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Reactive Red (RR141) Solution Adsorption by Nanochitin Particle via XAS and ATR-FTIR Techniques

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ABSTRACT

Adsorption of reactive dye solution on nanochitin and chitin particle under acidic, neutral and basic condition was studied. The percentage adsorption of reactive dye solution on nanochitin and chitin under basic condition was 98% and 59%, respectively. In this study, we used ATR-FTIR spectroscopy to study the adsorption mechanism between nanochitin and reactive dye. The results indicated that the amine group of nanochitin was a functional group for the adsorption of Reactive Red (RR141) under acidic condition while the hydroxyl group of nanochitin was the main site for adsorption of Reactive Red (RR141) under basic condition. Azo group (N=N) of reactive dye might be electron donor, while amide group (-$CONH_2$) of nanochitin was electron acceptor under neutral condition. XAS spectra obtained the changes of S atom in RR141 adsorbed onto nanochitin under acidic, whereas adsorption under neutral and basic condition caused no change in the form of S- atom in the dye.

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1. Introduction

Reactive dyes were high solubility and were considered as harmful to aquatic life in rivers and sea where they have been discharged by several industries (Annadurai *et al*., 1999). Therefore it is very important to get rid of them from the effluents not only for removal of the colour of water but also for environmental preservation. Chitin is a natural polymer polysaccharide, found in marine animals, insects, yeast and fungi (Austin *et al*., 1981). This biopolymer consists of repeated units of N-acetyl-β-D-glucosamine and normally contains a small number of β-D-glucosamine units in a chain (Figure 1). Chitin polymer has been utilized as an adsorbent for various substances such as metallic ions, ionic species of sulfonated azo dyes and inorganic and organic acids (Longhinotti *et al*., 1998). Since chitin has amino group it has the advantage of better adsorption capacity and easier desorption. It may be produced very cheaply and is harmless to humans (Muzzerelli, 1977; Hiroyuki *et al*., 1993). For the studied of adsorption mechanism between reactive dye and chitin-chitosan polymer, ATR-FTIR spectra confirmed that the amines on chitosan polymer tend to be effective functional groups for dye adsorption under acidic conditions, Whereas the hydroxyl group tended to be the effective functional group for dye adsorption under basic conditions (Sakkayawong *et al*., 2005). Moreover, the possible mechanism of dye removal from wastewater by Narrow-leaved cattail was studied by using X-ray adsorption spectroscopy (XAS) (Nilratnisakon *et al*., 2007). Therefore, this research aims to study adsorption efficiency of reactive red dye on nanochitin particle under various conditions and investigate that adsorption mechanism by ATR-FTIR Spectroscopy and X-ray absorption spectroscopy techniques.

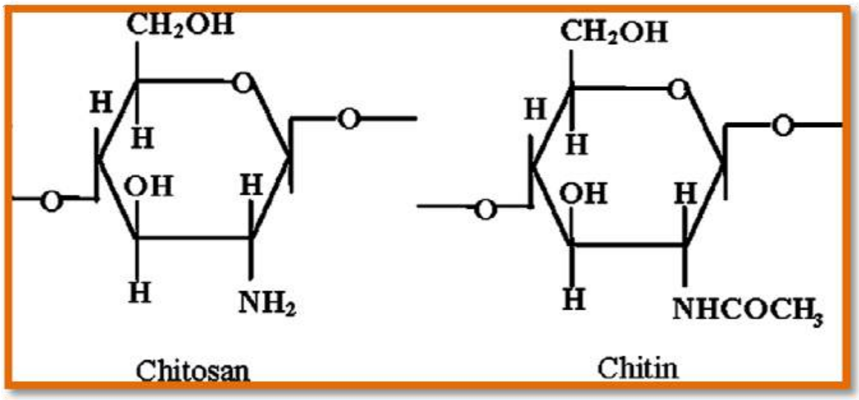

Figure 1: Structure of chitosan and chitin (modified from Sakkayawong *et al*., 2005).

2. Materials and Methods

2.1 Nanochitin Preparation

A gram of chitin (48%DD), approximate mean particle size of 740 nm, was hydrolyzed by addition of 3N HCl 100 ml at 104°C for 9 hours (removal of acid was done every 3 hours by centrifugation at 10,000 g for 5 minutes and new acid was added). Suspension was then transferred to a dialysis bag and dialyzed in running water for 2 hours and later in distilled water until it was neutral. Dehydration of nanochitin suspension was done by lyophilization in order to obtain nanochitin particle, size of approximately 220 nm.

2.2 Reactive Dye Solution Preparation

Reactive red (RR141, see Figure 2 for chemical structure) was used to prepare the reactive dye solution for this study. The reactive dye solution (800 mg/L) was prepared by dissolving 0.8 gram of RR141 in 1L distilled water.

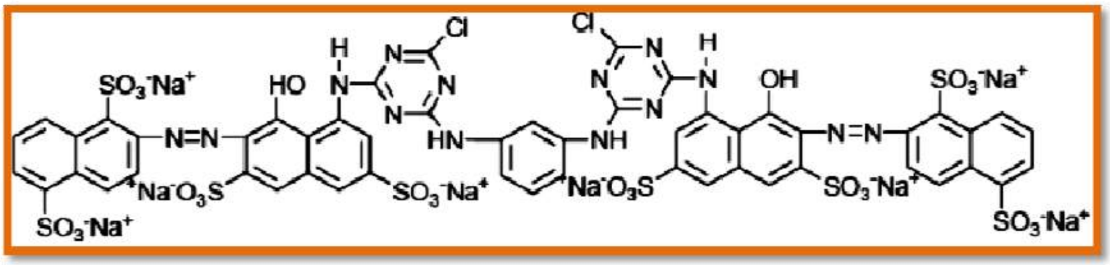

Figure 2. Chemical structure of Diazo C.I. Reactive Red (RR141) (Sakkayawong *et al*., 2005).

2.3 Effect of pH on Adsorption Efficiency

The reactive dye solution was prepared at three different pH systems (acid pH=2.0, neutral pH=7.0 and base pH=11.0) by using 0.1M H_2SO_4 or 0.1M NaOH for pH adjustment. Adsorption reaction was performed by adding 12 mL of reactive dye solution (pH2.0, 7.0 and 11.0) into a reaction bottle contains 0.5 g of chitin or nanochitin. The mixtures were shaken at 150 rpm, 37°C for 24 hours. The samples were centrifuged at 5,000 rpm for 5 minutes and then analyzed for color by a UV-visible spectrophotometer at λ_{544}. This study used adsorption percentage to describe reactive dye solution adsorption efficiency onto chitin and nanochitin under acidic, neutral and basic condition.

2.4 Adsorption Mechanism of Nanochitin

Nanochitin was separated from the dye solution after adsorption reaction at each pH system by centrifugation and filtration. Then the adsorbent was allowed to air dried prior to analysis by X-ray absorption spectroscopy. X-ray Adsorption Near Edge Structure (XANES)

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measurement was performed at BL-8 (XAS beamline) of Siam Photon Laboratory, Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand. XANES spectra of the sample were acquired from 30 eV below to 80 eV above the S K-edge (E_0= 2472 eV) in fluorescence mode with a Lytle detector at room temperature. Spectra obtained were analyzed using the ATHENA package (Ravel and Newville, 2005). Fourier transform infrared (FTIR) spectroscopy was used to investigate functional groups involved in adsorption of reactive dye onto nanochitin at different pH system (pH 2.0, 7.0 and 11.0). Nanochitin particles before and after RR141 adsorption were dried at 60°C by hot air oven. They were acquired by a Bruker TENSOR27 system (Bruker Optik GmbH, Ettlingen, Germany) equipped with a Pike MIRacle™ ATR (Pike Technologies, Madison, WI, USA) with a germanium crystal at Synchrotron Light Research Institute (Public organization), Nakhon Ratchasima, Thailand. A spectral resolution of 6 cm^{-1} with 64 co-added scans was employed. Spectral analysis was done using Win-IR Easy tm Version 3.30 and IR Mentor Pro 6.5 (Bio-Rad Laboratories, Philadelphia, USA).

3. Results and discussion

3.1 Effect of pH on Adsorption Efficiency

The percentages of reactive dye solution adsorption on nanochitin under acidic, neutral and basic conditions were 99.48%, 98.98% and 98.45%, respectively, whereas the RR141 adsorption percentages on chitin were 99.38%, 90.06% and 59.09%. The adsorption efficiency of nanochitin was higher than chitin under neutral and basic condition. While the effect of acidic condition on adsorption efficiency of nanochitin and chitin was not different. In addition to particle size of nanochitin after hydrolyzation was 223.66 nm, while original chitin was 740.93 nm. Therefore, surface area of nanochitin for reactive dye adsorption was increased. The best condition of reactive dye adsorption was acidic condition in both of adsorbents (Table 1). Chitin particle is a naturally occurring material a chelating polymer. In this polymer the presence of hydroxyl and amino groups make it a potential adsorbent for dye effluents. It seems likely that mechanism of adsorption may be the following. The acetamide group ($R\text{-}NHCOCH_3$) and amino group (NH_2) of nanochitin and chitin changed into ($R\text{-}NH_2COCH_3^+$) and (NH_3^+), respectively under acid condition. These groups may be absorbed by the electrostatic interaction with sulfonate (SO_3^-) group of reactive dye (Annadurai *et al.*, 1999; Sakkayawong *et al.*, 2005).

Table 1: The percentage of reactive dye solution adsorption by chitin and nanochitin under acidic, neutral and basic condition.

Initial pH	Adsorbent	Percentage of Reactive dye solution adsorption (%)
2	chitin	99.38 ± 0.08
	nanochitin	99.48 ± 0.00
7	chitin	90.06 ± 0.18
	nanochitin	98.98 ± 0.00
11	chitin	59.09 ± 0.31
	nanochitin	98.45 ± 0.03

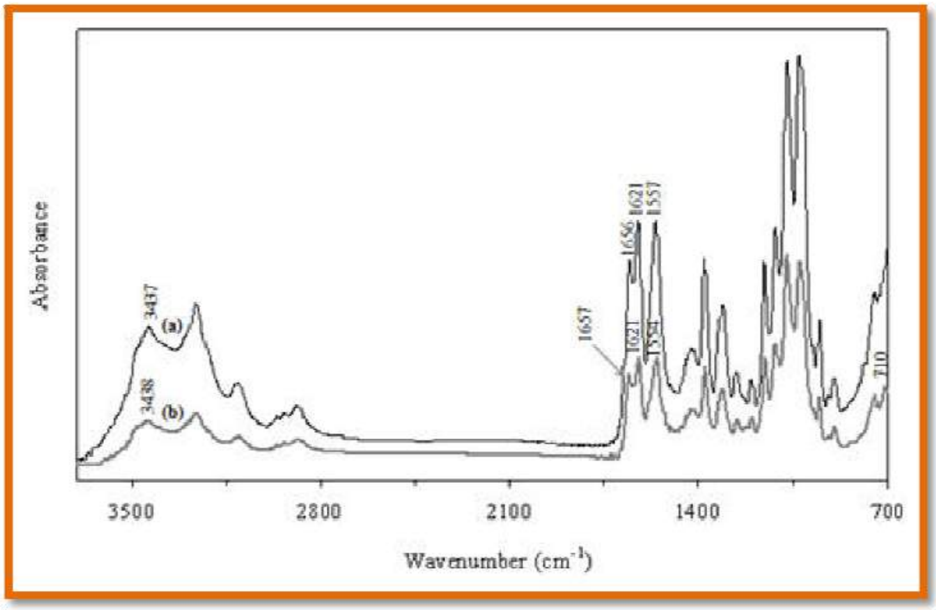

Figure 3: ATR-FTIR spectra of nanochitin before (a) and after (b) adsorption of reactive dye solution under acidic condition.

3.2 Adsorption Mechanism of Nanochitin by ATR-FTIR Technique

Adsorption mechanism under acidic condition

The ATR-FTIR spectra of nanochitin before and after dye adsorption under acidic condition were shown in Figs. 3a and 3b, respectively. The peaks of 1656 cm^{-1} (amide I: C=O), 1621 cm^{-1} (amide II: NH_2), 1557 cm^{-1} (-CNH), 3437 cm^{-1} (amine: N-H) and 3261 cm^{-1} (hydroxyl: OH) represented the nanochitin peak (Figure 3a), which involved the functional group of amine group (NH_2), acetamide group ($R\text{-}NHCOCH_3$) and hydroxyl group (OH) on nanochitin polymer. Accordingly, under acidic conditions, electrostatic interaction occurred between the protonated amine, acetamide and sulfonate (SO_3^-) group of reactive dye (Annadurai *et al.*, 1999; Sakkayawong *et al.*, 2005). In Figure 3b, the peak of amide I, (-CHN) and amine were shifted to 1657, 1554 and 3438 cm^{-1}, respectively. The results probably confirmed that amine and acetamide groups of nanochitin changed to become protonated amine (NH_3^+) and acetamide groups ($NH_2COCH_3^+$), respectively. In addition, new peaks appeared at 710 cm^{-1}. This peak might be analyzed to C-Cl or S-O of reactive dye which confirmed the attachment of dye on the nanochitin polymer. The main adsorption mechanism of reactive and nanochitin under acidic condition was electrostatic interaction.

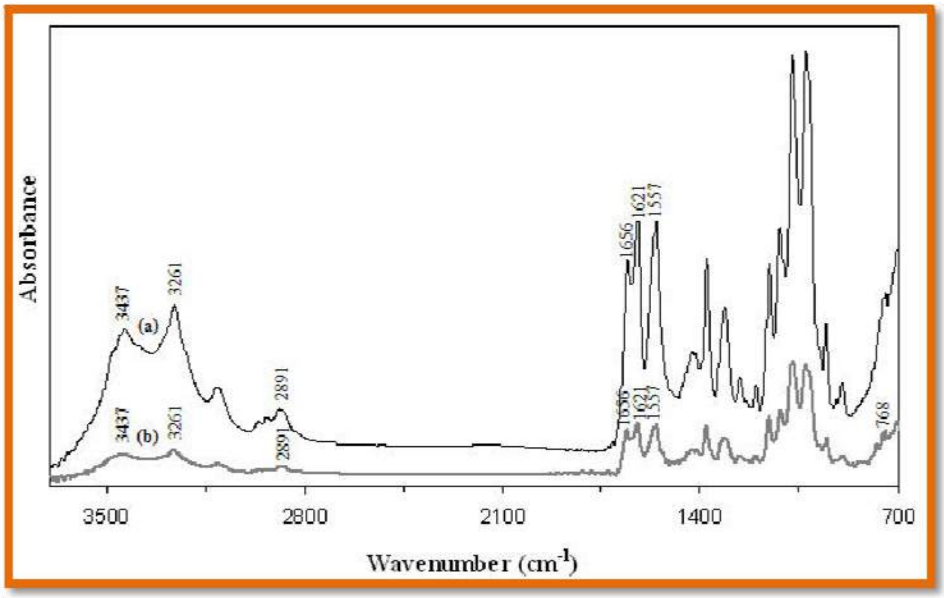

Figure 4: ATR-FTIR spectra of nanochitin before (a) and after (b) adsorption of reactive dye solution under neutral condition.

Adsorption mechanism under neutral condition

Figures 4a and 4b represented the ATR-FTIR spectra of nanochitin before and after reactive dye adsorption under neutral condition, respectively. The peaks of 1656 cm^{-1} (amide I: C=O), 1621 cm^{-1} (amide II: NH_2), 1557 cm^{-1} (-CNH), 3439 cm^{-1} (amine: N-H) and 3261 cm^{-1} (hydroxyl: OH) represented the nanochitin peak (Figure 4a), which involved the functional group of amine group (NH_2), acetamide group ($R\text{-}NHCOCH_3$) and hydroxyl group (OH) on nanochitin polymer. The flat peaks of nanochitin under neutral adsorption did not change from original position excepted the new peak of 748 cm^{-1}. This peak was C-Cl or S-O of dye which confirmed the attachment of dye on the nanochitin polymer as show in Figure 4b. In addition to, the adsorption under neutral condition might be Van der Waals forces are weak bonding of physical adsorption and electrostatic interaction dose not appear. Their forces occur between azo groups (-N=N-) of reactive dye as electron donor and hydroxyl groups (-OH) of chitin as electron acceptor. Therefore, no changing peak had occurred as Figure 4b.

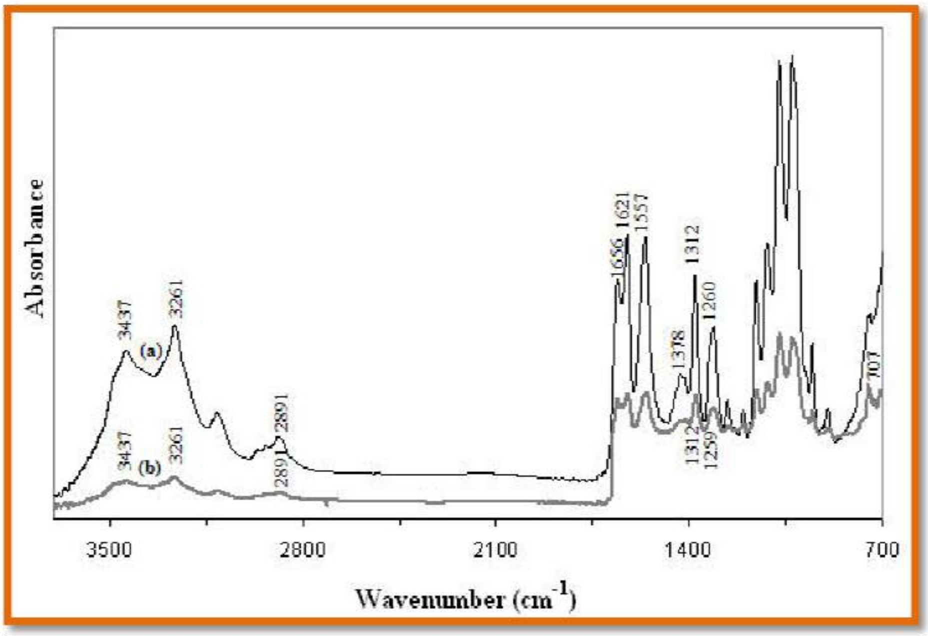

Figure 5: ATR-FTIR spectra of nanochitin before (a) and after (b) adsorption of reactive dye solution under basic condition.

Adsorption mechanism under basic condition

The ATR-FTIR spectra of nanochitin before and after reactive red dye adsorption under basic condition were shown in Figs. 5a and 5b, respectively. The peaks of 1656 cm^{-1} (amide I: C=O), 1621 cm^{-1} (amide II: NH_2), 1557 cm^{-1} (-CNH), 3437 cm^{-1} (amine: N-H) represented the nanochitin polymer. The peaks of hydroxyl group (OH) from naonchitin were obtained from the peak of 1260, 1312, 1378, 2890 and 3261 cm^{-1} (Figure 5a). Under basic condition implied that the hydroxyl group of chitin was the main functional group for reactive dye adsorption by covalent bonding (Sakkayawong *et al*., 2005; Dolphen *et al*., 2007). As Figure 5b, the peaks of hydroxyl group shifted to 1259 and 3263 cm^{-1} and the peak of 2891 cm^{-1} changed to be boarder peak. These results confirmed that the hydroxyl group at primary alcohol (CH_2OH) of nanochitin polymer changed to become a deprotonated hydroxyl group (CH_2O^-) and attached with reactive dye structure by covalent bond. In addition, new peaks of reactive dye also appeared at 707 cm^{-1} (C-Cl or S-O).

3.3 Adsorption Mechanism of Nanochitin by X-Ray Absorption Spectroscopy Technique

The XANES spectra comparison of reactive dye (RR141), Na_2SO_4 (standard chemical) and adsorbed reactive dye solution on nanochitin under acidic, neutral and basic condition as shown in Figure 6. Under acidic condition represented that S-atom into adsorbed dye was shifted from energy peak of S in RR141 (2,480.0 eV) toward the energy peak of new sulfur complex which peak indicated near sulphate (SO_4^{2-}) peak. This implied that S-atom in the dye underwent some change in its form after adsorption was taken place under acidic condition but we could not determine the exact form of S-atom after these changes occurred. This result probably confirmed that sulfonate (SO_3^-) group of reactive dye attached with protonated amine and/or protonated acetamide groups in electrostatic interaction. Under basic and neutral conditions represented that S-atom into adsorbed dye had still been energy peak of S-atom in RR141 (2,480.0 eV). The result implied that the hydroxyl group of chitin was the main functional group for reactive dye adsorption by covalent bonding. Therefore the structure of S-atom did not involve in adsorption mechanism. Reactive dye had chlorine (Cl) group which been main functional group for adsorption mechanism.

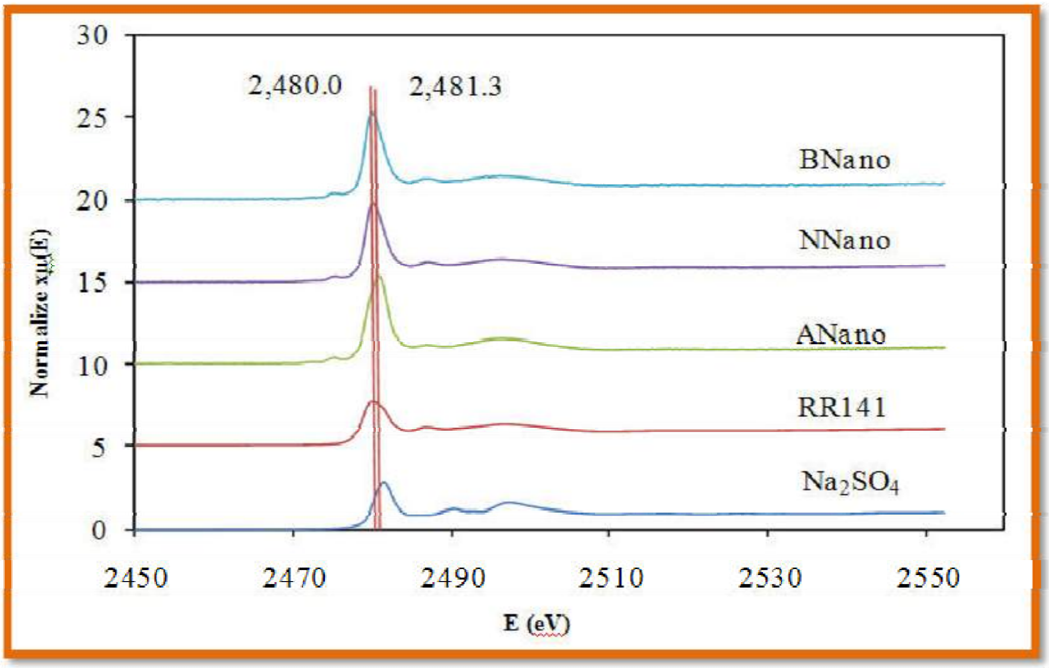

Figure 6: XANES spectra comparison of RR141, Na_2SO_4 standard and reactive dye solution adsorbed on nanochitin under acidic (ANano), neutral (NNano) and basic (BNano) condition.

In addition to, the adsorption under neutral condition might be Van der Waals forces while electrostatic interaction and covalent bonding did not appear. Their forces occur between azo groups (-N=N-) of reactive dye as electron donor and hydroxyl groups (-OH) of chitin as electron acceptor. Therefore the structure of S-atom of RR141 which attached on nanochitin under neutral condition was not main functional group for adsorption mechanism under neutral condition.

4. Conclusion

Nanochitin was effective adsorbent for Reactive red (RR141) dye solution adsorption. It had grater surface area than original chitin and it could adsorb RR141 in various conditions such as acidic, neutral and basic conditions. The ATR-FTIR spectra probably confirmed that electrostatic interaction, Van der Waals forces and covalent bonding occurred under acidic, neutral and basic conditions, respectively. These results corresponded to XANES spectra which implied that S-atom into adsorbed dye was shifted from energy peak of S in RR141 (2,480.0 eV) toward the energy peak of new sulfur complex which peak indicated near sulphate (SO_4^{2-}) peak under acidic condition. S-atom into adsorbed dye on nanochitin had still been energy peak of S-atom in RR141 (2,480.0 eV) under basic and neutral conditions.

5. Acknowledgements

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