Synthetic Reactive Dye Wastewater Treatment by Narrow-leaved Cattail : studied by XRD and FTIR

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Abstract: Narrow-leaved cattail (*Typha angustifolia* Linn) has been reported as being useful in the removal of textile dyes from industrial sources. This study investigated the possible mechanism for plant avoidance in this wastewater by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Evidence from XRD showed the precipitation of dye with silicon (Si) and calcium (Ca) oxalate in the plant tissue. FTIR spectra indicated that amide ($R(C=O)NH_2$) and siloxane (Si-O-Si) groups in the plant might be involved in the dye

removal. This implied that the decolorization of textile wastewater by narrow-leaved cattails involved an amide group or protein and silicon such as a complex of iron-calcium-silicate to bind with the negative charge of dye and/or wastewater. After uptake and translocation in the plant system, the semi-permeability system of plant might select and avoid the solute as dye molecule by several mechanisms such as precipitation by iron-calcium-silicate complexes or dye degradation. High intensity XRD peaks from calcium oxalate (CaC_2O_4), calcium silicate (Ca_2SiO_4) complexes and silica (SiO_x) were also observed in these samples suggesting that some metals might be involved in SRDW removal by this plant.

Keywords: Narrow-leaved Cattail, reactive dye, FTIR, XRD.

1. Introduction

In 2007, the export quantities of Thailand's garment and textile sectors were approximately 261 Billion Baht [1]. This corresponded to the release of 1.2 x 10^{11} liters of effluents from the textile industry into public streams [1]. The characteristics of textile wastewater are high pH, alkalinity and the presence of various soluble dye compounds which is highly visible, and it is very difficult to degrade or eliminate [2]. Decolorization of textile wastewater can be accomplished through many efficient methods, including physical, chemical and biological treatment. Treatment with algae, fungi and bacteria are biological methods that have been reported for the biodegradation of reactive azo dye [3-9].

Phytoremediation for treatment of textile wastewater is an alternative method and is sustainable for long-term treatment. It is a low cost technique, with low chemical and energy consumption. It is easy to operate and to maintain the treatment system using this method [10]. Decolorisations of azo dyes has been investigated in wetlands of *Phragmites* [8,11], and *Saccharum* [12]. Until recently there were no reports of the use of narrow-leaved cattails (*Typha angustifolia* Linn.) for textile dye removal from wastewater. Through our preliminary study, we found that this plant can efficiently remove dye and treat textile wastewater by decreasing pH, COD and TDS [13]. Therefore, the objectives of this study were to (a) identify the functional groups in the plant that might be involved in textile dye removal and (b) determine the possible mechanism for textile dye wastewater treatment by narrow-leaved cattail.

2. Materials and methods

2.1 Dyes and Synthetic Reactive Dye Wastewater (SRDW)

Synthetic Reactive Dye Wastewater (SRDW) was prepared in a laboratory dyeing process and contained 400 mgl^{-1} of RR141, with 90 gl^{-1} of sodium sulphate and 20 gl^{-1} sodium carbonate being added to increase the dye substance and to improve the fastness in the dyeing process. The commercial diazo C.I. Reactive Dye (Reactive Red 141: Molecular Structure = $C_{52}H_{26}Cl_2N_{14}Na_8O_{26}S_8$) used in this study was obtained from DyStar, Thai Co.,Ltd. Thailand. The final pH of the SRDW was approximately 10-11. The maximum absorbance of SRDW was at λ_{max} = 544 nm (determined by UV-visible

spectrophotometer, model UNICO-2100, USA). In this study, the SRDW was diluted from 400 mgl^{-1} to 20 mgl^{-1}, which is similar to the concentration of dye residues from textile effluents in public waterways [14], and the initial pH was adjusted to 9.0.

2.2 Plant culture conditions

Narrow-leaved cattails (*Typha angustifolia* Linn.) were collected from a freshwater pond near King Mongkut's University of Technology Thonburi (KMUTT) Bangkhuntien Campus, Thailand, and maintained in plastic boxes until new shoots were produced. Plants were selected and cultured in fresh pond water containing added SRDW as described in section 2.1. Plants were selected at the same stage of growth (4-5 leaves per plant, 20-30 roots per plant, 90-100 cm. height,) for growing in 10″ width x 15″ length of glass bottles with and without added clay. The volumes of solution in each treatment were adjusted to 1500 ml. per bottle. Plants were cultured for 28 days, samples analyzed at days 0, 7, 14, 21, and 28.

2.3 Functional groups analysis and mechanism of textile wastewater treatment by narrow-leaved cattail.

2.3.1 X-ray Diffraction (XRD) Study

XRD was used to measure the crystalline dye and the other chemical compounds in plants after treatment with SRDW. Samples were analyzed by X-ray diffractometer (JEOL, JDX-3530) using a 30 kV voltage and 40 mA current. The diffraction angel of 5- 100°2θ were scanned in steps of 0.02 degree per second.

2.3.2 Fourier Transmission Infrared (FTIR) Spectrophotometer Study

Narrow-leaved cattail before and after treatment with 20 mgl^{-1}SRDW were air dried using solar energy. Plants were then ground with an agate pestle and then analyzed by FTIR (PerkinElmer Spectrum One) to determine the functional groups involved in the dye degradation mechanism. The spectra were obtained using the KBr disc technique with a ratio of 1 mg of sample per 100 mg of KBr.

3. Results

3.1 Effect of calcium oxalate (CaC_2O_4), calcium silicate (Ca_2SiO_4) and silicon (SiO_x) for enhancing SRDW treatment of narrow-leaved cattail by XRD

XRD results revealed that the polyaniline structure of reactive red 141 and the sodium salts (Na_2SO_4 and Na_2CO_3), which were added to the SRDW, were present in the leaves and roots of narrow-leaved cattails after treatment with SRDW (Figures 1-2). High intensity XRD peaks from calcium oxalate (CaC_2O_4), calcium silicate (Ca_2SiO_4) complexes and silica (SiO_x) were also observed in these samples suggesting that some metals might be involved in SRDW removal by this plant. Therefore, this plant might deal with the toxic dye by cutting it into smaller molecules, which could be easily translocated to areas (e.g. vacuole, golgi body, vesicle and etc.) by semi-permeable membrane of plant, that do not interrupt photosynthesis and solute transport.

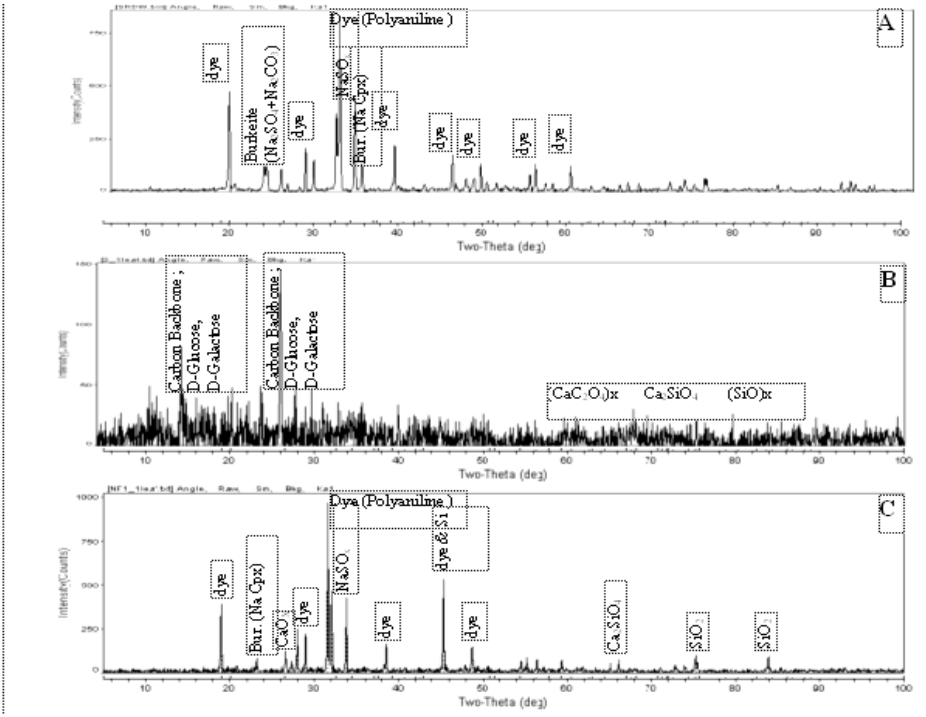

Figure 1. X-ray Diffraction patterns of leaf before and after SRDW treatment (A) SRDW showing the dye structure with polyaniline and Na_2SO_4 + Na_2CO_3 (Bur.=Burkeite) (B) leaf of narrow-leaved cattail as a control plant showing the pattern from the C-6 backbone (D-glucose, D-galactose) and (C) leaf of narrow-leaved cattail after 28 days exposure to SRDW showing the pattern from the dye, Na_2SO_4 + Na_2CO_3 , calcium (mono-, di-) oxalate, calcium silicate and silica. At $2\theta \sim 45°$ peaks from dye and silica overlap.

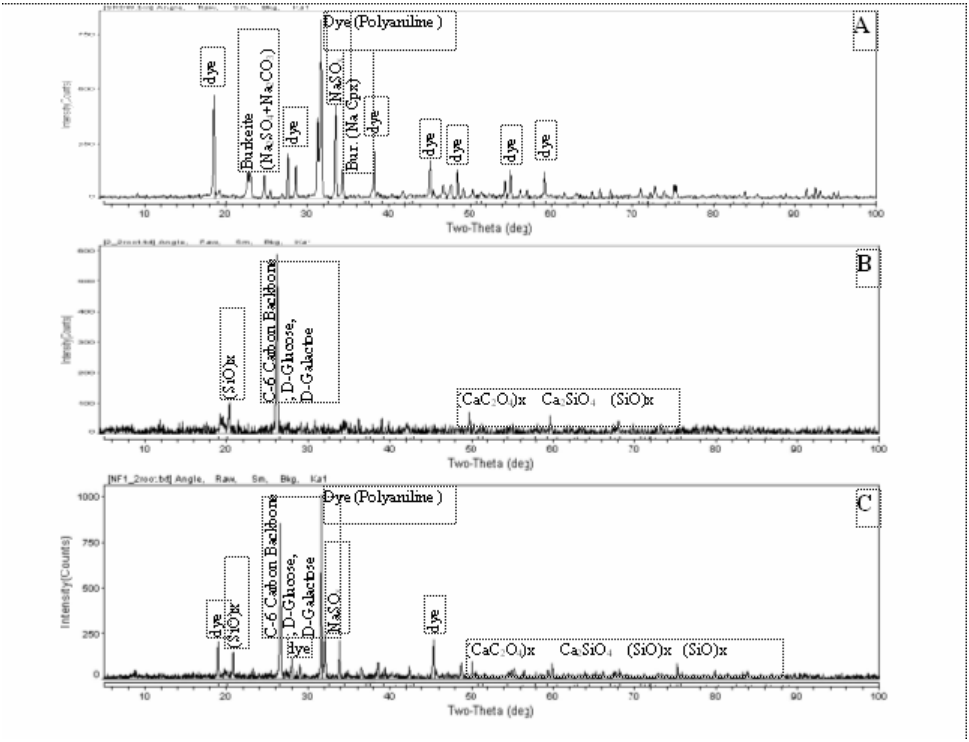

Figure 2. X-ray Diffraction patterns of root before and after SRDW treatment (A) SRDW showing the dye structure with polyaniline and Na_2SO_4 + Na_2CO_3 (Bur.=Burkeite) (B) root of narrow-leaved cattail as a control plant showing the pattern from the C-6 backbone (D-glucose, D-galactose) and (C) root of narrow-leaved cattail after 28 days exposure to SRDW showing the pattern from the dye, Na_2SO_4 + Na_2CO_3 , calcium (mono-, di-) oxalate, calcium silicate and silica. At $2\theta \sim 45°$ peaks from dye and silica overlap.

3.2 Effect of SRDW treatment of narrow-leaved cattail on FTIR of amide and siloxane groups

FTIR spectra of narrow-leaved cattail were investigated after 28 days of exposure to SRDW. The spectrum of control set revealed that SRDW consisted of peaks from primary and secondary amines (around 3500-3200; NH stretching and 1568 cm^{-1}; O=C-NH bending), aromatic azo bond (2112.5 cm^{-1}), sulfonate (1117.6; SO_3^- and 900 cm^{-1}; R-$SO_3^-Na^+$) and chloride (600 cm^{-1}). The spectra of plant leaves and roots, before and after SRDW treatment, indicate that the primary (I) and secondary (II) amide groups (3314.5, 2932.2, 1738.4, 1642.9, 1515.6, 1436 and 1332.5 cm^{-1}) and the siloxane group (1038 cm^{-1}) of the plant leaf were affected by the SRDW. The band from amide I and II were shifted and the band from the siloxane group shifted and decreased. The aromatic ring (2112.5 cm^{-1}) and sulfonate group (1117.6 cm^{-1}) of the azo compound replaced the amide II (NH-bending) and C-OH bending of plant cellulose, respectively (Tables 1 – 2).

Table 1. Peak positions and assignments of FTIR spectra from narrow-leaved cattail leaf (control and SRDW plants).

Characteristics	Wavenumber (cm^{-1})		Wavenumber (cm^{-1}) Change	Absorbance change	Remarks
	Control leaf	SRDW leaf			
Peak Shift	3314.5	3401.8	+77.6	↓0.15	amide I, II NH-stretching
	2932.2	2940.2	+8.0	↓0.15	amide I, II NH-stretching
	1738.4	2112.5	+384.1	↑0.05	Ph-N=N-Ph instead of amide II NH-bending
	1515.6	1467.8	-47.8	↓0.35	C=C of amide II
	1436	-	-	↓0.1	O=C-NH of amide II
	1332.5	-	-	↓0.3	C=C-NH of amide II
	1245	1117.6	-127.4	↑0.4	SO_3 group of dye instead of C-OH bending of cellulose
	1046	1038	-8.0	↓0.35	Si-O-Si in plant
	-	624.2	-	↑0.3	Cl^- Halogen group of dye
Absorbance Change	1642.9	1642.9	-	↓0.2	O=C-NH bending

Table 2. Peak positions and assignments of FTIR spectra from narrow-leaved cattail root (control and SRDW plants).

Characteristics	Wavenumber (cm^{-1})		Wavenumber (cm^{-1}) change	Absorbance change	Remarks
	Control leaf	SRDW leaf			
Peak Shift	3704.2	3688.3	-15.9	-	amide I, II NH-stretching
	3632.6	3624.6	-8.0	-	amide I, II NH-stretching
	3338.1	3417.7	+79.6	-	CH asymmetric and symmetric stretching
	2924.2	2932.2	+8.0	-	CH asymmetric and symmetric stretching
		1873.7	-	↑0.05	R′R″C=CH_2 of dye
	1658.8	1642.9	-15.9	↓0.2	O=C-NH bending of amide II in plant
	1046.0	1038.0	-8.0	↓0.35	Si-O-Si open chain in plant
Absorbance Change	-	-	-	-	-

4. Discussion

4.1 Effect of calcium oxalate (CaC_2O_4), calcium silicate ($CaSiO_4$) and silica (SiO_x) on enhancing SRDW treatment by narrow-leaved cattail by XRD

Peaks from calcium oxalate (CaC_2O_4), calcium silicate ($Ca_xSi_yO_z$) and silica (SiO_x) were found in narrow-leaved cattail after culturing in SRDW. This suggested that silica, calcium mono,di-oxalate and calcium silicate might enhance the tolerance mechanism of the plant by forming metal-*dye*$^-$ complexes which are precipitated in leaf and root cells. Because the dye molecule can act as a barrier to the photosynthesis system, and hence translocation and transportation of nutrient in the plant system, precipitation of the dye compound with CaC_2O_4, Ca_2SiO_4 and SiO_x are a good mechanism for achieving tolerance. Observation of Si, Ca, S and Fe in leaf and root cells of narrow-leaved cattail by TEM-EDX [13] support this explanation based on XRD results. Therefore, it should be noted here that the principal roles for Si and Ca are to facilitate precipitation of the dye to avoid damages to plant cells. Calcium competes with sodium from salt stress and leads defenses to salt stress as with SRDW by releasing Si into cell walls and/or membranes. Silicon in cell walls in the form of polymeric silica will be converted to silica gel, which will act as a buffer and enable the plant to adjust the optimum osmotic pressure in the stem and reduce the toxicity from Na. At high Na levels, plants will produce CaC_2O_4, Ca_2SiO_4 in order to reduce ion-toxicity and to precipitate crystalline forms and suspensions in cells [15-19]. Calcium ions form Ca^{2+} links in cell

walls. However, in plant cells Ca mainly functions in the signal transduction pathways which involve large numbers of different proteins. External factors that affect plants (e.g. light, temperature, wind, CO_2, pathogen, heavy metal, drought, salt stress) are sensed by Ca^{2+} in cell walls which turns on the signal transduction to induce protein kinase activity. The Ca^{2+} in signal transduction is involved with the proton release in cells, and is correlated with siloxane bond formation by enhancing the activity of homologous enzymes that catalase the formation of siloxane bonds [20]. The proton generate by Ca^{2+} might help plant for relieve the toxic of dye, this proton might play the major role for dye degradation to the small molecule and deposit in plant leaves and roots. Plant of this type might use the phytochemical by releasing the smaller molecules into soil to control pH, and the gaseous composition of the soil, and leading to the altered toxic compound being fixing in the soil. Supporting results relate to the system pH of SRDW-treated plants. During the first week of exposure, the system pH decreased from 9 to close to 7, but during the second week it was close to 8. During this time the plant optimized the systematic pH for biochemical processing of the foreign molecule.

Azo dye degradation or decomposition has been reported in bioremediation by various plants and microorganisms (Table 3). The dye structures with several different numbers of carbon atoms were determined by matching the XRD peaks with the library program. Degradation of the reactive di-azo dye can be explained by 2 possible mechanisms. First, the reactive C-52 atom di-azo dye might

break at the linkage group (Figure 3) to produce one azo dye with C-16 and another with C-29 atoms that still retain the linkage group. This mechanism can be understood in terms of the di-azo dye synthesis, in which two azo dye molecules with C-16 atoms are combined initially. Then one side of the linkage group is modified to enable attachment of another azo dye molecule [21-23].

Table 3. The azo dye degradation or decomposition by bioremediation processes [8,11-12,24-25].

Dye (Azo)	Degradation (%)	Methods	References
Acid Orange 7	N/A*	Ascorbate-glutathione pathway by *Phagmite australis*	Carias *et al.*, 2008
Methyl Orange	N/A*	*Lactobacillus casei* TISR1500	Seesuriyachan *et al.*,2007
Reactive Red 120	N/A*	Ozonation	Zhang *et al.*, 2007
Acid Orange 7	100% in 120 h	Peroxidase of *P. australis*	Davies *et al.*, 2007
Procion Green (HE-4BD)	100% in 1 h	Peroxidase of *Saccharum spontaneum*	Shaffiqu *et al.*, 2002
Supranol Green	100% in 1 h	Peroxidase of S. *spontaneum*	Shaffiqu *et al.*, 2002
Direct Blue	>70% in 1 h	Peroxidase of S. *spontaneum*	Shaffiqu *et al.*, 2002
Procion Blue (H-7G)	>70% in 1 h	Peroxidase of S. *spontaneum*	Shaffiqu *et al.*, 2002
Chrysoidine	>70% in 1 h	Peroxidase of S. *spontaneum*	Shaffiqu *et al.*, 2002

*N/A = Not Available

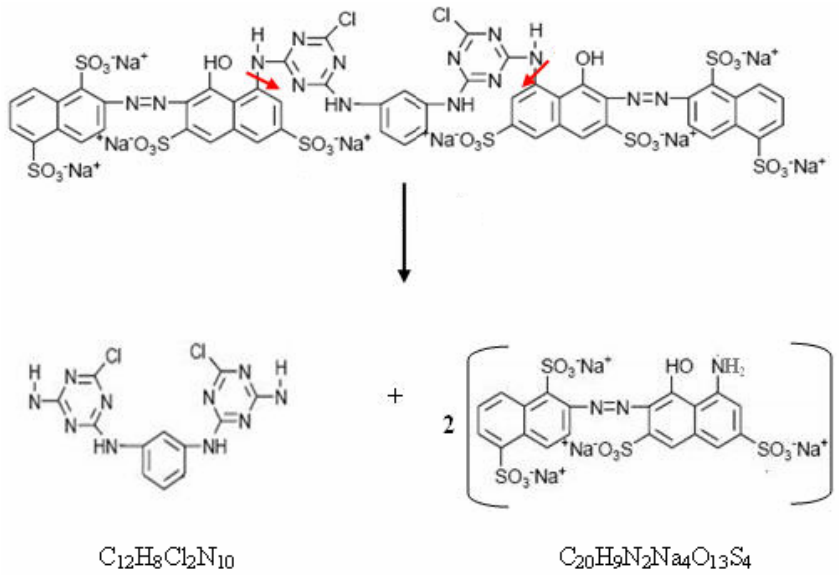

Figure 3. Possible dye molecular breaking from C-52 molecule to C-20 molecule and linkage group (pathway 1).

For the second mechanism, the C-52 molecule might degrade produce a C-29 molecule by breaking at 1,6-di-aminebenzene ring and modified structure of another *O*-chloro-1,3,5-trinitrobenzene. This process will produce 2 molecules of C-29 atoms and C-23 atoms. Then C-23 molecule will break *O*-chloro-1,3,5-trinitrobenzene to be C-20 molecule. Then C-20 molecules will modify one side of naphthalene to be C-16 molecule (Figure 4). In the case of narrow-leaved cattail, the possible degradation of reactive azo dye might reduce C-52 to C-20 atoms. Hence, the modification of dye molecule by breaking at the linkage group of dye from C-52 to C-20 are easier than modified *O*-chloro-1,3,5-trinitrobenzene in the case of C-29, C-20 and C-16 atoms, respectively.

4.2 Effect of amide and siloxane groups on SRDW treatment of narrow-leaved cattail

FTIR spectra suggest that primary and secondary amide and siloxane (Si-O-Si) groups in the plant play important roles in SRDW tolerance. $O=C^{(+)}$ and NH^{+} of amide I, II and siloxane groups or Si-O-Si bridges can bind with the negatively charged dye compound (dye^{-}) [26]. The aromatic ring with azo bond (2112.5 cm^{-1}) and sulfonate group (SO_3^{-}) at 1117.6 cm^{-1} which replaced amide II (NH-bending), C-OH or C-O-C bending of cellulose and the increase in Cl^{-} peak (624 cm^{-1}) indicate that this plant has a mechanism for SRDW translocation and transportation [27]. Evidence for dye movement in the plant stem could be seen as patches along the length of vein in the vascular bundle within 3 hr of exposure. These then reduced progressively and were not observed after 3 days. This suggests that after culturing narrow-leaved cattail in SRDW, semi-permeable membrane properties of plant and tolerance mechanisms function by detecting and selecting ions or molecules that are less toxic to the cells [28-29]. Functional groups which play crucial roles might be amide I, II and siloxane.

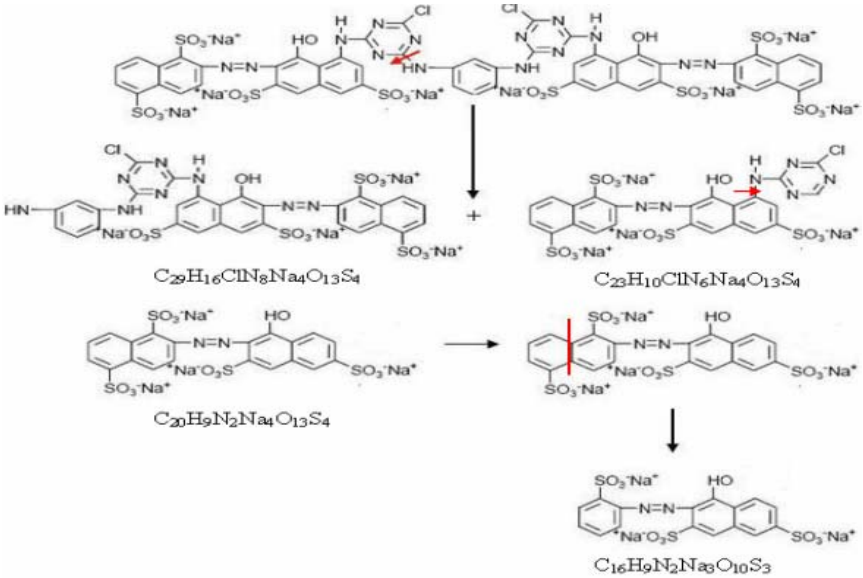

Figure 4. Possible dye molecular breaking from C-52 molecule to C-29, C-20 and C-16 molecule (pathway 2).

In salt stress conditions, as with SRDW under alkaline conditions, plants have levels for avoidance, tolerance and finally resistance to this kind of stress. Increasing the number of silica groups (Si-O-Si or SiO_2) might help the morphological and chemical changes which responded to the salt stress condition [15,30]. In monocotyledon plant, Si mainly in the cell wall helps maintain the integrity, stability, and function of the plasma membrane, and mitigate salinity toxicity by decreasing the Na^+ concentration in shoots. The consequent increased H^+ in leaves from salt stress and then Si maintains the optimal membrane fluidity [31-33]. Dye and some metal precipitation (e.g. Si), in the leaf and root cell of narrow-

leaved cattail was also seen in studies using TEM-EDX [13]. The amide I, II or proteins are discussed in detail in section 4.3.

The FTIR pattern for the polysaccharide skeleton (C-O-C) of the plant might represent common mechanism with the cotton dyeing process by attaching the carboxylic group, as occurs in the case of dye deposited in old leaves [8,34].

4.3 The possible mechanism for textile wastewater removal by Narrow-leaved Cattail

The mechanism for textile wastewater by narrow-leaved cattail involves both external and internal mechanisms. The external mechanism found that siloxane (Si-O-Si) was involved in dye absorption and precipitation of the sodium salt in the outer membrane of the plant. For the internal mechanism, FTIR and TEM-EDX showed that Si, Ca and Fe were involved in dye absorption indicating that silica production was induced by SRDW. FTIR showed that the amide groups (NH) have changed, implying that SRDW removal by this plant needs NH from amide groups.

Si, Ca and protein might have functions that are related to each other. At the beginning of the stress condition from SRDW, the alkaline conditions will induce protein kinase and other proteins activity. Protein will then increase from accumulated free proline in the stem, and will help to maintain the moisture and fluidity of the plant and to avoid the toxicity from osmotic stress that results from the salt stress (data not shown). Silica also functions to mitigate salinity toxicity by decreasing the Na^+ concentration in shoots of monocotyledon

plants [31-33,35-37]. Ca might help plants by functioning as a signal transducer, which involves proton released in the cell and acts involves many different proteins. The formation of siloxane bonds also requires Ca to achieve the maximum activity [20].

5. Conclusions

Narrow-leaved cattail shown its effective in dye removal from textile wastewaters and functional groups analyses have found that siloxane (Si-O-Si) and amide (NH) groups in the plant played major roles. XRD showed precipitation of silica (SiO_x), calcium-silicate (Ca_2SiO_4) and calcium oxalate (CaC_2O_4) in the plant tissues. These would be possible that plant could survive in the stress condition of this wastewater which contained of dye and salt by several mechanisms such as the external and internal mechanism. The precipitation with calcium complex or the semi-permeability by silicon might be the avoidance process via external mechanism. The internal mechanism, plant might have the proton or enzyme generation for degradation of reactive azo dye might reduce to C-29 and C-16 by breaking at the linkage group of dye. FTIR spectra of plants showed an increase in the peak from sulfur groups, along with decreases in amide ($R(C=O)NH_2$) and siloxane (Si-O-Si) groups in plants treated with SRDW. Protein or amide groups might therefore, be involved in the mechanism for textile wastewater treatment by this plant. FTIR and XRD results suggest that silica, calcium-silicate, and calcium oxalate are involved in the precipitation of metals, such as calcium complexes by release silicon and/or calcium from cell

walls and cell membranes. Under the caustic conditions as SRDW, calcium will compete with sodium and Ca^{2+} will bind with oxalate. Calcium oxalate may bind with negative charge and/or sulfur of dye and produce the crystalline deposit in cell. Protein or amide groups of plant might play a role to bind with dye at NH-group of amide.

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