

## GC-MS STUDY OF THE REMOVAL OF DISSOLVED AND COLLOIDAL SUBSTANCES IN RECYCLED PAPERMAKING BY FLOCCULATION WITH NANO-SIZE TiO<sub>2</sub> COLLOIDS

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In the papermaking process, the removal and control of dissolved and colloidal substances (DCS) is a key issue for reducing the usage of fresh water. Nano-size TiO<sub>2</sub> is an excellent capturing and flocculating agent for DCS due to its large surface area and positive charge. The composition of dissolved and colloidal substances in a system and the removal of these substances by flocculation with nano-size TiO<sub>2</sub> colloids were determined by gas chromatography and mass spectrometry (GC-MS). The samples were obtained from non-deinked pulp (non-DIP), deinked pulp (DIP), and whitewater. The research results indicated that the removal efficiencies of the DCS, which are associated with the molecular structures, were sequenced from large to small as follows: resin acids and sterols, benzene derivatives containing carboxyl, fatty acids, and the phthalic acid esters. Then, the mechanism of flocculation removal of DCS was considered. With hydrogen bonding between the surface hydroxyl (Ti<sup>4+</sup>-OH) and the functional groups containing oxygen, the nano-size TiO<sub>2</sub> particles can capture dissolved substances (DS), and bridge colloidal substances (CS) and complexes to induce agglomerate flocculation. The flocculating removal efficiencies were influenced by the functional groups and alkyls of the DCS. Greater numbers and polarities of functional groups produced higher removal efficiencies. Long alkyl chains shield functional groups, thereby inhibiting the formation of hydrogen bonding, which results in a decrease in removal efficiencies.

*Keywords:* GC-MS; Dissolved and colloidal substances; Nano-size TiO<sub>2</sub>; Recycled papermaking

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### INTRODUCTION

During the closure of water circuits in the paper industry, DCS, which includes lipophilic extractives, paper and ink chemicals, carbohydrates, lignin, and lignin-related substances, accumulate in the process water, interfering with the papermaking process and affecting the paper quality (Wearing et al. 1985; Stroem et al. 1985; Donat et al. 2003; Li et al. 2002; Dunham et al. 2002). The methods used for removing DCS involve membrane filtration (Fälth et al. 2001; Paleologou et al. 1994), bio-treatment (Huuhiho et al. 2002; Tardif, Hall 1997; Zhang et al. 2000), evaporation (Stevenson 1990), and freezing crystallization (Kenny et al. 1992; Ramamurthy and Dorica 1992). For these operations it is necessary to purchase new equipment and maintain them in running condition. An alternative option for removing DCS from papermaking water circuits

involves ensuring that DCS are retained and fixed in the paper sheet itself and carried out of the circuits while the paper machine runs. This option appears to be both cost-efficient and protective of the environment, as it can take full advantage of materials, reduce the treatment load of wastewater, and avoid the costs of external equipment and material consumptions.

The usage of polyelectrolytes to remove DCS (Dunham et al. 2002) is a conventional technique that is mainly based on colloidal flocculation. This approach is effective towards the colloidal substances (CS) but ineffective towards dissolved substances (DS) due to the weak association between soluble contaminants and polyelectrolytes. However, because the dissolved substances can account for up to 85% of the total organic carbon (TOC) in DCS (Dunham et al. 2000), they cannot be ignored. Xiao and coworkers (Huang et al. 2006) reported a process for the removal of DCS from pulp and paper wastewater by a dual-component system consisting of a cationic-modified microporous zeolite HY and an anionic polyacrylamide-based polymer. Zeolite HY was selected as an absorbent towards the hydrophobic, anionic aromatic contaminants. Alternatively, Wågberg et al. (2007) used hyperbranched polymers (polyesteramides) as a cationic fixing agent to remove DCS.

Nano-size  $\text{TiO}_2$  colloidal particles with a positive charge and high specific surface area are a potential excellent capturing agents towards negatively-charged DCS. The removal efficiencies of DCS in TMP (thermo-mechanical pulp) and DIP (deinked pulp) with nano-size  $\text{TiO}_2$  colloid were previously reported (Chen et al. 2004, 2006, 2009; Kou et al. 2008). It was found that the dual-component systems with retention aids containing nano-size  $\text{TiO}_2$ , nano- $\text{TiO}_2$ /APAM, and nano- $\text{TiO}_2$ /AmS, could perform well for the removal and control of DCS in DIP during whitewater closure. The present work described here focuses mainly on the use of GC-MS to study the mechanism of removing DCS by nano-size  $\text{TiO}_2$  colloids.

## MATERIALS AND EXPERIMENTAL METHODS

### Materials and Chemicals

The recycled pulp (pulp consistency 19.7%, ONP/OMG=4/1), non-deinked (ab. non-DIP, pH=9.0), and deinked (ab. DIP, pH=8.5), were supplied by Yuexiu Guangzhou Paper Group (China). The whitewater (pH=7.3) was taken from the paper mill.

Nano-size  $\text{TiO}_2$  colloids were synthesized by the hydrolysis of titanyl organic compounds [ $\text{TiO}(\text{OOCCH}_3)_2$  and  $\text{Ti}_2\text{O}(\text{OC}_4\text{H}_9)_2(\text{OOCCH}_3)_4$ ] at low temperature and ambient pressure according to the literature (Chen and Shen 2008). The colloidal particles were spherical with a mean size of 6.5 nm. The isoelectric point was 6.67 (pH), and the zeta potentials of the colloid were between 14 mV and 30 mV at a pH between 4.5 and 6.0 in the presence of  $5.0 \text{ mol}\cdot\text{L}^{-1}$  of  $\text{NaNO}_3$  as an electrolyte.

The chromatographic grade agents, including N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA), trimethylchlorosilane (TMCS), methyl tert-butylether (MTBE), heptadecanoic acid, and pyridine, were purchased from Sigma-Aldrich. Pyridine was dehydrated before being used, and the other reagents were used without any further purification.

### **Preparation of the DCS Solution**

With reference to Francis and Ouchi (2001), the preparation of the DCS solution was as follows: 100 mL of diluted non-DIP or DIP (solid content 2 %) was heated in a water-bath for 30 min at 60 °C and squeezed to about 20% solids content, then diluted with the pressate. The operation was repeated eight times. The eighth pressate was centrifuged for 20 min at 2000 rpm, and the supernatant was used as the DCS solution. The papermill whitewater was heated for 30 min at 60 °C in a water-bath and then centrifuged. The supernatant was used as the DCS solution prepared from whitewater.

### **Flocculation of the DCS Solution by Nano-size TiO<sub>2</sub> Colloids**

0.5 mL of a nano-size TiO<sub>2</sub> colloid (solid content 0.2 %) was added to 50 mL of the DCS solution, inducing flocculation. The mixed liquid was centrifuged at 5000 rpm for 20 min and then 10 mL of the supernatant, and 2 mL of the flocculated mixture were used for GC-MS analysis.

### **Liquid-liquid Extraction and Derivative Reaction**

10 mL of the DCS solution, 2 mL of MTBE (extractant), and 10 µg of heptadecanoic acid (internal standard) were mixed in a screw-capped glass tube. The mixture was vigorously shaken for 3 min and then centrifuged at 2000 rpm for 5 minutes. The extracted liquid was carefully picked up with a pipette. The second extraction process was carried out after adding 2 mL of MTBE. The extracted liquids were combined, and the extractant was removed under the sweeping of nitrogen to obtain the DCS for chemical derivation.

The extracted DCS were dissolved in 100 µL of pyridine and then mixed with 100 µL of BSTFA and 50 mL of TMCS (silanizing agent). After holding for 20 minutes at 70 °C, the derivative products were used for GC-MS analysis within 12 hours.

### **GC-MS Analysis**

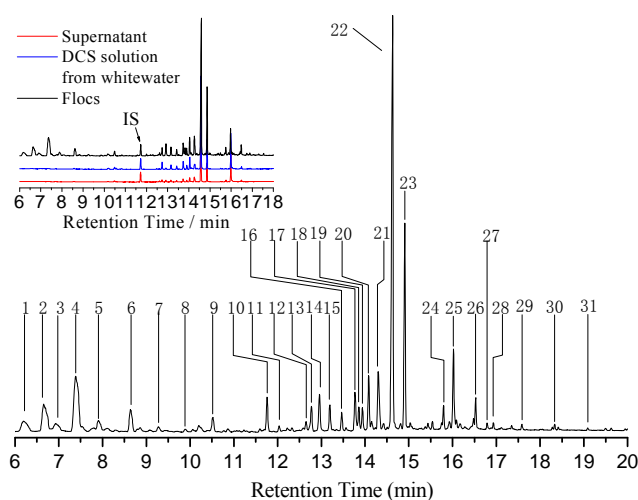
A 6890N GC system gas chromatograph (Agilent Technologies Co., Ltd. USA) coupled with a 5973 mass spectrometer (Agilent Technologies Co., Ltd. USA) was used for the analysis. The GC was equipped with a HP-5MS column (HP 19091S-433). The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. All injections were done in the split mode (5:1), and 1 µL of the sample was injected. The GC column temperature was programmed. The oven temperature was first held at 150 °C for 1 minute before being increased to 230 °C at a rate of 7 °C per minute. The temperature was then increased to 290 °C at a rate of 10 °C per minute and finally held at 290 °C for 7 minutes. The employed mass spectrum database was NIST05.

## **RESULTS AND DISCUSSION**

### **Component Analysis and Flocculating Removal of DCS**

The non-DIP sample was used for determining the DCS due to its abundant amount of DCS compared with that of DIP. Figure 1 displays a chromatogram of the

flocs in the DCS solution of non-DIP by flocculating with nano-size TiO<sub>2</sub> colloids, and compares it with the chromatograms of the supernatant and the DCS solution from the whitewater (top left corner). The names and matching degrees of the DCS are listed in Table 1. The results revealed that the DCS included benzene derivatives (1,3,4,11,13), fatty acids and fatty glycerides (6-9,12,14,27,30,31), resin acids (15-17, 19-24, 26), sterols (28,29), phthalic acid esters, and others (2,5,18,25). Most of those components could be removed by flocculation with nano-size TiO<sub>2</sub> colloids, which was indicated distinctly by comparing the chromatograms from both of supernatant and flocs (top left corner of Fig. 1). In particular, benzene derivatives and binary acids, for which the retention times were less than 10 minutes, were almost completely removed. Because those components are almost all removed, and because they are found in trace quantities in the DCS solution from whitewater (referring to the small figure in Fig. 1.), they were neglected in the subsequent research.



**Fig.1.** GC-MS analysis of DCS components and the flocculation effect of the DCS solution by nano-size TiO<sub>2</sub>

### Flocculating Removal Efficiencies of Different DCS by Nano-size TiO<sub>2</sub> Colloids

The flocculating removal efficiencies of DCS in non-DIP, DIP, and whitewater by nano-size TiO<sub>2</sub> colloids could be determined with GC-MS. Firstly, solutions of DCS (from non-DIP, DIP, or whitewater) were treated by means of extraction, derivatization, and analysis with GC-MS. Secondly, the supernatants of the flocculated DCS solution by nano-size TiO<sub>2</sub> colloids also went through the same processes. The spectral results are shown in Figs. 2 to 4. Lines A, C, and E, represent the GC-MS analysis before flocculation, and the lines B, D, and F represent analysis after flocculation. The flocculating removal efficiencies of the DCS can be calculated from the peak areas of the DCS solutions and supernatants in the chromatograms.

**Table 1.** Main Components in the Floccs Flocculated from the DCS Solution of Non-DIP

Serial Numbers	Component Names	Integral Area (%)	Matching Degrees (%)
1	1,2-Benzenedicarboxylic acid	2.60	95
2	Tricarballic acid	5.11	87
3	1,3-Benzenedicarboxylic acid	1.82	60
4	1,4-Benzenedicarboxylic acid	10.92	96
5	1-Pentamethyl-di-oxycyclopentane	1.59	62
6	Sebacic acid	2.62	90
7	n-Pentadecanoic acid	0.50	62
8	1,11-Undecanedioic acid	0.12	53
9	Hexadecanoic acid	1.39	99
10	Heptadecanoic acid(IS)	2.21	96
11	Vanillylmandelic acid	0.38	64
12	trans-9-Octadecenoic acid	0.70	95
13	2,2-bis(4-Hydroxyphenyl)propane	1.76	98
14	Octadecanoic acid	2.64	99
15	Pimaric acid	1.89	55
16	Sandarapimaric acid	1.14	58
17	Isopimaric acid	2.38	95
18	Methyl prostaglandin E1	1.45	71
19	Palustric acid	1.37	94
20	Levopimaric acid	3.15	99
21	Abietic acid	4.62	69
22	Dehydroabietic acid	26.85	70
23	Neoabietic acid,	10.02	90
24	15-hydroxy-dehydroabietic acid	1.50	56
25	Octyl phthalate	4.48	48
26	7-Oxodehydroabietic acid	2.52	99
27	Docosanoic acid	1.50	77
28	Pregn-5-en-11-one,3,17,20-tris(hydroxyl) sterol	0.43	57
29	Methyl ((24-oxo-3,7,12-tris(hydroxyl) cholane-24-yl)amino)acetate	0.12	62
30	Tetracosanoic acid	0.11	91
31	1-Monolinoleoylglycerol	0.11	73

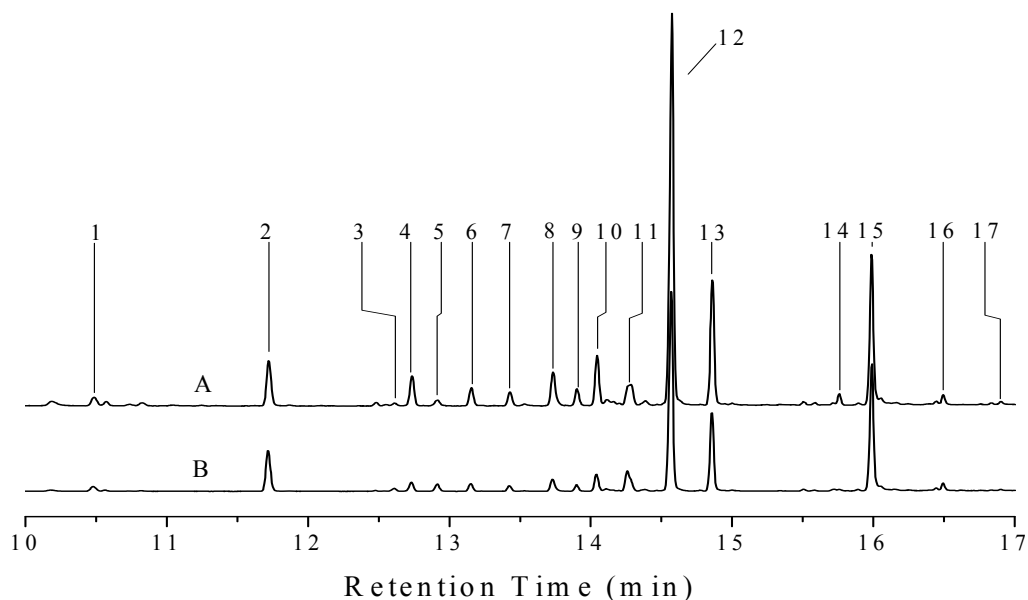
Rigo et al. (2002) measured response factors of hexadecanoic acid, oleic acid, stearic acid, and dehydroabietic acid with a GC equipped with an HP 19091S-433 chromatogram column (same as what was used in this study), and found that the response factors were constant with the injected content from 5 ng to 100 ng. Based on the present results, the removal efficiencies of DCS were calculated according to the internal

standard method with heptadecanoic acid as the internal standard substance (IS). The calculating equation is shown in Formula (1),

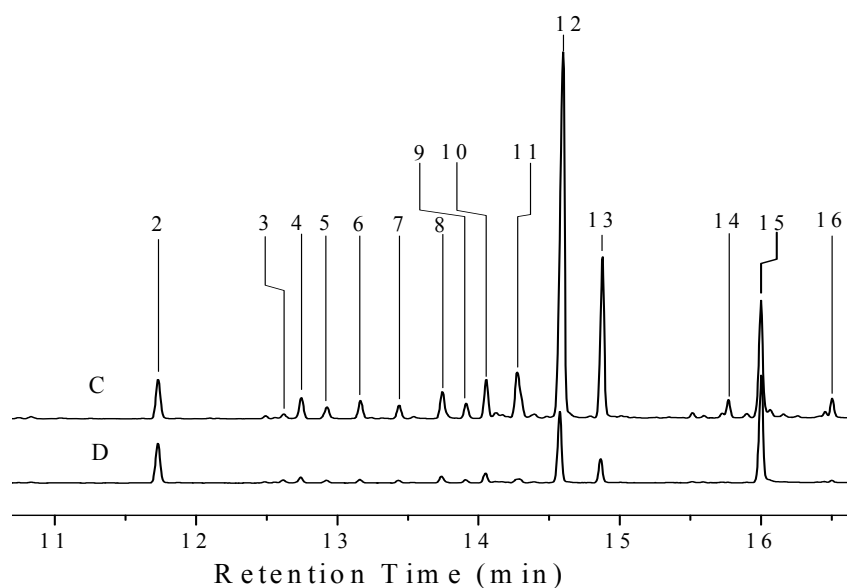
$$R\% = \left(1 - \frac{S'_X / S'_{IS}}{S_X / S_{IS}}\right) \times 100\% \quad (1)$$

where,  $R\%$  is removal efficiency;  $S'_X$  is the chromatographic peak area of component X that remained in the supernatant after flocculation;  $S'_{IS}$  is the peak area of the internal standard substance after flocculation;  $S_X$  is the peak area of component X in the DCS solution before flocculation; and  $S_{IS}$  is the peak area of the internal standard substance before flocculation.

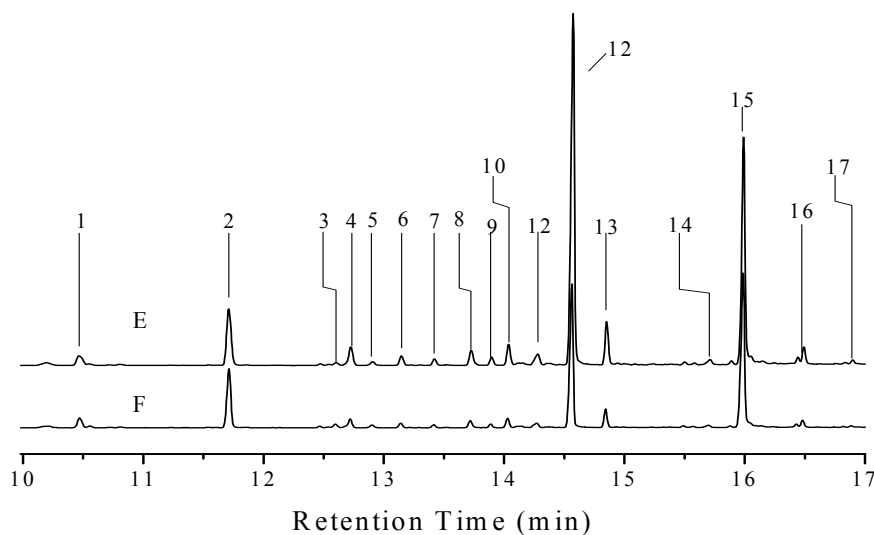
According to the chromatograms in Figs. 2 to 4, it can be concluded that the DCS solution from non-DIP, DIP, and whitewater had similar compositions, which included resin acids, fatty acids, phthalic acid esters, polyhydric phenol, and sterols. The removal efficiencies of DCS in different samples are listed in Table 2. Table 3 lists the aggregate integral area and aggregate removal efficiencies of different DCS. Analyzing the data listed in Table 2 and Table 3, it was concluded that most of the DCS could be removed flocculently by nano-size  $\text{TiO}_2$  colloids. The average removal efficiency was greater than 60%, and the removal efficiency of resin acids, which is the main component of DCS, was greater than 70%. From large to small, the sequence of removal efficiencies was as follows: resin acids, sterols, benzene derivatives containing carboxyl, fatty acids, and phthalic acid esters. The abietic acid and neoabietic acid (11 and 13) in the non-DIP are an exception.



**Fig. 2.** GC-MS analysis of DCS in non-DIP before and after flocculation by nano-size  $\text{TiO}_2$  colloids. A: GC-MS analysis before flocculation; B: GC-MS analysis after flocculation



**Fig. 3.** GC-MS analysis of DCS in DIP before and after flocculation by nano-size TiO<sub>2</sub> colloids. C: GC-MS analysis before flocculation; D: GC-MS analysis after flocculation



**Fig. 4.** GC-MS analysis of DCS in whitewater before and after flocculation by nano-size TiO<sub>2</sub> colloids. E: GC-MS analysis before flocculation; F: GC-MS analysis after flocculation

**Table 2.** Removal Efficiencies of DCS Components in non-DIP, DIP, and Whitewater by Flocculation with Nano-size TiO<sub>2</sub> Colloids

Serial Numbers		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Average
Removal Efficiency (%)	Non-DIP	37	-	21	86	32	87	81	75	79	67	12	61	36	92	3	47	89	57
	DIP	27	-	68	75	70	81	85	77	79	77	91	84	86	100	2	97	-	73
	White water	21	-	12	69	19	63	72	69	78	74	49	76	69	81	11	78	100	59

**Table 3.** Sorts of DCS in the Non-DIP, DIP, and Whitewater

Sorts	Serial Numbers	Aggregate Integral Area (%)*	Aggregate Removal efficiency (%)			Average Removal efficiencies (%)
			Non-DIP	DIP	Whitewater	
Fatty acids	1,3,5	4.73	30	55	17	34
Resin acids	6,7,8,9,10,11,12,13,14,16	55.44	64	86	63	71
Polyhydric phenols	4	1.76	86	75	69	77
sterols	17	0.43	89		100	95
Phthalic acid esters	15	4.48	3	2	11	6

\* From Table 1

### Bridging Flocculation Removal of DCS by Nano-size TiO<sub>2</sub> Colloids

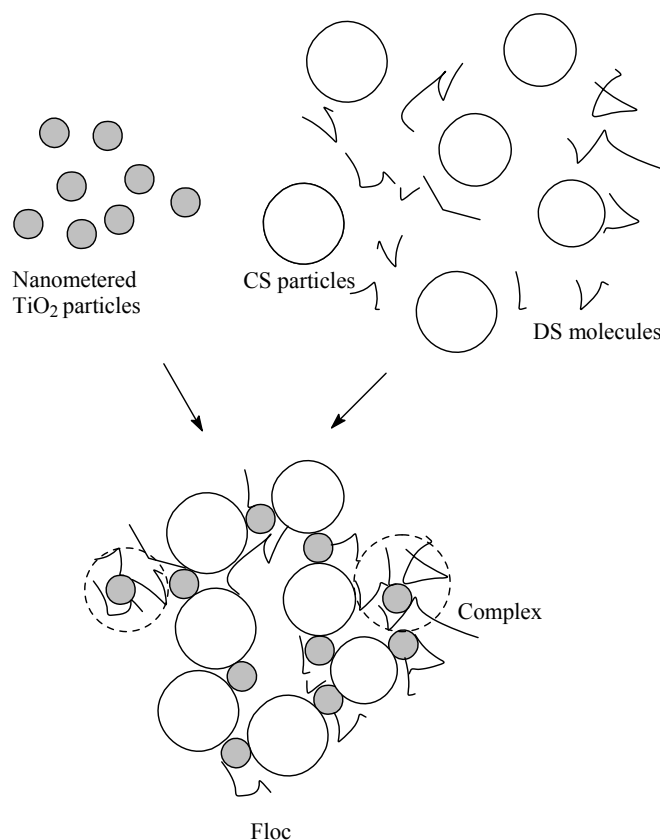
In previous research it was discovered that when a DCS solution is titrated with a nano-size TiO<sub>2</sub> colloid, the flocculation of DCS did not correspond to the reduction of the zeta potential towards zero. Therefore, it was speculated that the flocculation arose from bridging flocculation rather than charge neutralization (Chen et al. 2009).

In the present study, the nano-size TiO<sub>2</sub> used as the flocculating agent possess a great deal of surface hydroxyls due to its low temperature synthetic process in the liquid phase. Those surface hydroxyls (Ti<sup>4+</sup>-OH), which dissociate into Ti atoms with a charge of positive four, display favorable behavior for forming hydrogen bonds with hydroxyl groups in the structures of DCS molecules, as a result of the induction effect of the quadrivalent Ti atoms; therefore, we can speculate that hydrogen bonding adsorption is the main reason for the flocculation of DCS by nano-size TiO<sub>2</sub> colloids. The groups forming hydrogen bonds with nano-size TiO<sub>2</sub> particles may be hydroxyl, aldehyde, carboxyl, etheric, or carbonyl groups. The molecules contained in those groups may be the free molecules of dissolved substances (DS) or the surface molecules existing on the surface of colloidal substance (CS) particles. With hydrogen bonds, the nano-size TiO<sub>2</sub> particles can adsorb DS molecules to form a complex, which performs the capturing effect, and can also interact with CS particles or the formed complexes. The bridging flocculation process activated by the adsorbing action between nano-size TiO<sub>2</sub> and DCS is illustrated in Fig. 5.

### Influence of Polar Functional Groups on the Removal Efficiency of DCS by Nano-size TiO<sub>2</sub> Colloids

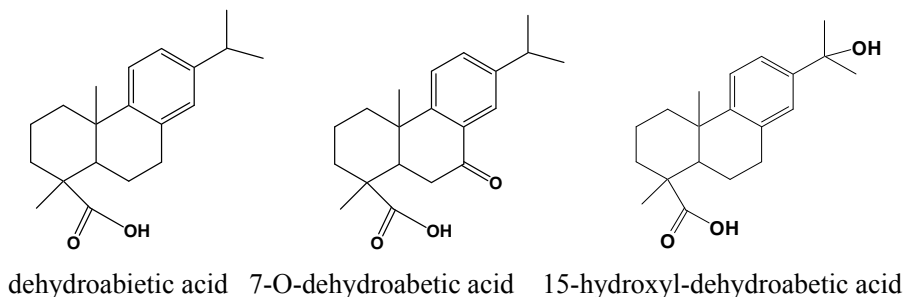
The bridging flocculation of DCS by nano-size TiO<sub>2</sub> colloids relies on the interaction between DCS molecules and nano-size TiO<sub>2</sub> particles. The actions are influenced by the numbers and polarity of the groups that can form hydrogen bonds with the Ti<sup>4+</sup>-OH. The resin acids possess a high removal efficiency owing to carboxylic groups, which can easily form hydrogen bonds.





**Fig. 5.** The bridging flocculation process of DCS by nano-size TiO<sub>2</sub> particles

The molecular structures of the resin acids, such as dehydroabietic acid (12), 7-O-dehydroabietic acid (16), and 15-hydroxyl-dehydroabietic acid (14), are shown in Fig. 6. The removal efficiencies were improved with the increase in polar groups within the molecules. The removal efficiency sequence of DCS in DIP were as follows: 15-hydroxyl-dehydroabietic acid (100 %) > 7-O-dehydroabietic acid (97 %) > dehydroabietic acid (84 %), which was the same as that of the whitewater. The situation of non-DIP is complicated, and the resin acids do not show higher removal efficiency. This can be due to there being more CS in non-DIP than in DIP, and some resin acid molecules existing inside the CS particles cannot ideally display the influence of the functional groups on the removal efficiencies.



**Fig. 6.** Structures of three resin acids

Sterols, such as 3,17,20-tris (hydroxyl) pregn-5-en-11-one (17), were also detected in non-DIP; the corresponding molecular structure is shown in Fig. 7. With numerous hydroxyl and carbonyl groups in the molecules, the sterols exhibited a high flocculation efficiency (97 %); therefore, the carboxyls, hydroxyls, and carbonyls in the DCS molecules are beneficial in enhancing the removal efficiencies of DCS by nano-size  $\text{TiO}_2$ , and moreover the removal efficiencies were improved by increasing the number and polarity of functional groups.

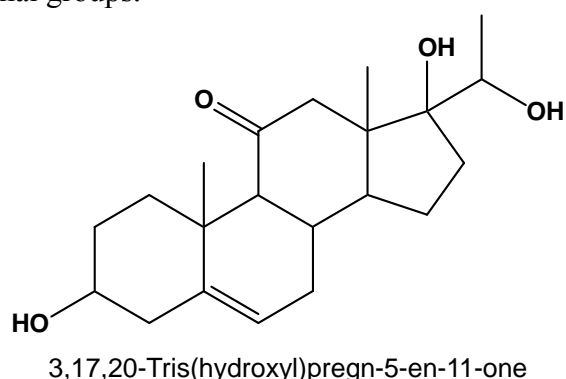


Fig. 7. Structure of sterol compound (17)

### Influence of the Alkyl Structure in Molecules on Removal Efficiencies of DCS with Nano-size $\text{TiO}_2$ Colloids

In the process of flocculating DCS with nano-size  $\text{TiO}_2$  colloids, the formation of hydrogen bondings is affected by the alkyl structures in the DCS molecules. As shown in Table 3, all resin acids with multi-ring alkyls showed high removal efficiencies, and yet the fatty acids with long-chain alkyl groups exhibited comparatively lower efficiencies, though both of them have the same carboxyl functional group. The difference in removal efficiencies of DCS with the same functional groups is probably due to the diversity of alkyl structures in the molecules. Comparing hexadecane acid (1) and pimaric acid (6) (the molecular structures are shown in Fig. 8), for example, the removal efficiency of pimaric acid (resin acid) was much higher than that of hexadecane acid (fatty acid); the former was 86% (in non-DIP) and 81% (in DIP), whereas the latter was 37% (in non-DIP) and 27% (in DIP).

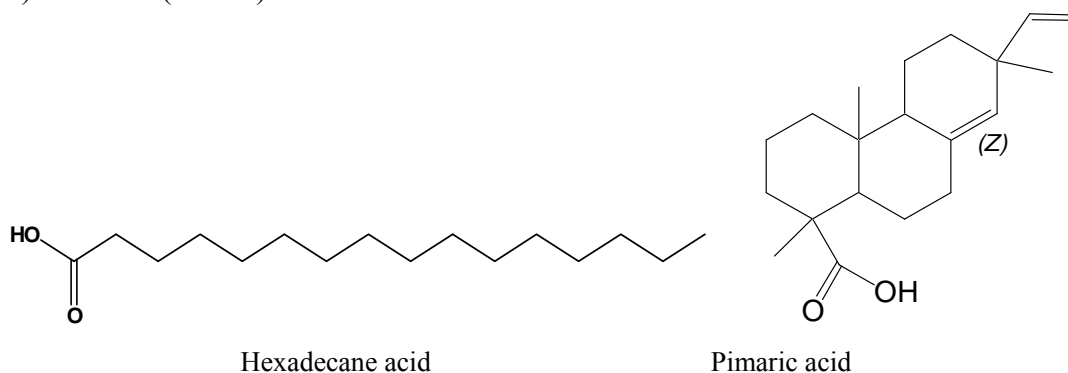
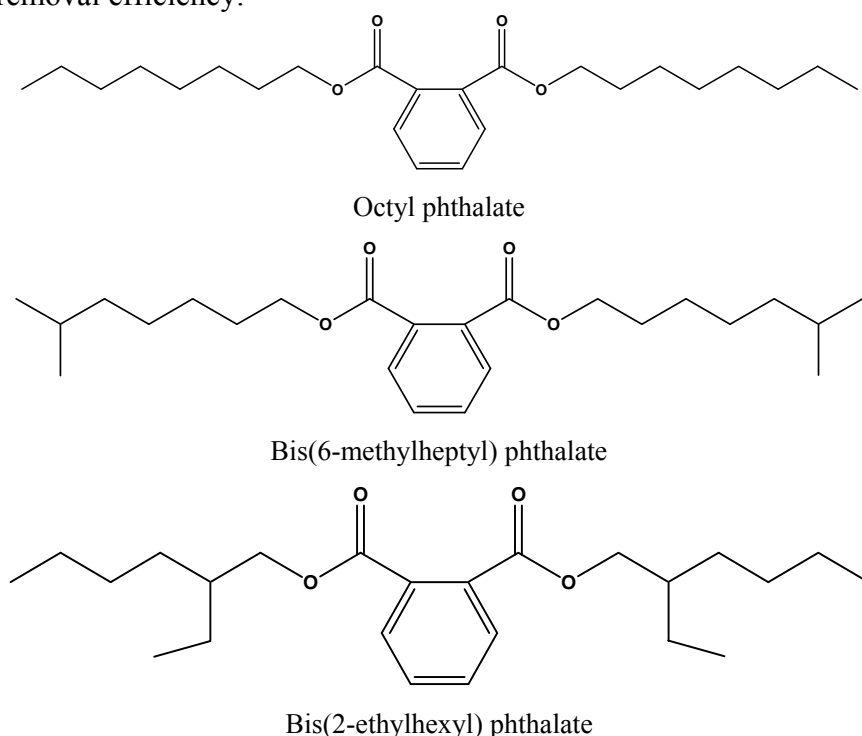


Fig. 8. Structures of two compounds with the same functional group carboxyl (1 and 6)

The reason is that carbon-carbon single bonds in the alkyl chain of fatty acids can rotate so that the long-chain alkyl generates twisting and folding, which shields the carboxyl functional group. The shielding effect prevents the formation of hydrogen bonds between DCS molecules and nano-size  $\text{TiO}_2$  particles, leading to inferior flocculation efficiency. By contrast, the resin acids with rigid multi-cyclic structures cannot perform rotating or distorting, and so there is no shielding effect unfavorable for the flocculation removal

The shielding effect has also appeared in the structures of phthalic acid ester compounds (15); three possible molecule configurations are shown in Fig. 9 (based on NIST05 spectral library). Two symmetric chain alkyls in the molecular structures have given strong shielding effects to carboxyl functional groups to weaken the flocculation efficiency. Furthermore, the symmetric configuration of molecules decreases the overall molecular polarity, which results in a very weak interaction with nano-size  $\text{TiO}_2$  particles and a low removal efficiency.



**Fig. 9.** The possible structures of the phthalic acid ester compounds (15)

## CONCLUSIONS

1. Most of the DCS could be removed through flocculation by their interaction with nano-size  $\text{TiO}_2$  colloids. The removal efficiencies, which correlate with the molecular structures, are sequenced from large to small as follows: resin acids and sterols, benzene derivatives containing carboxyl, fatty acids, and phthalic acid esters.
2. The mechanism of removal of DCS by nano-size  $\text{TiO}_2$  colloids is bridging flocculation. The key step is the formation of hydrogen bonds between the surface

hydroxyl ( $\text{Ti}^{4+}$ -OH) and the functional groups containing O atoms, with which the nano-size  $\text{TiO}_2$  particles can capture DS molecules, bridging CS and complex particles to form chemical complexes.

3. The functional groups and alkyls in DCS molecules influence the flocculating removal efficiencies. In the DCS molecules, high polarity of the functional groups, and high numbers of functional groups, which are more favorable for forming hydrogen bonds, account for high flocculating removal efficiencies of DCS. On the other hand, the long-chain alkyls shield the functional groups and inhibit the formation of hydrogen bonds, which results in the decrease of removal efficiencies.

## ACKNOWLEDGMENTS

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## REFERENCES CITED

- Chen, X. Q., Kou S. L., and Liu H. B. (2006). "Study on the mechanism of flocculation of DCS in TCMP with nanosized  $\text{TiO}_2$ ," *Proc. 25th CCS Congress*, Changchun, China, 230.
- Chen, X. Q., Liu, H. B., Zhao, G. L., He, B. H., and Qiao, L. Y. (2004). "Application of nanosized  $\text{TiO}_2$  microparticle in the retention system of newsprint," *Paper Sci. & Tech.* 23(2), 25-28.
- Chen, X. Q., and Shen, W. H. (2008). "Preparation and properties of stable nanocrystalline anatase  $\text{TiO}_2$  colloids," *Chem. Eng. Technol.* 31(9), 1277-1281.
- Chen, X. Q., Shen, W. H., Liu, H. B., and Kou, S. L. (2009). "Study on removal of dissolved and colloidal substances in deinked pulp by dual-component system retention aids containing nanosized  $\text{TiO}_2$  colloid," *Appita J.* 62(5), 345-350.
- Donat, V., Van de Ven, T. G. M., and Paris, J. (2003). "Distribution of dissolved and colloidal substances in the forming and press sections of a paper machine," *J. Pulp Paper Sci.*, 29(9), 294-298.
- Dunham, A. J., Sherman L. M., and Alfano J. C. (2002). "Effect of dissolved and colloidal substances on drainage properties of mechanical pulp suspensions," *J. Pulp Paper Sci.*, 28(9), 296-310.
- Dunham, A. J., Tubergen, K.R., Govoni, S.T., and Alfano, J. C. (2000). "The effect of dissolved and colloidal substances on flocculation of mechanical pulps," *J. Pulp Pap. Sci.*, 26(3), 95-101.
- Fälth, F., Pfromm, P. H., and Bryant, P. S. (2001). "Ultrafiltration of E1 stage effluent for partial closure of the bleach plant," *Pulp and Paper Can.* 102(1), 46-48.
- Francis, D. W., and Ouchi, M. D. (2001). "Effect of dissolved and colloidal solids on newsprint properties," *J. Pulp Pap. Sci.*, 27(9), 289-295.

- Huang, L., Xiao H., and Ni, Y. (2006). "Cationic-modified microporous zeolites/anionic polymer system for simultaneous removal of dissolved and colloidal substances from wastewater," *Sep. Purif. Technol.*, 49(3), 264-270.
- Huuhilo, T., Suvilampi, J., and Puro, L. (2002). "Internal treatment of pulp and paper mill process waters with a high temperature aerobic biofilm process combined with ultrafiltration and/or nanofiltration," *Paper and Timber* 84(5), 50-53.
- Kenny, R., Gorgol, R. G., and Martineau, D. (1992). "Freeze crystallization of Temcell's BGTMP effluent," *Pulp and Paper Can.* 93(10), 55-58.
- Kou, S. L., Chen, X. Q., and Liu, H. B. (2008). "Study on the flocculation of dissolved and colloidal substances in secondary fibre suspension with nano-titania/anionic polyacrylamide," *Intl. Conf. on Pulping, Papermaking and Biotechnology*, Nanjing, China, 462-466.
- Li, H., Ni, Y., and Sain, M. (2002). "The presence of dissolved and colloidal substances in BCTMP and their effects on sizing," *J. Pulp Paper Sci.* 28(2), 45-49.
- Tardif O., and Hall E. R. (1997). "Alternatives for treating recirculated newsprint whitewater at high temperatures," *Wat. Sci. Tech.* 35(2-3), 57-65.
- Paleologou, M., Cloutier, J. N., and Ramamurthy, P. (1994). "Membrane technologies for pulp and paper applications," *Pulp and Paper Can.* 95(10), 36-40.
- Ramamurthy, P., and Dorica, J. (1992). "Separation processes for treatment of effluents from pulp and paper mills," *AICHE First Separations Topical Conference*, Miami Beach, Florida, November (2-6), 947-952.
- Rigol, A., Latorre, A., and Lacorte, S. (2002). "Determination of toxic compounds in paper-recycling process waters by gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry," *J. Chromatography*, 963(1), 265-275.
- Stevenson, S. (1990). "With a zero-effluent mill millar western will meet the stringent saskatchewan standards," *Pulp and Paper Can.* 91(4), 16-18.
- Stroem, G., Barla, P., and Stenius, P. (1985). "The formation of polyelectrolyte complexes between pine xylan and cationic polymers," *Coll. Surf. A.* 13, 193-207.
- Wågberg, L., Ondaral, S., and Enarsson, L. E. (2007). "Hyperbranched polymers as a fixing agent for dissolved and colloidal substances on fiber and SiO<sub>2</sub> surfaces," *Ind. Eng. Chem. Res.* 46(7), 2212-2219.
- Wearing J. T., Barbe, M. C., and Ouchi, M. D. (1985). "The effect of white-water contamination on newsprint properties," *J. Pulp Paper Sci.*, 11(4), J113-121.
- Zhang, X., Derrick, W. S., and John, N. S. (2000). "Enzyme treatments of the dissolved and colloidal substances present in mill white water and the effects on the resulting paper properties," *J. Wood Chem. Technol.* 20(3), 321-318.

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