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Preparation of Water Soluble Chitosan Blendmers and Their Application to Removal of Heavy Metal Ions from Wastewater†

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Abstract: High purity water soluble chitosans (WsCs) were employed as a flocculant to remove heavy metal ions from wastewater of industrial plating wastewater treatment complex. Their weight average molecular weights and polydispersities were 272,000~620,000 g/mol and 1.4~1.9 range, respectively and were readily soluble in water in the pH range of 3~11. Heavy metal ions such as chromium, iron and copper were removed well by WsCs. When WsCs was blended with either sodium N,N-diethyldithiocarbamate trihydrate ($SDDC_T$) or sodium salicylate (SS_C), the removal efficiency was further increased primarily due to the excess amount of hydrophilic sulfonic and carboxylic groups. Especially, in the case of WsCs-SS_C the remaining chromium and copper concentrations were 0.1 mg/L and 9.5 mg/L, which are 1/15 and 1/3 compared with that of pure WsCs, respectively. The former is within the acceptable limit, but the latter is not. Therefore, the effective copper flocculant remains to be studied.

Keywords : blending, sodium *N,N*-diethyldithiocarbamate trihydrate, sodium salicylate, chitosan, heavy metal ions, wastewater treatment, plating.

Introduction

Heavy metal ions in wastewater such as chromium, copper, iron and lead are very toxic and should be removed. Inorganic and synthetic polymer flocculants have been conventionally used to remove such heavy metal ions in wastewater. In many cases, however, they are not environmentally friendly because they are not readily decomposed by microorganisms.[1] Therefore, natural flocculants are more preferable than conventional inorganic or synthetic polymer flocculants.[2,3] For example, natural adsorbents such as chicory, green tea leaves and coffee residues have been commonly used to treat wastewater because of their excellent adsorptivity of heavy metals.[4-10]

Meanwhile, chitosan extracted from shells of a crustacean, e.g., crab and shrimp, constitutes many amino groups having an excellent affinity to heavy metal ions.[11,12] Thus, chitosan has been developed as an adsorbent for heavy metal ions as well as a scavenger for useful metal ions. However, since chitosan is only sparingly soluble in water and has high molecular weight, its efficiency is not so high. Therefore, water soluble chitosans are desirable. They are successfully prepared by proprietary techniques of enzyme and ultrasonic treatments, electrolysis and multistep membrane separation from Jakwang Co., Ltd (Ansung city, Korea).[13]

In this research, water soluble chitosans were characterized chemically and their separation properties of heavy metal ions from wastewater stream are evaluated. Further blendmers are prepared with sodium *N,N*-diethyldithiocarbamate trihydrate ($SDDC_T$) or with sodium salicylate (SSc) to enhance the removal efficiency of heavy metal ions from

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wastewater since they have active groups for heavy metal ions such as sulfonic and carboxylic groups.

Experimental

Materials. Three water soluble chitosans (WsCs) of EU-01, EU-02 and EU-03 were obtained from Jakwang Co., Ltd. (Ansung city, Korea), as schematically shown in Figure 1. The detailed procedure to make WsCs was described in the reference 13. Industrial wastewater containing heavy metal ions was taken from plating wastewater stream in Shiwha complex, Ansan city, Kyunggi province.

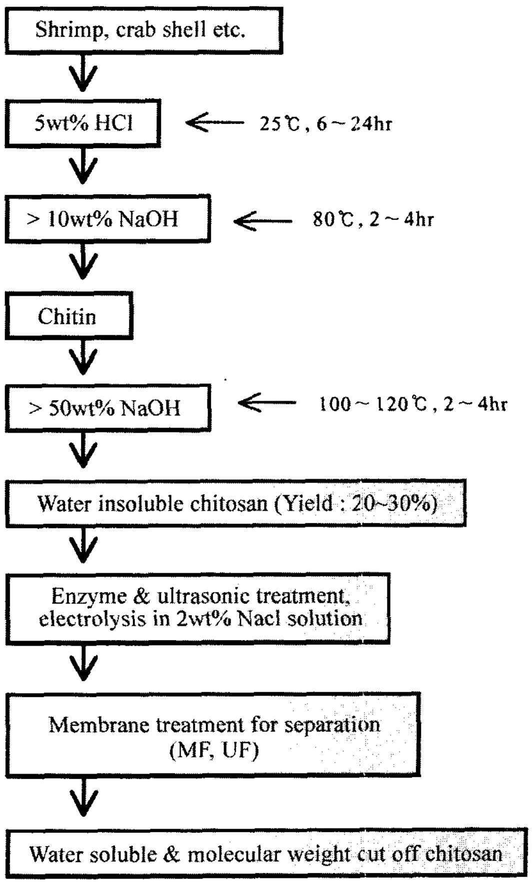

Figure 1. Manufacturing of water soluble and molecular weight cut off chitosan.[13]

Characterization of WsCs. FT-IR spectra were obtained using infrared spectrometer (Perkin-Elmer, System 2000, Buckinghamshire, UK) and molecular weight and molecular weight distribution were measured using gel permeation chromatography (Waters, Model 2690, Massachusetts, USA). The viscosity and pH were measured using viscometer (Brookfield, LVDV-II, Wisconsin, USA) and pH meter (Orion, Model 350, Massachusetts, USA), respectively.

Preparation of WsCs-blendmers. Sodium *N,N*-diethyldithiocarbamate trihydrate ($SDDC_T$) and sodium salicylate (SS_C) from Kanto Chemical Co., Ltd. (Japan) contain sulfonic and carboxylic groups, respectively and are water soluble. WsCs-blendmers of WsCs-$SDDC_T$ and WsCs-SS_C were prepared by adding certain amounts of $SDDC_T$ and SS_C, respectively, into the chitosan solution in water without any catalysts and other additives.

Measurement of Heavy Metal Removal. The concentration of heavy metal ions in wastewater and acceptable limits thereof were shown in Table I. A certain amount of flocculant was added to the previously pH-adjusted wastewater. The solution was stirred rapidly at 130 rpm for 5 minutes, and then stirred slowly at 20 rpm for 15 minutes, and placed to precipitate for 15 minutes. The remaining heavy metal concentrations were measured using atomic absorption spectrophotometer (Shimadzu, AA-6601F, Kyoto, Japan) from the collected 10~15 mL of supernatant within 5 cm deep from surface.

Results and Discussion

Characterization of Water Soluble Chitosan. The molecular characteristics of three different water soluble chitosans of EU-01, EU-02 and EU-03 are summarized in Table II. The weight average molecular weights of the 3 samples are within the range of 272,000~620,000 g/mol and

Table II. Molecular Characteristics of WsCs

Sample	$\overline{M_w}$ (g/mol)	Polydispersity	Viscosity (mN · s/m^2)
EU-01	272,000	1.6~1.8	101.1
EU-02	380,000	1.5~1.9	104.2
EU-03	620,000	1.4~1.9	109.8

Table I. Concentration of Heavy Metals in Plating Wastewater

	pH	*SS (mg/L)	Heavy Metal (mg/L)			
			Cr_{Total}	Cr^{6+}	Cu	Fe
Sample	1.7~1.8	1540.0	166.3	18.9	133.4	338.4
Acceptable Limit[14]	5.8~8.6	120.0	2	0.5	3	Not available

*SS ; Suspended solids.

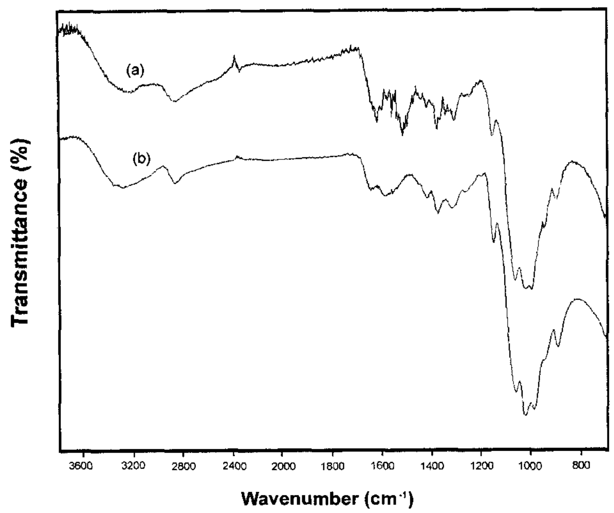

Figure 2. FT-IR spectra of chitosans ; (a) WsCs and (b) InCs.

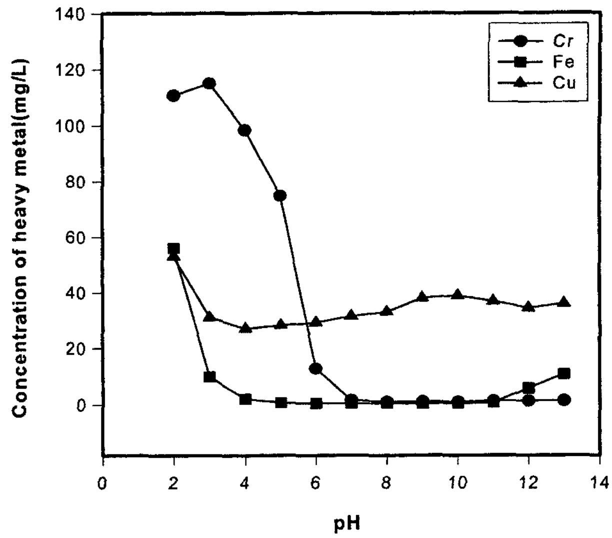

Figure 3. Heavy metal removals by WsCs.

the polydispersities and viscosities thereof are within the ranges of 1.4~1.9 and 101.1~109.8 mN · s/m^2, respectively.

FT-IR spectra of water insoluble chitosan (InCs) and WsCs were taken as depicted in Figure 2, which are very similar each other. It suggests that the chemical structure hardly change during the solubilization process as described in Figure 1.

Considering the removal of suspended materials and toxic metal ions in aqueous solution, it is preferred to use a flocculant of water soluble polymer having an excellent miscibility with water and dispersability in water. Therefore, the flocculant must contain appropriate hydrophilic or charged groups. When the flocculant was finely well dispersed, its surface area was largely increased and the flocculation efficiency was thus enhanced due to the increased contact probability between the flocculant and metal ions. Therefore, the hydrophilicity of flocculant is very important.[15]

The water solubility, a measure of hydrophilicity, of the chitosan samples over the change of pH was measured and listed in Table III. All chitosan samples exhibited an excellent water solubility in the broad range of pH from 3 to 11 except the strong acid (pH 1~2) and strong alkali (pH 12~14) ranges. It thus suggests that the chitosans used in this study were water soluble in the wide range of pH.

Heavy Metal Removals by WsCs. Figure 3 is a graph showing the remaining chromium, iron and copper concentrations versus pH. Chromium removal is not efficient in the acidic condition until the pH of the solution reaches to approximately 7. However it becomes very effective in the alkaline condition. The remaining chromium concentration was within the range of 1.5~0.9 mg/L in the alkaline condition. The iron removal behavior is analogous to the chromium one, i.e., low in acidic and high in alkaline condition. The remaining iron concentration was 0.5 mg/L or less in the pH range of 6~10. In the case of copper, the removal efficiency is not high even in the alkaline condition where chromium and iron are removed effectively. The remaining copper concentration was as much as 27 mg/L at pH 4 and exhibited low removal efficiency in the overall pH range. Since the copper ions can form complex compounds in wastewater, copper removal efficiency was relatively low and thus the remaining copper concentration was higher.

Heavy Metal Removals by WsCs-blendmers. Figure 4 is a graph of the remaining heavy metal concentrations versus $SDDC_T$ content at pH 7 when WsCs-$SDDC_T$ was used. The removal efficiency of chromium and iron are high but that of copper is still not high in the whole range of the $SDDC_T$

Table III. Water Solubility of WsCs vs pH Values

	pH													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
EU-01	-	±	+	+	+	+	+	+	+	+	+	-	-	-
EU-02	-	±	+	+	+	+	+	+	+	+	+	-	-	-
EU-03	-	±	+	+	+	+	+	+	+	+	+	-	-	-

+ ; Soluble, - ; Insoluble, ± ; Patially soluble.

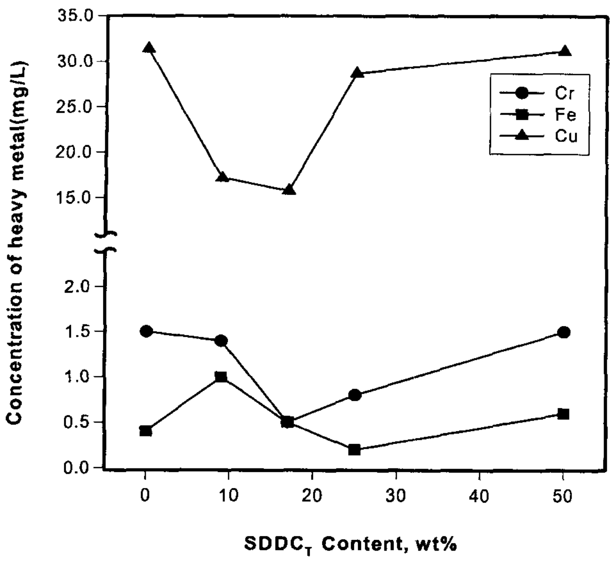

Figure 4. Heavy metal removals by WsCs-SDDC$_T$.

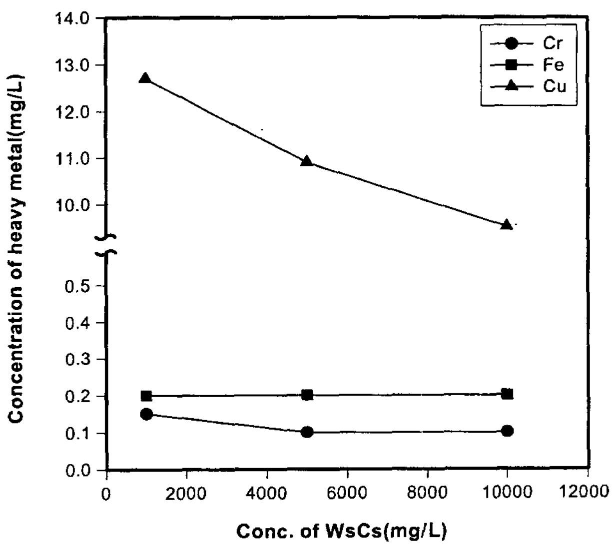

Figure 5. Heavy metal removals by WsCs-SS$_C$.

content studied. When the SDDC$_T$ content was in the range of 9~17 wt%, the remaining heavy metal concentrations were low, compared with pure WsCs.

In particular, when the SDDC$_T$ content was 17 wt%, the remaining chromium concentration was a minimum at 0.5 mg/L, which corresponds to about 1/3, compared with that of pure WsCs. When the SDDC$_T$ content was 25 wt%, the remaining iron concentration was 0.2 mg/L. Also, when the SDDC$_T$ content was 17 wt%, the remaining copper concentration was 15.8 mg/L, which corresponds to 1/2, compared with that of pure WsCs. This results suggest that WsCs-SDDC$_T$ blendmer is much more effective than pure WsCs.

Figure 5 is a graph showing the flocculation experimental results of WsCs-SS$_C$ blendmer with the SSc concentration fixed at 1,000 mg/L and the WsCs concentration varying from 1,000 to 10,000 mg/L at pH 7. SS$_C$ contains many carboxylic groups. When the WsCs concentration was 5,000 mg/L, the remaining chromium concentration was dropped to 0.1 mg/L. When WsCs concentration was 10,000 mg/L, the remaining copper concentration was 9.5 mg/L. These concentrations correspond to about 1/15 and 1/3, respectively, compared with that of pure WsCs. Thus, WsCs-SS$_C$ blendmer is more effective than WsCs-SDDC$_T$ one in removing heavy metal ions.

Conclusions

The weight average molecular weights and polydispersities of WsCs prepared through the processes of enzyme treatment, ultrasonic treatment and electrolysis were 272,000~620,000 g/mol and 1.4~1.9 range, respectively. WsCs is highly water soluble in the pH range of 3~11.

WsCs-blendmers such as WsCs-SDDC$_T$ and WsCs-SS$_C$ showed higher heavy metal removal efficiency than that of WsCs itself. Especially, in the case of WsCs-SS$_C$ blendmer the remaining chromium concentration and copper concentration were 0.1 mg/L and 9.5 mg/L, which are 1/15 and 1/3 compared with that of pure WsCs, respectively. However the remaining chromium concentration is within the acceptable limit, whereas the remaining copper concentration is over the limit. Therefore, the effective copper binding agent remains to be studied.

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