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Metal adsorption by quasi cellulose xanthogenates derived from aquatic and terrestrial plant materials

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Abstract

The FTIR spectra, SEM-EDXA and copper adsorption capacities of the raw plant materials, alkali treated straws and cellulose xanthogenate derivatives of *Eichhornia crassipes* shoot, rape straw and corn stalk were investigated. FTIR spectra indicated that of the three plant materials, the aquatic biomass of *Eichhornia crassipes* shoot contained more O-H and C=O groups which accounted for the higher Cu²⁺ adsorption capacities of the raw and alkali treated plant material. SEM-EDXA indicated the incorporation of sulphur and magnesium in the cellulose xanthogenate. The Cu²⁺ adsorption capacities of the xanthogenates increased with their magnesium and sulphur contents. However more copper was adsorbed than that can be explained by exchange of copper with magnesium. Precipitation may contribute to the enhanced uptake of copper by the cellulose xanthogenate.

23 *Keywords:* Cellulose xanthogenate; Cu²⁺ adsorption capacity; Sulphur; Magnesium; Biomass

24 **1. Introduction**

25 Plant fiber generally has a low adsorption capacity for metal ions in aqueous solution and
26 furthermore the fiber readily degrades. However, chemical modification of fiber has the
27 potential to both increase adsorption capacity and improve stability of fiber (Kamel et al.,
28 2006; O'Connell et al., 2008). Fiber may be modified by low molecular weight organic
29 compounds such as acrylic acid (Wei et al., 2005), high molecular weight substances such as
30 polyacrylonitrile (Okieimen et al., 2005), and many inorganic substances, including CS₂ (Tan
31 et al., 2008). The introduction of functional groups, such as -CS-S- and carboxyl, on the
32 cellulose backbone can enhance the heavy metal binding capacities of modified fibers. Due to
33 their high heavy metal chelation capacity and the intrinsic advantages of low cost, availability,
34 biodegradability and easy handling, there has been much recent research interest in adsorbents
35 derived from biomass resources. Studies have included their preparation, application
36 (Chakraborty and Tare, 2006; Chauhan and Sankararamakrishnan, 2008; Tan et al., 2008),
37 structural characterization and adsorption mechanisms (Panda et al., 2008; Zhou et al., 2009).

38 This paper focuses on differences in the structural characteristics of terrestrial and aquatic
39 sourced plant materials, their corresponding alkali-treated straws (intermediate products) and
40 cellulose xanthogenates (products), and the relationship between structural characteristics and
41 heavy metal adsorption capacities of these materials. Plant straws from aquatic *Eichhornia*
42 *crassipes* (*E. crassipes*) shoot were compared with terrestrial biomasses of rape straw and corn
43 stalk. *E. crassipes* biomass was of particular interest because of its nuisance factor in
44 eutrophic waters (Malik, 2007), and the relevance that chemical modification and utilization

1 45 of *E. crassipes* biomass as a cellulose based adsorbent for water remediation or other purposes
2
3 46 would have to the economic viability of large scale harvesting of this nuisance plant.
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5
6 47 Favorable results would provide a basis for its selection as an appropriate raw plant material
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9 48 for biomass adsorbents.

11 49 **2. Methods**

14 50 *2.1. Collection and pre-treatment of raw plant materials*

17 51 Plant samples of *E. crassipes* were collected from a pond near Huazhong Agricultural
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20 52 University (E114°23' , N30°33') in Wuchang, Wuhan City of China. The shoot and the root
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23 53 were separated. Rape straw and corn stalk were also collected from fields near Huazhong
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25 54 Agricultural University. All of the plant materials were washed with tap water, cut into small
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28 55 pieces (3~5 mm), air-dried, oven-dried, ground into fine powder, passed through a 40 mesh
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30
31 56 sieve and kept desiccated at 25°C.

34 57 *2.2. Preparation of cellulose xanthogenate*

36 58 A 5 g sample of dried plant biomass was treated with 50 ml 200 g/L NaOH for 90 min,
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39 59 and thoroughly washed with deionised water to obtain alkali-treated straw. The alkali-treated
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42 60 straw was then esterified with 0.15 ml CS₂ and 50 ml 100 g/L NaOH for another 90 min, and
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45 61 finally treated with 10 ml 50 g/L MgSO₄ for 10 min to prepare cellulose xanthogenate,
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48 62 according to the method of Tan et al. (2008). The nine materials studied included *E. crassipes*
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50 63 shoot, rape straw, corn stalk, their corresponding alkali-treated straws and cellulose
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53 64 xanthogenates. All of the samples were oven-dried and ground into fine powder, passed
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56 65 through a 100 mesh sieve and kept desiccated at 25°C until used.

58 66 *2.3. Structural characterization*

1 67 FTIR spectra of the different materials were obtained with a FTIR spectrophotometer
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3 68 (Nexus-470, USA) using KBr discs containing 2.5% finely ground sample (2.00 mg dried
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6 69 sample mixed with 80.0 mg KBr). They were recorded as absorption spectra in the range
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9 70 4000–400 cm^{-1} with an accumulation of 32 scans and a resolution of 4 cm^{-1} .

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11 71 Surface element concentration of the samples was investigated using a JSM-6390LV
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14 72 scanning electron microscope (SEM) equipped with energy dispersion X-ray spectroscopy
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17 73 analysis (EDXA). The samples were coated with platinum in a JFC-1600 sputter coater before
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20 74 observation.

21 22 75 *2.4. Cu^{2+} adsorption experiments*

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25 76 Cu^{2+} was selected as a model heavy metal for the adsorption experiments. The stock
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28 77 solutions of 1000 mg/L and 3000 mg/L Cu^{2+} were prepared in deionized water using the
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31 78 sulphate salt. To determine the adsorption capacity of raw plant materials and alkali-treated
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34 79 straws, 0.20 g samples were slurried in a 20-mL solution of 1000 mg/L Cu^{2+} initially at pH 4.5,
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37 80 stirred for 24 h and filtered prior to determination of the residual concentration of Cu^{2+} . In the
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40 81 case of cellulose xanthogenate a concentration of 3000 mg/L Cu^{2+} was used. Adsorption
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43 82 studies were carried out at 25 ± 1 °C and Cu^{2+} concentration was determined by AAS.

44 83 *2.5. Determination of sulphur and magnesium content of cellulose xanthogenate*

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46
47 84 Sulphur was determined by iodimetry. Magnesium was determined by EDTA titration
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50 85 after samples were dry ashed, and dissolved in 1 mol/L HCl solution.

51 52 86 **3. Results and discussion**

53 54 55 87 *3.1. IR functional group changes caused by chemical modification of plant materials*

1 88 The IR spectra of all the raw plant materials contained the same main absorbance bands,
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3 89 including bands at 3383cm^{-1} , 1643cm^{-1} and 1027cm^{-1} representing O–H stretching, aromatic
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6 90 ring C=O stretching, and symmetric C–O stretching (Viera et al., 2007), respectively. The
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9 91 absorbances of the three main bands were the highest for *E. crassipes* shoot, followed by those
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11 92 of rape straw with the bands for corn stalk being the lowest, indicating that the aquatic
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14 93 biomass of *E. crassipes* shoot contained more active O-H and C=O groups than the other two.
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16
17 94 In the alkali-treated materials, the intensity sequence of absorbances at 1504 cm^{-1} and
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19 95 1229 cm^{-1} , representative of lignin content (Viera et al., 2007), was rape straw > corn stalk > *E.*
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22 96 *crassipes* shoot consistent with literature reports (Tan et al., 2008). Compared with the
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24
25 97 alkali-treated straws, bands of O-H stretching in the vicinity of 3407 cm^{-1} and C=O stretching
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28 98 in the vicinity of 1637 cm^{-1} of the three cellulose xanthogenates all had diminished
29
30
31 99 absorbances. The aromatic ring C=C stretching (lignin) absorbance in the vicinity of 1523
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33 100 cm^{-1} became invisible, and symmetric CH_2 bending absorbances near 1454cm^{-1} all increased
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35
36 101 significantly. These results are consistent with the reduction or disappearance of hemicellulose
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38
39 102 and lignin, and a relative increase in cellulose content and its chemical modification by the
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41
42 103 formation of cellulose xanthogenate.

43 44 104 3.2. Incorporation sulphur and magnesium in modified materials

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46
47 105 **Table 1** Surface element atomic percentages determined by EDXA

48
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50 106 Surface element atomic percentages of the nine samples determined by EDXA are shown
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53 107 in Table 1. The main elements of the raw plant materials and alkali-treated straws are C and O,
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56 108 and there are no obvious changes in elemental composition between raw plant materials and
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59 109 alkali-treated straws. However, the Mg and S concentrations of cellulose xanthogenates are
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110 significantly higher indicating incorporation of Mg and S into the surfaces of the
111 modified materials. Of the three xanthogenates, Mg concentration of *E. crassipes* shoot and S
112 concentration of corn stalk were the highest.

113 3.3. The effect of chemical modification on Cu^{2+} adsorption capacities

114 The Cu^{2+} adsorption capacities of the raw plant materials of *E. crassipes* shoot, rape
115 straw and corn stalk were 39.2 ± 0.2 , 31.4 ± 0.1 and 23.6 ± 0.1 cmol/kg, respectively. Those of
116 their alkali-treated straws were 62.7 ± 0.5 , 55.0 ± 0.3 and 39.3 ± 0.2 cmol/kg, and those of
117 cellulose xanthogenates were 361.0 ± 2.5 , 303.1 ± 3.8 and 334.5 ± 4.3 cmol/kg, respectively.
118 Compared to raw plant materials, alkali treatment followed by CS_2 and Mg treatments
119 produced successive 1.67 to 1.75 fold and 9.2 to 14.2 fold enhancements of the Cu^{2+}
120 adsorption capacity. The Cu^{2+} adsorption capacities of the three raw plant materials and their
121 alkali-treated straws follows the trend: *E. crassipes* shoot > rape straw > corn stalk. This is
122 also the order of the relative IR absorbances of the main functional groups, O-H and C=O, for
123 these materials. For the xanthogenates however, the sequence of absorbance intensity of main
124 characteristic functional groups, -O- CS_2 - and O-H, is corn stalk > *E. crassipes* shoot > rape
125 straw, and is not completely consistent with the sequence of copper adsorption capacities
126 which is *E. crassipes* shoot > corn stalk > rape straw. Other factors, such as sulphur and
127 magnesium content, are likely to be involved in the copper adsorption process.

128 3.4. The mechanism of Cu^{2+} adsorption

129 **Table 2** The sulphur and magnesium contents of cellulose xanthogenates prepared from
130 different raw plant straws

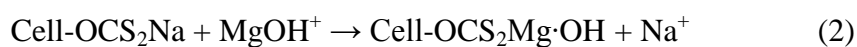
131 The sulphur and magnesium contents of the three cellulose xanthogenates are summarized

132 in Table 2. The bulk sulphur and magnesium contents of Table 2 are not completely consistent
 133 with the surface sulphur and magnesium concentrations determined by EDXA given in Table 1.
 134 This indicates a non-uniform distribution of sulphur and magnesium in these materials.
 135 Comparison of surface sulphur and magnesium concentrations with copper adsorption data
 136 reveals that *E. crassipes* shoot derived xanthogenate with the highest surface magnesium
 137 concentration and the corn stalk derived xanthogenate with the highest surface sulphur
 138 concentration correspond to the materials with the highest and the second highest Cu²⁺
 139 adsorption capacities. This indicates an association between surface sulphur and magnesium
 140 content of the cellulose xanthogenate and copper adsorption.

141 The sulphur contents of Table 2 allow calculation of the -O-CS₂- contents which are also
 142 summarized in the table. When the calculated -O-CS₂- contents are compared with the
 143 measured Mg contents, the expected stoichiometry is not observed. If, as according to Tan et
 144 al. (2008), the reaction of magnesium with sodium xanthogenate is:

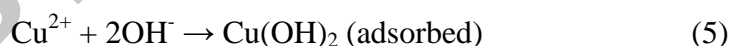


145 the -O-CS₂- : Mg mole ratio should be greater than or equal to 2:1. The ratios of the data are
 146 1.08, 2.48 and 1.28 for xanthogenates from *E. crassipes* shoot, rape straw and corn stalk,
 147 respectively (Table 2). Only the rape straw xanthogenate conforms. The other two samples
 148 contain more magnesium than can be accounted for by their sulphur contents. It is possible
 149 that hydrolysed magnesium species are involved in the magnesium treatment step and that
 150 magnesium reacts with sites other than sulphur sites:





From the sulphur and magnesium contents in Table 2 and the Cu^{2+} adsorption capacities, it is clear that there is no close relationship between the sulphur contents of the xanthogenate products and their Cu^{2+} adsorption capacities. There is a better relationship between the magnesium contents of the products and their Cu^{2+} adsorption capacities but this is not consistent with stoichiometric exchange of Mg^{2+} by Cu^{2+} . The greater than expected Cu retention capacities might be due to mildly alkaline conditions produced by hydrolysis of the xanthogenate products. When the xanthogenate samples were added to deionised water the pH was observed to rise to 8.0. Given that the solubility product of $\text{Cu}(\text{OH})_2$ is 2.2×10^{-20} (mol/L)³ and the concentration of Cu^{2+} in the adsorption solution was 3000 mg/L, i.e. 0.047 mol/L, precipitation of copper hydroxide can be expected while the pH remains above approximately 5.0. Thus a further possible mechanism for the high uptake of copper by xanthogenate might be:



4. Conclusion

Compared to the terrestrial rape straw and corn stalk, the aquatic *E. crassipes* shoot contain more active O-H and C=O groups. Cu^{2+} adsorption capacity of the raw and alkali-treated straw increased with the relative contents of the O-H or C=O groups, respectively. Due to the incorporation of sulphur and magnesium, the Cu^{2+} adsorption capacity of quasi-xanthogenate products increased significantly. Cu^{2+} adsorption capacity of quasi-xanthogenate products increased with magnesium and sulphur contents in products. Besides cation exchange between Mg^{2+} and Cu^{2+} , copper precipitation mechanism may be

1 176 present.

2
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Table 1

Surface element atomic percentages determined by EDXA

Element type	Raw plant materials			Alkali-treated straws			Cellulose xanthogenates		
	<i>E. crassipes</i> shoot	Rape straw	Corn stalk	<i>E. crassipes</i> shoot	Rape straw	Corn stalk	<i>E. crassipes</i> shoot	Rape straw	Corn stalk
C	51.85	67.07	58.37	54.30	56.92	55.88	17.79	15.37	17.99
O	43.92	29.36	40.79	44.88	41.85	43.61	61.85	65.63	60.84
Si	—	—	0.20	—	—	0.21	0.25	—	1.07
Na	0.52	0.44	—	0.33	0.11	—	0.27	0.61	1.16
Mg	0.30	0.13	—	0.23	0.22	0.16	15.69	13.65	12.72
P	0.38	—	—	—	—	—	—	—	—
S	—	0.34	0.15	—	0.08	—	4.09	4.64	6.21
Cl	1.26	0.80	—	—	—	—	—	—	—
K	1.53	1.07	0.12	—	—	—	—	—	—
Ca	0.24	0.79	0.38	0.27	0.83	0.13	0.07	0.10	—

— means no detection of the element.

Table 2

The sulphur and magnesium contents of cellulose xanthogenates prepared from different raw plant straws

Cellulose xanthogenate	<i>E. crassipes</i> shoot	Rape straw	Corn stalk
Sulfur content (%)	4.99±0.05	4.93±0.06	4.15±0.11
-OCS ₂ ⁻ (cmol/kg)	77.7±1.6	76.8±2.0	64.6±2.1
Mg content (cmol/kg)	73.0±1.9	31.0±1.3	49.9±1.4
The ratio of -OCS ₂ ⁻ to Mg ²⁺	1.08	2.48	1.28