS and removal efficiency.
Table 7 | The reusability of EAWNS

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q ) (mg/g)</td>
<td>104.87</td>
<td>102.59</td>
<td>101.63</td>
<td>100.81</td>
</tr>
<tr>
<td>( W_r ) (%)</td>
<td>92.18</td>
<td>90.17</td>
<td>89.33</td>
<td>88.61</td>
</tr>
</tbody>
</table>

Reusability of EAWNS

To assess the reusability of EAWNS, the recycling experiments were carried out and the results are listed in Table 7. From Table 7, the recycled EAWNS maintains high adsorption capacity which is equivalent to 88.61% of fresh adsorbents despite four cycles.

In order to regenerate the used EAWNS, the ionic interaction between \( \text{OH}^- \) and \( \text{A–NH}_3^+ \) was the main desorption mechanism (Cao et al. 2014). The desorption of \( \text{KN} \)-R from EAWNS was due to deprotonation of the amine groups under alkaline conditions (Atia et al. 2009). The related chemical reaction (an electrostatic reaction) could be described by Equation (25)

\[
\text{EAWNS–COONH}_3^-\text{–A + NaOH} \\
\rightarrow \text{EAWNS–COONa} + \text{A–NH}_2^- + \text{H}_2\text{O}
\] (25)

This equation shows the bonds between \( \text{KN} \)-R and EAWNS would substantially break after alkali treatment. Thus, the EAWNS adsorbent can be reused in \( \text{KN} \)-R adsorption.

CONCLUSIONS

The EAWNS synthesized from walnut shell after reaction with epichlorohydrin and alkaline solution of aspartic acid was a novel adsorbent for removal of reactive dye (\( \text{KN} \)-R) in aqueous media. This adsorbent was characterized through FTIR spectroscopy and SEM. The optimal initial pH in the initial \( \text{KN} \)-R concentration of 350 mg/L is 2.0. The equilibrium data of \( \text{KN} \)-R adsorption onto EAWNS could be best explained by the Langmuir model rather than the Freundlich model, which reveals the adsorption process is homogeneous and favorable, and the maximum monolayer adsorption capacity for \( \text{KN} \)-R is 224.42 mg/g at 318 K. The values of \( E \) from the D–R model show that the \( \text{KN} \)-R adsorption onto EAWNS takes place chemically. Compared with the pseudo-first-order model, the adsorption kinetics of \( \text{KN} \)-R onto EAWNS are fitted better with the pseudo-second-order model. The high \( R^2 \) of the Elovich model \( (R^2 > 0.98) \) suggests chemisorption is probably rate-controlling in the process of \( \text{KN} \)-R adsorption onto EAWNS. The intraparticle diffusion model shows adsorption of \( \text{KN} \)-R onto EAWNS involves intraparticle diffusion, but it is not the sole rate-controlling step. The calculated mass-transfer coefficient decreases from \( 2.93 \times 10^{-4} \) to \( 2.95 \times 10^{-5} \text{ cm/s} \) as the \( \text{KN} \)-R concentration increases from 50 to 1,000 mg/L. The thermodynamic results show that the adsorption of \( \text{KN} \)-R onto EAWNS is spontaneous, endothermic and entropy driven. The EAWNS adsorbent could be effectively utilized for the design of a single-stage batch adsorption system. Furthermore, the depleted EAWNS could be recycled through alkali treatment, and maintains high adsorption capacity despite four cycles. Thus, EAWNS is an effective adsorbent for removing \( \text{KN} \)-R from aqueous media.

REFERENCES


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