Adsorption of Reactive Red 141 from wastewater onto modified chitin

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Abstract

This research involved the adsorption of synthetic reactive dye wastewater (SRDW) by chitin modified by sodium hypochlorite and original chitin in batch experiments. The comparison of maximum adsorption capacity used the Langmuir model to describe SRDW adsorption onto chitin and modified chitin under a system pH of 11.0. Maximum dye adsorption by chitin increased from $133\,\mathrm{mg\,g^{-1}}$ to $167\,\mathrm{mg\,g^{-1}}$ at temperatures of 30–60 °C, respectively. For modified chitin, the capacity decreased from $124\,\mathrm{mg\,g^{-1}}$ to $59\,\mathrm{mg\,g^{-1}}$ when the temperature increased from 30 °C to 60 °C, respectively. Both Na_2SO_4 and Na_2CO_3 increased in dye adsorption. The spectra of attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry confirmed the hydroxyl groups as functional groups of modified chitin, which affected the modification and the SRDW adsorption. The adsorbed dyes were eluted by distilled water and 1 M NaOH to confirm the dye adsorption mechanism. Total elution of modified chitin and chitin were 92.76% and 55.29%, respectively. Although modified chitin had a maximum adsorption capacity less than chitin, elution of the dye from modified chitin was easier than chitin. Therefore, modified chitin could be suitable in a column system for dye pre-concentration as well as wastewater minimisation. In addition, the column study showed that modified chitin could be used for more than four cycles of adsorption and elution by distilled water.
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1. Introduction

The wastewater produced by textile industries is currently an important problem in Thailand. These industries produce a lot of wastewater, which includes a large number of contaminants such as acids, caustics, toxic organics, inorganics, dissolved solids, and dyes [1,2]. Among textile effluents, reactive dye wastewater has limited biodegradability in an aerobic environment, while many azo dyes, constituting the largest dye groups, may, under anaerobic conditions in the environment, decompose into potential carcinogenic aromatic amines [3,4]. Furthermore, it is difficult to remove reactive dyes using chemical coagulation due to the dyes' high solubility in water [5]. Adsorption with activated carbon appears to be the best prospect for elim-

ination of this dye. Despite its effectiveness, this adsorbent is expensive and difficult to regenerate after use. Therefore, many researches in recent years have focused on the use of various low-cost adsorbents to replace activated carbon [6].

Chitin is usually obtained from waste materials from the seafood processing industry, mainly shells of crab, shrimp, prawn and krill [7]. Shrimp shell waste is a plentiful waste from the Thai seafood processing industries (200,000 t per year). This polymer is also known to be an effective adsorbent in the adsorption of reactive dyes [8–11]. Accordingly, chitin has the potential to be an inexpensive and effective adsorbent for reactive dye wastewater removal, but the problem with chitin is the difficulty in the elution of adsorbed-dye adsorbent, making this adsorbent suitable for only one time use. Therefore, modified chitin is pretreated by sodium hypochlorite solution, which allows elution easily by water. Therefore, modified chitin was selected as the adsorbent in this study.

The objective of this research is to study the feasibility of using modified chitin as a new adsorbent for the removal of azo reactive dye from SRDW. The SRDW, which contains C.I.

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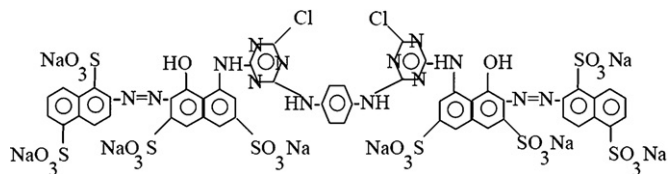[1] Present address: Division of Biotechnology, Thammasat University, Bangkok, Thailand.

Fig. 1. Chemical structure of diazo C.I. Reactive Red (RR141).

Reactive Red 141, a bright red colour of azo reactive dye, sodium sulphate and sodium carbonate, imitated real dyeing wastewater from the textile industry. The adsorption isotherms and elution tests were investigated in comparison with chitin. Additionally, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were applied for analysis of the functional groups of modified chitin before and after pretreatment and before and after SRDW adsorption under caustic conditions. The mechanism of modified chitin in dye adsorption was also investigated.

2. Materials and methods

2.1. Modified chitin

Chitin (48% DD) from shrimp shell waste was supplied by Seafresh Chitosan (Lab) Co. Ltd., Thailand. The average particle sizes were 400 μm to 1 mm and were bleached with sodium hypochlorite solution (as available chorine 6% (w/w)) at a ratio of 1:30 (w/v). Then, the modified chitin was washed with an excess of distilled water until the pH of washing solution was about 7 before it dried. The BET surface area, total pore volume and average pore volume of chitin and modified chitin 1:30 (w/v) were analyzed by a surface area analyzer (Quantachrome, Autosorb-1).

2.2. Dye

C.I. Reactive Red 141 (RR141) was obtained from DyStar Thai. Co. Ltd., the structure is shown in Fig. 1. The wavelength of maximum absorbance (λ_{max}) for RR141 is 544 nm. RR141 has a molecular weight and solubility of 1774 and $50 \, g \, l^{-1}$, respectively.

2.3. Synthetic reactive dye wastewater (SRDW)

The dyeing process was obtained from DyStar Thai. Co. Ltd. The laboratory dyeing process consisted of $4 \, g \, l^{-1}$ of RR141, $90 \, g \, l^{-1}$ of sodium sulphate, and $20 \, g \, l^{-1}$ of sodium carbonate, which were added during the dyeing process. Sodium sulphate and sodium carbonate were added to increase the dye substantivity and improve fastness, respectively. Moreover, the ratio of fabric and dyeing solution was 1:10 (w/v). After the dyeing process, the dyeing wastewater contained $400 \, mg \, l^{-1}$ of RR141 and was used as the SRDW sample for this research. However, λ_{max} for SRDW and RR141 were the same, at 544 nm.

2.4. Adsorption isotherm and thermodynamic study

Adsorption equilibrium experiments were obtained by contacting 10 ml of SRDW solution with varying dosages of adsorbents at a range of 0.05–3% (w/v) in a 15 ml vial under caustic conditions. The mixtures were shaken at a speed of 150 rpm at temperature of 30 °C, 40 °C and 60 °C for an equilibrium time of 6 h. The samples were centrifuged at 4500 rpm for 10 min. The changing pH of the supernatant was detected by a pH meter (Mettler Delta 340, England) and then analyzed for colour by a UV–Vis Spectrophotometer (DR/4000, HACH, USA).

This study used the non-linear Langmuir isotherm to describe synthetic reactive dye wastewater adsorption onto chitin and modified chitin is shown in Eq. (1).

$$q_e = \frac{q_{max} C_e}{1/b + C_e} \qquad (1)$$

where b = Langmuir constant related to energy $(1 \, mg^{-1})$; C_e = concentration of dye at equilibrium concentration $(mg \, l^{-1})$; q_e = amount of dye adsorbed at equilibrium $(mg \, g^{-1})$; q_{max} = maximum adsorption capacity $(mg \, g^{-1})$.

2.5. Functional groups of modified chitin

ATR-FTIR Spectrometry (Magna-IR 750 Series II, USA) was applied for confirmation of functional groups which are involved in modification and SRDW adsorption.

2.6. Elution test

1% (w/v) of adsorbed-dye adsorbents was dried and added into a syringe, which connected to a Vacuum manifold (Ashcroft, USA) with a flow rate ranging between $0.29 \, ml \, min^{-1}$ and $0.31 \, ml \, min^{-1}$. Adsorbed-dye adsorbents were eluted by 10 ml of deionised water until no colour appeared in the solution and then 1 M NaOH was used as a second eluent. The colour analysis of the solution was obtained by UV–Vis Spectrophotometer.

3. Results and discussion

3.1. Surface area and porosity

BET surface area, total pore volume and average pore volume of chitin and modified chitin 1:30 (w/v) are shown in Table 1. The decrease in BET surface area and total pore volume of chitin after modification with sodium hypochlorite might be due to the shrinking of modified chitin and/or the effect of sodium and hydrate to the interior pores. However, the average pore diameters of both chitin and modified chitin are classified as mesopores (20–500 Å) [12].

3.2. Adsorption isotherm and thermodynamic study

The effect of temperatures of 30 °C, 40 °C and 60 °C on the adsorption isotherm of SRDW by chitin and modified chitin are

Table 1
Surface area, total pore volume and average pore diameter of chitm and modified chitin 1:30 (w/v)

Sample	BET surface area[a] ($m^2\,g^{-1}$)	Total pore volume ($ml\,g^{-1}$)	Average pore diameter (Å)
Chitin	10.14	0.0256[b]	101.20
Modified chitin 1:30 (w/v)	3.01	0.0052[c]	69.83

[a] Specific surface area.
[b] Total pore volume for pore with diameter less than 1843.8 Å at $P/P_0 = 0.98948$.
[c] Total pore volume for pore with diameter less than 3265.7 Å at $P/P_0 = 0.99410$.

Table 2
Langmuir constants and separation factor for the adsorptions of SRDW by chitin and modified chitin at different temperatures

Adsorbent	Temperature (°C)	q_{max} ($mg\,g^{-1}$)	R^2	b ($1\,mg^{-1}$)	R_L
Chitin	30	133	0.9882	0.0108	0.197
	40	145	0.9827	0.0103	0.202
	60	167	0.9871	0.0088	0.230
Modified chitin	30	124	0.9824	0.0068	0.273
	40	101	0.9945	0.0060	0.307
	60	59	0.9789	0.0054	0.332

shown in Fig. 2. They were fitted by the Langmuir isotherm better than the Freundlich isotherm (data not shown). The dye adsorption of chitin increased when increasing the temperature, while the adsorption of modified chitin decreased with the rise in temperature of the system.

The values of q_{max} and b at different temperatures were determined from DeltaGraph 5 (Red Rock software, Inc., 1998–2005). All constant values obtained by this model are represented in Table 2. The effect of temperature on chitin shows that the adsorption capacity increased with increasing temperatures while the capacity of modified chitin was decreased. Maximum dye adsorption by chitin increased from 133 mg g^{-1} to 167 mg g^{-1} at temperatures of 30 °C to 60 °C, respectively. For modified chitin, the capacity decreased from 124 mg g^{-1} to 59 mg g^{-1} when the temperature increased from 30 °C to 60 °C, respectively.

However, the q_{max} values of chitin were higher than those of modified chitin. This might explain why chitin had maximum SRDW adsorption capacity more than the adsorption by modified chitin. But the q_{max} value of chitin at low temperature was lower than at high temperature at equilibrium conditions on the Langmuir plots. This might indicate that chitin can adsorb SRDW at higher temperature. In addition, it had a high affinity and strength for SRDW adsorption at initial concentration at low temperature which was opposite of modified chitin. For practical application, the concentration of dye in wastewater, the values of q_{max} and b were also considered for the determination of the most suitable temperature for wastewater treatment.

The influence of the adsorption isotherm shape has been discussed to determine whether adsorption is favourable in terms of R_L [13], a dimensionless constant referred to as the separation factor. R_L is calculated using Eq. (2) [14].

$$R_L = \frac{1}{1 + bC_0} \qquad (2)$$

C_0 is the initial SRDW concentration (mg l^{-1}). The values of R_L calculated in the above equation are incorporated into Table 2. The results showed that increasing the temperature from 30 °C to 60 °C induced a higher maximum adsorption capacity. All of the R_L values were between 0 and 1. This indicated that chitin and modified chitin were favourable adsorbents for SRDW removal [13,14].

The decreasing of maximum adsorption capacity for SRDW of modified chitin might be due to the action of sodium hypochlorite (NaOCl) in bleaching processing as shown in Eq. (3) [15].

$$NaCIO + H_2O \rightleftharpoons Na^+ + HClO + OH^- \qquad (3)$$

The hypochlorous acid (HClO) in solution affected with alcohol groups (CH$_2$OH) of cellulose polymer and transformed into CH$_2$OCl [15]. Accordingly, hydroxyl groups of alcohol groups on cellulose polymers were the effective functional group of covalent linkage for dye adsorption under caustic conditions. Therefore, the transformation of alcohol groups also affected the decreasing of dye adsorption by modified chitin.

3.3. The effect of Na$_2$SO$_4$ and Na$_2$CO$_3$ in dye adsorption

In the dyeing process, dye is dissolved in water. Salt is then added, causing the dye to be exhausted on the fabric and Na$_2$SO$_4$

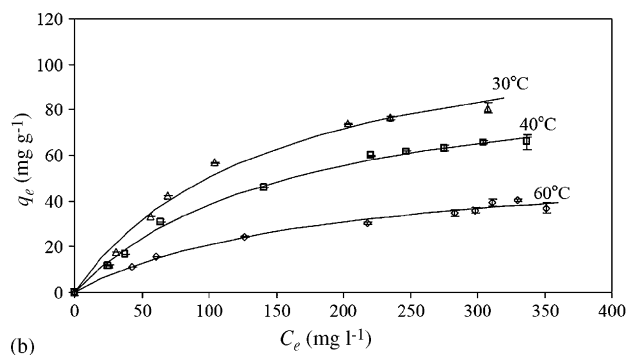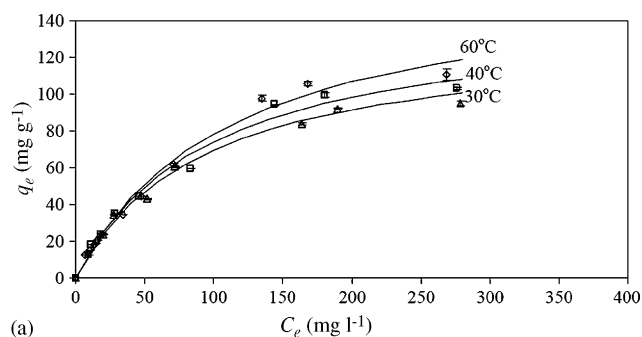
Fig. 2. The adsorption isotherms of synthetic reactive dye wastewater by (a) chitin and (b) modified chitin at different temperatures (△) 30 °C, (□) 40 °C and (◇) 60 °C.

Table 3
Effect of Na$_2$SO$_4$ and Na$_2$CO$_3$ on the dye adsorption by chitin and modified chitin

Sample	pH		% Colour removal
	Initial	System	
RR 141 + chitin	6.99	8.84	6
RR 141 + Na$_2$SO$_4$ + chitin	8.36	9.69	63
RR 141 + Na$_2$CO$_3$ + chitin	11.13	10.73	31
SRDW[a] + chitin	11.47	11.12	93
RR 141 + modified chitin	6.99	9.66	13
RR 141 + Na$_2$SO$_4$ + modified chitin	8.36	10.02	8
RR 141 + Na$_2$CO$_3$ + modified chitin	11.13	10.63	11
SRDW[a] + modified chitin	11.47	11.07	64

[a] SRDW = RR 141 + Na$_2$SO$_4$ + Na$_2$CO$_3$.

was added at the first step of dyeing to prevent dye hydrolysation and increase physical adsorption between dye and fabric. After that, Na$_2$CO$_3$ is added as alkali, used to get better penetration. The SRDW also consisted of reactive dye, Na$_2$SO$_4$ and Na$_2$CO$_3$. As expected from the salt effect on adsorption, an increase in apparent substantivity of the dyes by the crossing of diffusion profiles at intermediate dye concentrations occurs. As a result, the increase in surface concentrations results in the penetration of dye into adsorbents [16]. From Table 3, both Na$_2$SO$_4$ and Na$_2$CO$_3$ affected adsorption of chitin rather than modified chitin, possibly because the hydroxyl group of modified chitin was transformed into CH$_2$OCl by HOCl which decreased the dye adsorption by modified chitin.

3.4. Functional group of modified chitin

Fig. 3a and b represents the ATR-FTIR spectra of chitin before and after SRDW adsorption under caustic conditions, respectively. The peaks of 1558 cm^{-1} (−NH$_2$), 1621 cm^{-1} (amide II), 1654 cm^{-1} (amide I), 1205 cm^{-1} (CNH), 1258 cm^{-1}
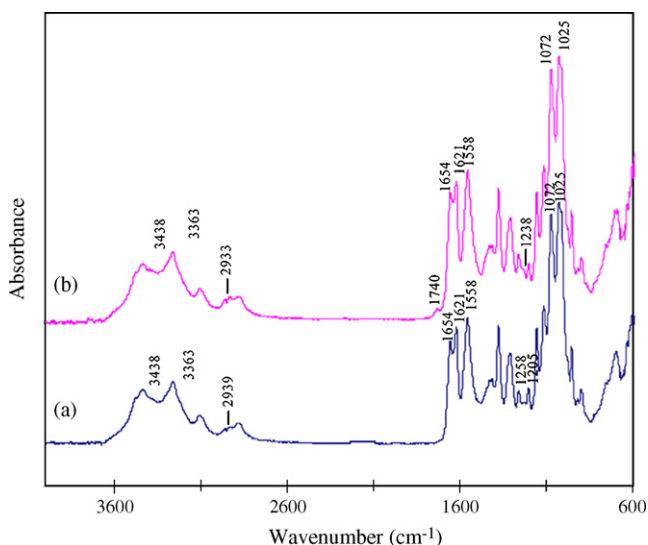

Fig. 3. ATR-FTIR spectra of chitin before (a) and after (b) adsorption of synthetic reactive dye wastewater under caustic conditions.
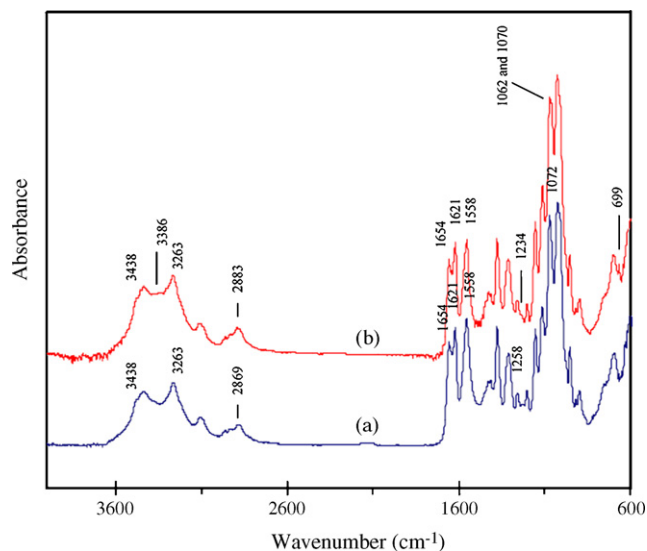

Fig. 4. ATR-FTIR spectra of chitin (a) before and (b) after modification by sodium hypochlorite.

(CNH), 1025 cm^{-1} (C−N), 3363 cm^{-1} (N−H) and 3438 cm^{-1} (N−H) are the original peaks of chitin (Fig. 3a). Accordingly, the hydroxyl group of chitin was the mainly effective functional group for SRDW adsorption caused by covalent bond formation under caustic conditions. Therefore in Fig. 3b, the peak at 2939 cm^{-1} (OH) was slightly shifted to be 2933 cm^{-1}, and the new shoulder peak occurred at 1238 cm^{-1} (C−O). Furthermore, the peak at 1740 cm^{-1} (H$_3$O)$^+$ of sulphate anion of dye appeared in Fig. 3b. The result implied that the hydroxyl group of chitin was the effective functional group for SRDW adsorption under caustic conditions.

Fig. 4a and b shows ATR-FTIR spectra of chitin before and after modification by sodium hypochlorite. The peaks of 1558 cm^{-1} (−NH$_2$), 1621 cm^{-1} (amide II), 1654 cm^{-1} (amide I), 1205 cm^{-1} (CNH), 1258 cm^{-1} (CNH), 1025 cm^{-1} (C−N), 3363 cm^{-1} (N−H) and 3438 cm^{-1} (N−H) are the original peaks of chitin (Fig. 4a). Accordingly, sodium hypochlorite affected the alcohol group (CH$_2$OH) of chitin and transformed it to CH$_2$OCl. Therefore, Fig. 4b shows the peak at 2869 cm^{-1} (C−O) was shifted to 2883 cm^{-1} and the peak 1072 cm^{-1} (C−O) was divided into two small peaks at 1062 and 1070 cm^{-1}. Furthermore, the new small peaks appeared at 669 cm^{-1} (Cl), 1234 cm^{-1} (C−O) and 3386 cm^{-1} (OH). Therefore, the result implied that the transformation of the alcohol group to CH$_2$OCl had affected SRDW adsorption.

The ATR-FTIR spectra of modified chitin before and after SRDW adsorption under caustic conditions are represented in Fig. 5a and b. In addition, the elution studied using water showed that it could elute SRDW from modified chitin to 83%. Therefore, physical adsorption might be occurring in the adsorption mechanism. Fig. 5b shows the small peak at 3386 cm^{-1} (OH) and the peak at 669 cm^{-1} (Cl) disappeared. Furthermore, the small peaks of 1062 cm^{-1} and 1070 cm^{-1} were changed to a single peak at 1072 cm^{-1} (C−O). That might be due to bonding of (O−Cl), which was destroyed under caustic conditions when the Cl group came out of modified chitin.
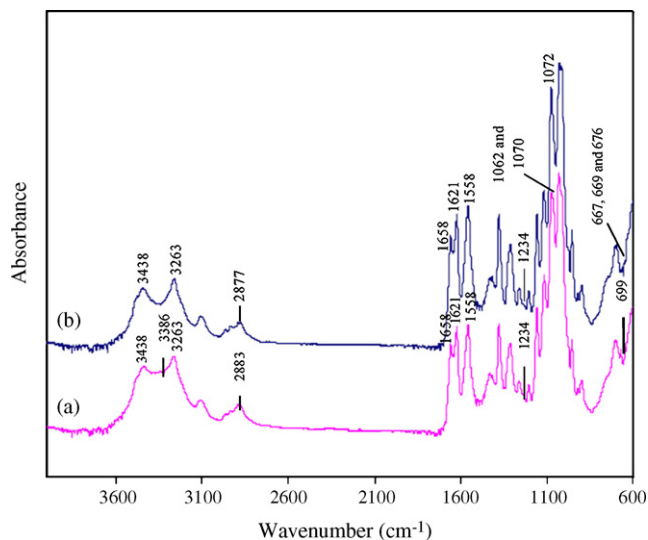
Fig. 5. ATR-FTIR spectra of modified chitin (a) before and (b) after synthetic reactive dye adsorption under caustic conditions.

3.5. Elution test

After adsorption of SRDW by chitin and modified chitin, the elution test was performed to confirm the dye adsorption mechanism of chitin and modified chitin in order to know the nature of the process by which the dye remains adhered to the surface of the adsorbents.

The result showed that distilled water could elute the dye from chitin and modified chitin to 37% and 89%, respectively. Accordingly, water can destroy the van der Waals' force between the azo group (−N=N−), amine group (−NH$_2$) and amide group (−CO−NH−) of chitin and modified chitins. Table 4 indicates that modified chitin was eluted by distilled water more than chitin. This might be due to transformation of the hydroxyl group of the primary alcohol position in modified chitin to CH$_2$OCl, while this position of chitin can be formulated as CH$_2$−O$^-$, when the leaving group (Cl) of the dye can undergo nucleophilic displacement by the hydroxyl group, so that the covalent linkage is difficult to destroy with only distilled water.

However, NaOH is also used as another eluent. This substance may destroy the covalent linkage between the dye and absorbents. Therefore, NaOH could elute the dye out of chitin and modified chitin by 18% and 3%, respectively. These were correspondent to the theory of dyeing, during which the leaving group can undergo nucleophilic displacement by a hydroxyl group of the cellulose.

Therefore, the main dye adsorption mechanism of modified chitin was physical adsorption, while the adsorption mechanism of chitin was chemical adsorption.

3.6. Regeneration of chitin and modified chitin

The experiment was performed for five cycles of adsorption and desorption. The adsorbents were studied in a column which connected to a vacuum manifold. After that, elution tests using distilled water as the first eluent were carried out until no dye occurrence was visible. NaOH was used as the second eluent to elute dye-adsorbed adsorbents.

In regards to the efficiency of desorption, chitin was lower than modified chitin. Chitin was slightly changed from 65% to 48%, while modified chitin exhibited a slightly change from 97% to 71%. This indicated that modified chitin could remove synthetic reactive dye wastewater less efficiently than chitin. It can desorb dye higher than chitin. These column studies showed that modified chitin could be used for more than four cycles of adsorption and elution by distilled water.

4. Conclusions

Modified chitin has the potential to be a new adsorbent for removal of reactive dye from textile wastewater because it can adsorb reactive dyes under caustic conditions and can elute the dyes using distilled water. In addition, physical adsorption occurred during the adsorption mechanism. However, the ATR-FTIR spectra confirmed that the hydroxyl group on the modified chitin polymer transformed into CH$_2$OCl that cannot react with the dye solution. This caused the maximum adsorption capacity of chitin to be higher than that of modified chitin. Therefore, dye adsorption by modified chitin involves mainly physical adsorption.

Acknowledgments

Table 4
Elution test of dye-adsorbed chitin and modified chitin under caustic conditions by using water and 1 M NaOH as eluents

Absorbent	pH		% Desorption
	Initial	System	
(a) Water elution			
Chitin	7.96	7.63	37.09
Modified chitin		7.38	89.46
(b) NaOH elution			
Chitin	13.17	12.87	18.20
Modified chitin		12.75	3.30
(c) Total elution			
Chitin			55.29
Modified chitin			92.76

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