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Use of polyethyleneimine-modified wheat straw for adsorption of Congo red from solution in batch mode

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ABSTRACT

It is essential and important to remove dyes from solution and adsorption is considered as a promising technology for removal of dyes from solution. In this study, wheat straw was modified with polyethyleneimine to enhance adsorption capacity for anionic dye, Congo red (CR). The presence of the amine group on modified wheat straw (MWS) was confirmed by FTIR and elemental analysis. The CR adsorption onto the surface of MWS was performed in batch mode. The effects of pH, salt concentration, initial CR concentration, contact time, and solution temperature on adsorption quantity were performed. The results showed that the maximum adsorption capacity was reached at pH 5.0 and inorganic salt had little effect on CR adsorption. Isotherm and kinetic analysis showed that Langmuir and intraparticle model described the adsorption behavior very well, suggesting a monolayer adsorption and the rate-controlling step of intraparticle diffusion, respectively. The adsorption quantity was 89.7 mg g^{-1} at 303 K from Langmuir model. MWS can be efficiently regenerated with 0.1 mol L^{-1} sodium hydroxide solution and reused for CR adsorption. It was concluded that MWS might be a promising agent to adsorb anionic dye from solution.

Keywords: Adsorption; Congo red; FTIR; PEI-modified wheat straw; Regeneration

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1. Introduction

China is the world's largest country in wheat planting area and is the highest one in wheat consumption capacity. The wheat planting area is about 20–30% of the arable land every year and 90 million tons of wheat straw would be produced annually [1]. Because the yields of natural wheat straw (NWS) from agriculture are vast, it is very low cost and easily harvested. One part of these wheat straws are utilized as animal feed, rest is not properly utilized or is burnt in open environment, which is an unsustainable and non-recommendable practice [2]. There are various floristic fibers and some functional groups (hydroxyl, carboxyl, and amide) in NWS and these groups are available for adsorption process. NWS is selected as adsorbent according to its own structure and the surface chemical functional groups, which not only solves

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the problem of handling wheat straw issue but also finds a cheap raw material for adsorption. Natural or modified wheat straw (MWS) has been used as an available adsorbent to remove heavy metals and dyes from water/wastewater [3–7]. But the adsorption capacity of anionic pollutants is very low.

Dye wastewater is a serious problem if directly discharging into environment without any treatment and anionic dye waste is difficult to deal with. As the dyes usually contain azoaromatic groups, there is of extreme environmental concern due to their carcinogenic, mutagenic, and inert properties [8,9]. It is also a difficult degradation process and may result in ecological imbalance. So it is necessary to develop effective adsorbents to remove anionic dye from solution. Congo red (CR) is an anionic dye and it is widely used for cotton, hemp, silk, leather, paper, and wood products dyeing as its structural stability and good dying effect. Discharging CR into wastewater can cause great damage to the environment. In addition, this anionic dye can be metabolized to benzidine, a known human carcinogen [10]. Therefore, the removal of CR from solution is essential and important. Because of economic feasibility and simple implementation, adsorption has been employed as an effective method for the removal of refractory pollutants from wastewater.

In our previous study, cationic surfactants such as cetyltrimethyl ammonium bromide [11] and hexadecylpyridinium bromide [12] were used to modify wheat straw to remove anionic dye CR and light green, respectively. There was an enhancement of adsorption capacity after surfactant modification. The experiments indicated that positive surfactant-MWS was effective to remove anionic dye from solution.

Polyethyleneimine (PEI, a water-soluble polymeric amine) as a polymer contains a large number of $-NH$ and $-NH_2$ groups which may be beneficial for the removal of anionic dye. It can be used as a coagulant. There were several papers that native plant-derived materials modified by PEI were selected as adsorbent to remove anionic pollutants. Adsorbent and adsorbate can be combined strongly by electrostatic attraction as nitrogen atoms can be protonized in acid environment. M.S. Sajab et al. [13] reported that the adsorption capacity of phenol red was 171 mg g^{-1} with the initial concentration of 300 mg L^{-1} by PEI-modified oil palm empty fruit bunch. Deng and Ting [14] investigated PEI-modified fungal biomass as biosorbent for removal of Cr(VI) anions from solution. Sadaf et al. [15] used PEI-treated peanut husk biomass as adsorbent to remove direct dyes efficiently. The result indicated that electrostatic interaction between adsorbent and adsorbate played an important role in the process of adsorption. According to the reports, it is concluded that PEI is an effective cationic-modified reagent. So PEI-NWS may be an appropriate adsorbent for removal of anionic dye. However, there is no similar research.

In this study, PEI was physically adsorbed onto wheat straw surface and the weakly bound PEI was then cross-linked with glutaraldehyde (GA) to reinforce the stability of the adsorbent. PEI-MWS was characterized and was used as environment-friendly and low-cost adsorbent to remove CR from solution. The influence of initial solution pH, salt concentration, contact time, and dye concentration on adsorption quantity had been performed. Adsorption isotherms and kinetics parameters were also estimated. The CR-loaded MWS was regenerated and reused.

2. Materials and methods

2.1. Reagent

The NWS was obtained from suburb of Zhengzhou city, China. PEI (molecular weight 600, 99%, PEI) and GA (50%) were used to modify the wheat straw. The stock solution of CR (500 mg L^{-1}) was prepared in distilled water. All working solutions were prepared by diluting the stock solution with appropriate volume of distilled water. Other reagents such as HCl, NaOH, NaCl, and Na_2SO_4 are all analysis reagent.

2.2. Preparation of MWS

The collected wheat straw was washed with tap water to clean dust, soaked in the distilled water for 12 h to remove other impurities, washed with distilled water for several times, and oven dried at 80℃ for 12 h. The dried straw was milled and sieved to size range from 20 to 40 mesh, and preserved in the desiccators for use.

Two gram of dried NWS was treated with 70 mL PEI solution (25%) and stirred for 3 h at 303 K. The mixture was filtered and transferred into 100 mL GA (1%) solution and stirred for 20 min at 303 K. MWS was thoroughly washed with distilled water to remove the excess PEI and GA, and dried at 353 K in the oven.

2.3. Characterization

Samples of NWS and MWS were analyzed with FTIR spectrum in KBr matrix in the range of 4,000–400 cm^{-1} (PE-1710FTIR). The elemental analysis of NWS and MWS was performed (Thermo, FLASH EA1112).

2.4. Kinetic and equilibrium adsorption experiments

Batch experiment was carried out to evaluate the adsorptive behavior of MWS. 0.010 g of MWS was added in 50 mL flask with 10 mL CR solution at different dye concentrations and pH values of the solution. The initial pH of the solution was adjusted using NaOH and HCl solutions. The effect of pH of the solution was investigated within 2–12 and the effect of initial CR concentration was from 50 to 200 mg L^{-1}. The adsorption experiment was carried out at different temperatures of 293, 303, and 313 K, respectively. The effect of salt concentration on adsorption quantity was also evaluated. The mixture was agitated in the thermostatic oscillator for 8 h. After the equilibrium, the mixture was filtered and the residual concentration of CR in the solution was measured by UV–vis at a maximum wavelength of 498 nm. The experiments were duplicated and average values were shown.

The adsorbent quantity adsorbed per unit mass (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

Where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentration of CR, respectively. V is the volume of the dye solution (L), and m is the mass of adsorbent used (g).

2.5. Regeneration of dye-loaded adsorbent

MWS was recovered after batch equilibrium studies. The CR-loaded MWS were dealt with different methods. Some were put in different solutions (0.1 mol L^{-1} NaOH, 0.01 mol L^{-1} NaOH, 0.01 mol L^{-1} HCl, and 50% methanol) for 12 h. Some were treated with microwave in different power ranges (350, 500, and 600 W). The adsorbents were recovered and then repeated the batch adsorption process. Ten milligram of adsorbent was added in 10 mL solution of initial dye concentration of 100 mg L^{-1} and shaken for 8 h. This cycle was repeated for three times. The regeneration efficiency was calculated by the following equation:

$$\eta = \frac{q_i}{q_b} \times 100\% \tag{2}$$

where q_i is the adsorption quantity of recovered adsorbent (mg g^{-1}) and q_b is of the first adsorbent.

3. Results and discussion

3.1. Characteristic of MWS

In order to compare the difference of functional groups between NWS and MWS, FTIR spectrum of NWS and MWS were shown in Fig. 1, respectively. From Fig. 1, it was observed that spectra of NWS and MWS displayed many absorption peaks, reflecting the complex of the materials. There were hydroxyl group and carbonyl group on surface of NWS from analysis [16] and several of bands from lignin and hemicellulose were observed. The strong and broad peaks at 3,415 cm^{-1} were originated from O–H stretching vibration and this indicated significant hydrogen bond interactions. C–H stretching vibrations near 2,918 cm^{-1} from methylene group were also clearly observed. The peaks located at 1,732 and 1,634 cm^{-1} were contributed to stretching vibration of carbonyls. The absorption band at 1,377 cm^{-1} corresponded to the $-CH_3$ symmetrical deformation mode. The absorption bands, indicative of alcohols –OH and aliphatic ethers (C–O–C) (1,160–1,030 cm^{-1}), were related to oxygenated functional groups existed in cellulose [16]. The region below 1,000 cm^{-1} was the fingerprint zone and the peak could not clearly be assigned to any particular vibration because they corresponded to complex interacting vibration systems.

Compared to NWS, the absorption intensity at 1,731 cm^{-1} became lower and this may be related to a large number of the PEI molecules on the surface of NWS, which rendered the C=O group absorption in the FTIR analysis. The broad overlapping peak at 3,416 cm^{-1} became strong because a large number of amine groups were introduced on the surface. The peak evident at 1,150 cm^{-1} attributed to the C–N stretching vibration indicated that PEI reacted with GA on the surface.

Table 1 listed the results of elemental analysis. As shown in Table 1, the content of N, C, and H all increased after modification, and the proportion of the growth of the content was 22:15:5. The proportion was nearly equal to the proportion of the three elements in PEI, which indicated that the modified process was successful. It was well indicated from FTIR spectrum of MWS and elemental analysis that groups $-NH_2$ and –OH were present in abundance. These groups may function as proton acceptor, and hence they can bind anionic ions from solution by electric attraction, hydrogen bond, etc.

From all these evidences, it was clear that the PEI had been successfully coated onto the surface of NWS.

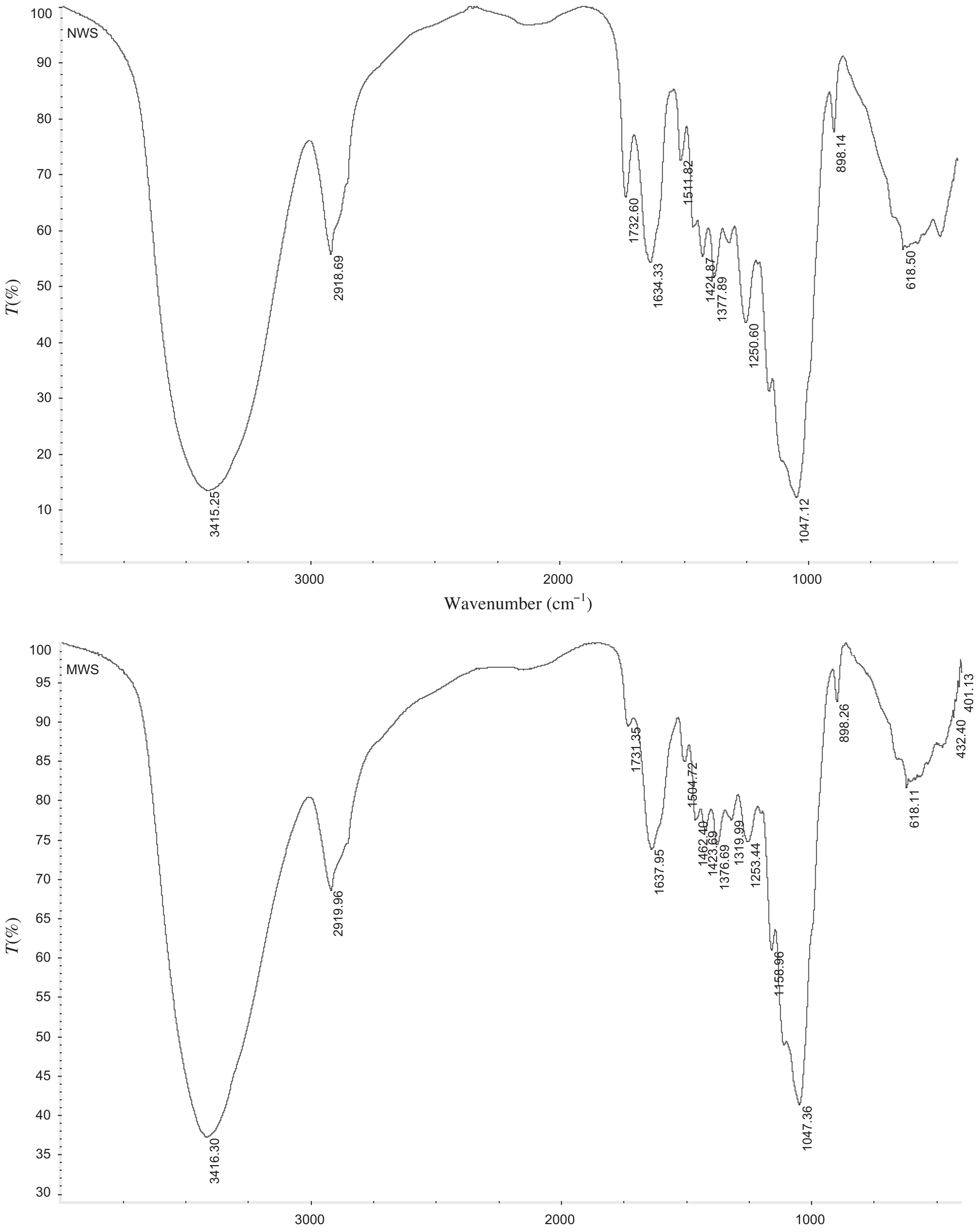

Fig. 1. FTIR of MWS and NWS.

Table 1
Element analysis (%)

Element	N	C	H
NWS	0.11	43.17	5.65
MWS	2.28	44.86	6.05

3.2. Batch adsorption

3.2.1. Effect of pH

pH of the solution is an important parameter influencing the adsorption process. The surface charge of an adsorbent and dissociation of functional groups on its active sites are both affected by pH of the solution. The degree of ionization and structural changes of dye molecules can also be influenced by pH of the solution [17]. Effect of various pH values of the solution on adsorption quantity was shown in Fig. 2. From Fig. 2, the adsorption quantity was enhanced with increase in pH from 1–5, and remained nearly constant in the base environment. The maximum adsorption capacity was shown at pH 5.0. As there were a lot of amine groups as protonation, the surface of MWS should be positively charged in acid solution. There was existed an electrostatic attraction between CR (anionic ions) and MWS. In theory, the electrostatic attraction force may be decreased with the increase in pH [18]. But the adsorption quantity became larger and remained nearly constant above pH 5.0. This implied that the electrostatic attraction is not the sole role and other actions might exist. Combing the FTIR spectrum of MWS, it was deduced that the main force may be a hydrogen bond between nitrogen element and hydrogen element in MWS and CR, while there may be conjugate between C=C in MWS and aromatic ring in CR. The optimum pH of the solution was selected as 5.0 in next experiments.

3.2.2. Effect of salt concentration

In the process of practical wastewater treatment, there are common salts in wastewater containing dyes, so it is necessary to study the effect of common salt. The effect of various concentrations of NaCl and Na_2SO_4 on CR adsorption was investigated using an initial concentration of 100 mg L^{-1} and pH 5.0 and the results were shown in Fig. 3. It was observed from Fig. 3 that the dye adsorption capacity of adsorbent increased from 75.8 to 81.0 mg g^{-1} when the concentration of common salt was from 0 to 0.12 mol L^{-1}, and a further increase in salt concentration leads to a smaller decrease in adsorption quantity.

Two reasons could explain the phenomenon. The first reason may be salting-out effect (with the increase in salt, the solubility of weak polar and non-polar compound decreased). There was a slight coagulation about CR which resulted in the increase in adsorption capacity. Another reason may be that the addition of salt reduced the thickness of electric double layer and it made easier for dye spread to the adsorbent surface. Similar results were reported about CR adsorption on chitosan [19]. In summary, inorganic salt that coexisted in solution was slightly preferred for adsorption and this was beneficial for practical application. This also showed that other actions (hydrogen bond,

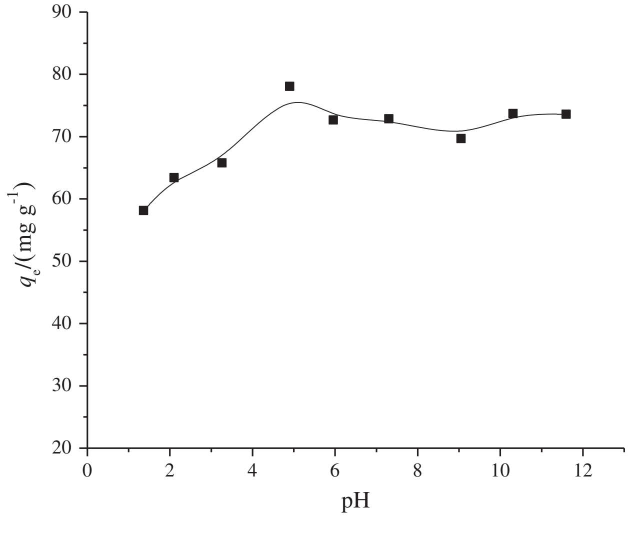

Fig. 2. Effect of pH on adsorption of CR on MWS (C_0 = 100 mg L^{-1}, T = 303 K).

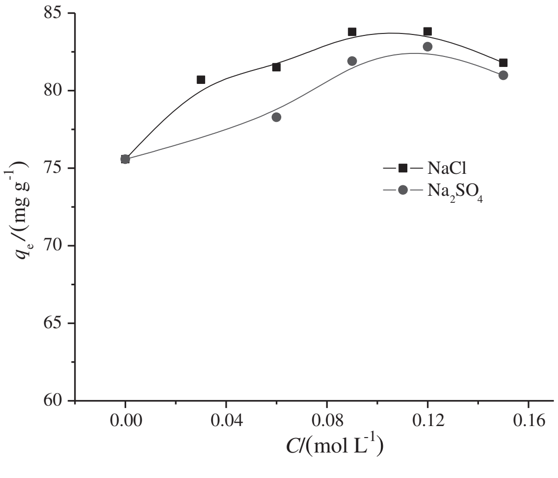

Fig. 3. Effect of salt concentration on sorption of CR on MWS (C_0 = 100 mg L^{-1}, pH 5.0, T = 303 K).

Van der Waals' force) were existed as well as electrostatic attraction between interaction of CR and MWS.

3.2.3. Isotherm study

The adsorption isotherms of CR at different temperatures were shown in Fig. 4. It was seen from Fig. 4 that the values of adsorption quantity (q_e) increased with the increase in CR equilibrium concentration (c_e). The driving force from concentration gradient was larger at higher CR concentration and this was the advantage of overcoming the resistances to the mass transfer of dye between the solution and solid phases. The increase in c_e enhanced the action between dye and adsorbent. Therefore, there were higher values of q_e with larger CR equilibrium concentration. The higher adsorptive capacity was also observed at higher temperature and this showed that the process was endothermic and it was in favor of adsorption at higher temperature. The value of q_e was up to 100.5 mg g^{-1} at 313 K.

According to the equilibrium isotherm, the maximum adsorption capability of the adsorbent can be evaluated and it can provide practical instruction in the design of adsorbent system to remove dyes from effluent. Also, the way of action between adsorbent and adsorbate can be described. In order to evaluate the nature of the interaction, two common models were selected: the Langmuir and Freundlich equations.

Langmuir model proposes a theory to describe the adsorption of gas molecules onto solid surfaces in 1916. It is now widely applied in solution adsorption process. The model assumed monolayer adsorption, once the active site was occupied, other adsorbent cannot be adsorbed at that site [20]. Moreover, the model depends on the assumption that there is no interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [21]. As we all known, each adsorbent has finite sites, so when the sites were all occupied, adsorption saturation was reached. The Langmuir model is expressed as

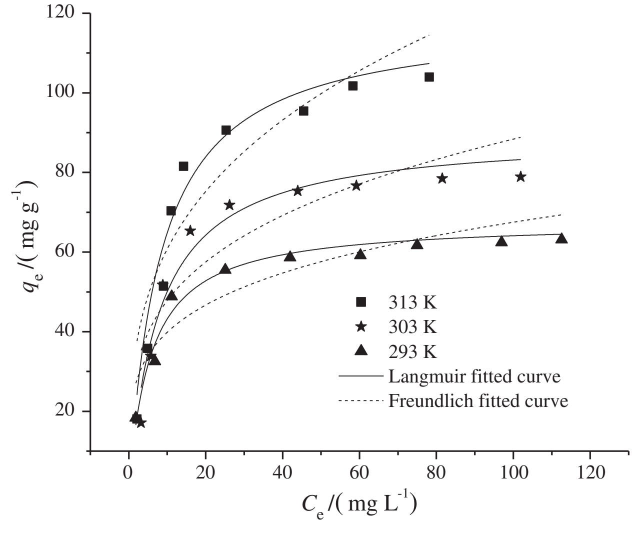

Fig. 4. Adsorption isotherms of CR on the MWS.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_e is the amount of dye adsorbed per unit weight of an adsorbent at equilibrium (mg g^{-1}), q_m is the adsorption capability (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), and K_L is a constant related to the adsorption energy (L mg^{-1}).

Freundlich model is known to describe the multilayer adsorption process with a uniform energy distribution [22]. It is derived by assuming an exponential decay energy distribution function inserted into the Langmuir equation [23]. It is widely used in heterogeneity adsorption process as the equation is convenient for calculation. Freundlich isotherm can be written as

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F and $1/n$ are the Freundlich constants representing the extant of adsorption and the degree of non-linearity between solution concentration and adsorption.

The q_e, q_m, R_L, K_F, $1/n$, and the determined coefficients R^2 and errors sum of the absolute errors (SAE), average relative standard error (ARS) were presented in Table 2 according to non-linear regressive analysis. Fig. 4 also showed the Langmuir model and Freundlich model fitted curves. According to Fig. 4 and the fitted results listed in Table 2, the better fit was achieved with Langmuir model, which was explained by the fact that this had two adjustable parameters and CR adsorption onto MWS was monolayer adsorption. The high degree of correlation for the non-linearity Langmuir relationship suggested a single surface reaction with constant activation energy would be the predominant adsorption step and possibly the predominant rate-controlling step [23]. The maximum adsorption quantity from Table 2 was 67.7, 89.7, and 118 mg g^{-1} at 293, 303, and 313 K, respectively. The adsorption capacity toward CR became higher with the increase in temperature at experimental conditions. There was a similar trend for parameter of K_L.

From Table 2, both parameters of Freundlich equation, K_F and $1/n$, became larger with the

Table 2
Parameters from modeling of CR adsorption using the Langmuir and Freundlich adsorption isotherm equations

Langmuir T/K	$q_{e\ (exp)}$ (mg g^{-1})	K_L (mg^{-1})	q_m (mg g^{-1})	R^2	SAE	ARS × 10^{-2}
313	104	0.120 ± 0.032	118.0 ± 9.0	0.900	66.3	1.69
303	78.9	0.126 ± 0.023	89.7 ± 4.0	0.945	38.2	1.89
293	66.1	0.176 ± 0.025	67.7 ± 1.8	0.968	20.1	0.247
Freundlich T/K	$q_{e\ (exp)}$ (mg g^{-1})	K_F	$1/n$	R^2	SAE	ARS × 10^{-2}
313	104	29.9 ± 7.6	0.308 ± 0.071	0.755	105	9.17
303	78.9	25.9 ± 5.9	0.267 ± 0.60	0.768	78.4	7.95
293	66.1	23.5 ± 3.6	0.229 ± 0.038	0.869	41.5	1.83

Note: $\text{SAE} = \sum |(q_c - q_e)|$, $\text{ARS} = \sqrt{(\sum((q_c - q_e)/q_e)^2)/(n-1)}$, q_e and q_c are the values of adsorption quantity from experiments and calculation according to adsorption model, respectively; n is the number of experimental points.

increase in temperature. The obtained values of $1/n$ ($0.1 < 1/n < 0.5$) indicated a higher adsorption ability of CR at all temperatures studied.

According to Langmuir isotherm, Webber and Chakkravorti [24] proposed the separation factor (R_L) equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where K_L is the Langmuir constant, C_0 refers the initial concentration of the adsorbate. The nature of the adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). By calculation, R_L is 0.077, 0.074, and 0.054 at 293, 303, and 313 K, respectively, that they are fall between 0 and 1, which shows the adsorption process is favorable in this study. Similar result was reported by Madrakian et al. [25].

3.2.4. Kinetic adsorption

Kinetic adsorption process describes the rate of the reaction, which can reveal the mechanism of adsorption. Fig. 5 showed the kinetic adsorption behavior of MWS in pH 5.0. As shown in Fig. 5, there were mainly two stages in adsorption process, the reaction stage from 0 to 360 min and the equilibrium stage from 300 to 540 min. The initial adsorption rate and the equilibrium adsorption quantity increased at higher temperature. This implied that higher temperature was favor of adsorption and the process was endothermic. So it was concluded that the adsorption

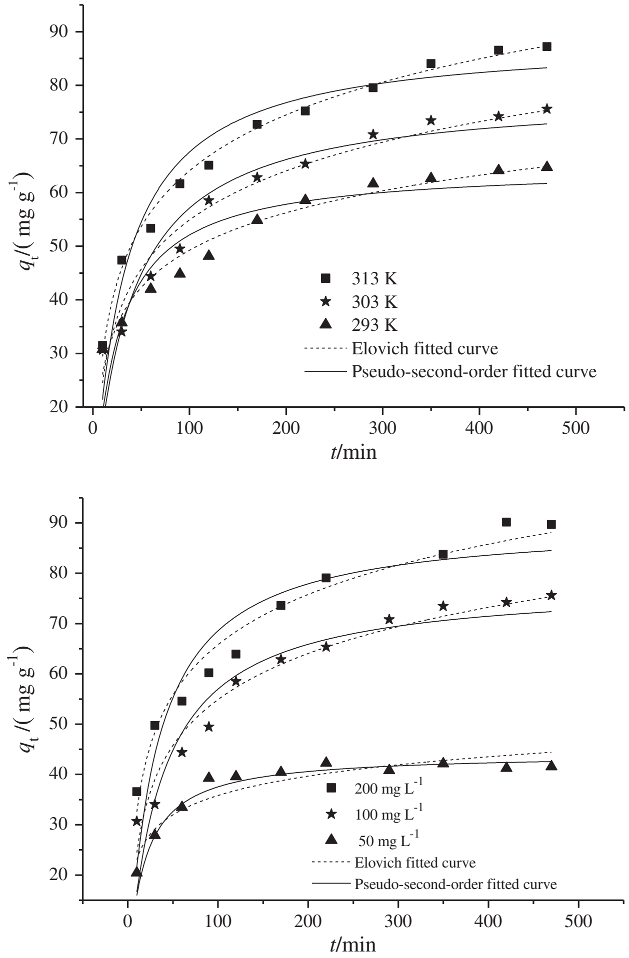

Fig. 5. Effect of contact time on adsorption quantity at different temperatures ($C_0 = 100$ mg L^{-1}, pH 5.0) and different initial concentrations (pH 5.0, $T = 303$ K).

reaction not be a simple physical adsorption, there must be a physical-chemical reaction.

The adsorption quantity of MWS toward CR was 74.2 mg g^{-1} for MWS ($T = 303$ K, $C_0 = 100$ mg L^{-1}, and dose 10 g L^{-1}), while the value of NWS was 8.1 mg g^{-1} (kinetic curve not shown) at the same experimental condition. This showed that the adsorptive capacity was strongly enhanced after PEI modification due to the nitrogen-containing functional groups after modification which was in favor of CR adsorption. Fig. 5 also showed that the equilibrium time increased with the increase in CR initial concentration. As dosage of adsorbent was constant, it would take long time to attain high adsorption quantity.

Pseudo-second-order model, Elovich model, and intraparticle diffusion model were applied to analyze the result of kinetic adsorption.

Pseudo-second-order model [26] is based on the adsorption capacity which predicts the behavior over the whole range of studies supporting a pseudo-second-order equation and is in agreement with chemisorptions being the rate-controlling step. The expression is following:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{6}$$

where k_2 refers to the second-order rate coefficient, q_t and q_e are the amounts of dyes adsorbed at time t and at equilibrium (mg g^{-1}), respectively.

The Elovich equation [27] assumes that the surface of adsorbent is energetically heterogeneous and that the adsorption rate index decreases with the increasing amount of adsorbate adsorbed onto adsorbent.

$$q_t = \beta \ \ln \ t + \beta \ \ln \ (\alpha\beta) \tag{7}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}) during experiment.

Intraparticle diffusion model is used to evaluate the rate-controlling step in CR adsorption process. It is based on the following mechanistic steps: (1) adsorbate molecular transported the boundary layer surrounding the adsorbent; (2) internal diffusion (transfer within the internal structure of the adsorbent particles); (3) adsorption on the surface. The intraparticle diffusion model [28] is generally expressed as follows:

$$q_t = K_p t^{1/2} + C \tag{8}$$

where K_p is the rate constant of intraparticle diffusion (mg g^{-1} min^{-2}), and C (mg g^{-1}) is the constant which is determined by the thickness of boundary layer; the larger the value of C, the greater the thickness of the boundary layer. C and K_p is the intercept and slope of the linear plot of q_t vs. $t^{1/2}$. A liner fitting curve through the origin suggested that adsorption was controlled by the internal diffusion. If not through the origin, the external mass transfer resistance cannot be neglected, so the adsorption process may be controlled by more than one process.

Parameters of three kinetic models and determined coefficients were listed in Table 3 according to non-linear regressive analysis. From Table 3, the results with higher values of R^2 and low errors showed a good compliance with the pseudo-second kinetic model. The values of equilibrium adsorption capacity calculated by pseudo-second-order model were close to the experimental data at the same condition, respectively. So the equilibrium capacity of adsorption can be evaluated with the pseudo-second-order rate equation. Furthermore, the fitted curves of pseudo-second-order model (also shown in Fig. 5) were also close to experimental data. These implied that this model is best to describe the kinetic process.

From Table 3, higher values of R^2 with lower values of *SAE* for Elovich equation showed that this equation was also available to describe the kinetic process. The fitted curves were also close to experimental data. This result suggested that the ion exchange as interaction would be existed between MWS and CR.

In this study, only the initial adsorption stage was fitted by the intraparticle diffusion model. The parameters at three temperatures were shown in Table 3. The values of R^2 for the intraparticle diffusion models were between 0.95 and 0.99, so the rate of adsorption was an intraparticle diffusion model mechanism (fitted curves were not shown). From Table 3, the reaction stage data showed good linearity and the lines had non-zero intercepts. So the rate-controlling step was not only the intraparticle diffusion. However, the intraparticle diffusion played an important role in the adsorption as the C value was smaller than q_e. It was concluded that the reaction rate is mainly controlled by the intraparticle diffusion meanwhile affected by the layer diffusion.

3.2.5. Regeneration of CR-loaded MWS

Regeneration of the exhausted adsorbent is a crucial step in order to increase its practical applicability [29–32]. The batch experiment demonstrated the preferred removal of CR by MWS. Because of its low cost

Table 3
Parameters from modeling of CR using the pseudo-second-order equation, Elovich equation, and intraparticle diffusion equation

Pseudo-second-order equation

T/K	C_0 (mg L^{-1})	q_e (exp) (mg g^{-1})	k_2 (g mg^{-1} min^{-1}) × 10^{-4}	q_e (mg g^{-1})	R^2	SAE	ARS × 10^{-3}
303	50	41.5	17.4 ± 2.2	43.3 ± 0.67	0.960	12.1	1.05
303	100	75.6	3.36 ± 0.91	78.7 ± 3.8	0.882	37.9	12.1
303	200	89.7	4.07 ± 1.3	88.7 ± 4.8	0.832	55.9	10.5
293	100	66.7	6.24 ± 2.0	64.9 ± 3.3	0.792	45.1	10.6
313	100	87.2	3.57 ± 0.85	88.9 ± 3.6	0.905	49.2	7.3

Elovich equation

T/K	C_0 (mg L^{-1})	q_e (exp) (mg g^{-1})	α	$\beta \times 10^2$	R^2	SAE	ARS × 10^{-4}
303	50	41.5	35.6 ± 6.7	18.1 ± 9.1	0.876	21.9	23.9
303	100	75.6	8.39 ± 0.58	7.58 ± 7.1	0.956	25.5	39.0
303	200	89.7	13.8 ± 0.67	6.94 ± 0.21	0.966	25.1	16.5
293	100	66.7	13.4 ± 1.1	9.92 ± 9.1	0.927	30.9	28.9
313	100	87.2	10.6 ± 0.26	6.65 ± 6.4	0.985	18.2	7.09

Intraparticle diffusion equation

T/K	C_0 (mg L^{-1})	q_e (exp) (mg g^{-1})	K_t	C	R^2	SAE	ARS × 10^{-3}
303	50	41.5	14.1 ± 0.86	−5.01 ± 2.2	0.989	2.10	0.215
303	100	75.6	18.3 ± 1.0	−5.05 ± 3.5	0.975	15.3	1.85
303	200	89.7	19.0 ± 0.96	3.09 ± 3.1	0.982	13.6	0.462
293	100	66.7	11.9 ± 1.4	8.29 ± 3.7	0.950	4.93	0.907
313	100	87.2	20.2 ± 0.93	−2.36 ± 2.9	0.985	212.3	0.701

and simple method of preparation, MWS was available for removal of pollutants from wastewater. The regeneration efficiency was also an important parameter in practical application. Fig. 6 showed the results of regeneration efficiency with various methods. As shown in Fig. 6, the best solution of regeneration was 0.1 mol L^{-1} NaOH and the regeneration efficiency was 78.9%. This may be because the hydrogen bond was broken in base environment. So the infinity between adsorbent and adsorbate decreased, and desorption of the adsorbate from the adsorbent resulted in regeneration ability of MWS. The efficiency of regeneration was 78.9, 75.6, and 73.7% with three cycle adsorption–desorption process. This implied that MWS can be reused with loss of part adsorption quantity.

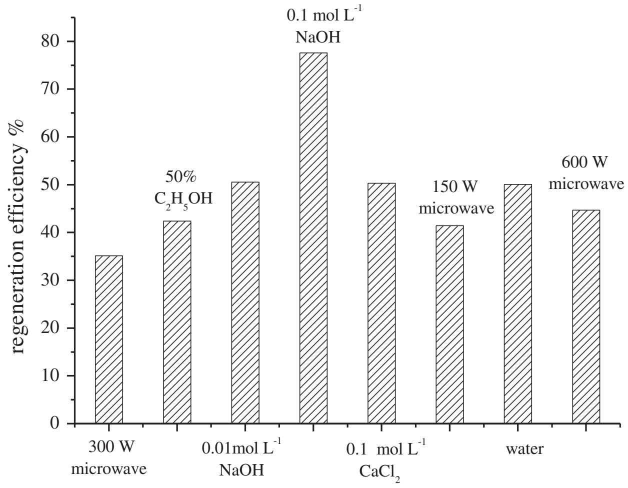

Fig. 6. Regeneration efficiency at various conditions.

3.3. Comparison of adsorption capacity with other adsorbents

The adsorption capacity of wheat straw toward CR was significantly improved through PEI modification. Other adsorbents were also published to remove CR from solution. Generally, the q_m (obtained from the Langmuir constant) can describe the adsorption capacity of one adsorbent to some extent. Values of q_m

Table 4
CR adsorption capacity toward CR: a selection of the Langmuir constant, q_m, of various related materials from the literatures

q_m (mg g^{-1})	Adsorbent	T/K	References
31.25	Eucalyptus wood sawdust	303	[33]
72.4	Neem leaf powder	300	[34]
18.2	Banana peel	303	[35]
14.0	Orange peel	303	[35]
35.7	Jute stick powder	303	[36]
73.4	Ethylenediamine-modified wheat straw	303	[37]
6.72	Activated carbon prepared from Coir pith	298	[38]
39.8	Sugarcane bagasse	298	[39]
17.39	Grafted *Luffa cylindrica* cellulosic fiber	303	[40]
300	Activated carbon	308	[41]
5.44	Zeolite	303	[42]
3.77	Kaolin	303	[42]
35.84	Na–Bentonite	303	[42]
67.7	MWS	293	This study
89.7	MWS	303	This study
118.0	MWS	313	This study

toward CR from the literatures were listed in Table 4. From Table 4, the values of q_m of CR onto MWS were relatively higher compared to some adsorbents, while lower than the slightly expensive adsorbents such as activated carbon. This implied that MWS is an efficient, competent, and promising adsorbent for CR adsorption.

4. Conclusion

Batch adsorption of CR using PEI MWS had been investigated in present work. The highest adsorption capacity reached at pH 5.0. Common salt that coexisted in solution was the advantage of CR adsorption. Adsorption capacity increased with temperature showed the adsorption was endothermic. The results indicated that the adsorption mechanism was hydrogen bond interaction rather than electrostatic attraction. The experimental isotherm data were analyzed by Langmuir and Freundlich equations and Langmuir equation was found to provide the better prediction for the sorption of CR which demonstrated monolayer adsorption. Value of q_m was 89.7 mg g^{-1} at 303 K. The kinetic process was available described by pseudo-second-order model. The adsorption of CR may be controlled by intraparticle diffusion step as the kinetic adsorption data fitted the intraparticle diffusion model very well. The regeneration studies proved that MWS can be reused with higher efficiency of regeneration. It was concluded that MWS be effective, low cost, and promising to remove anionic dye from solution.

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