Radiation synthesis and heavy metal ions removal of cellulose microsphere based adsorbent

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Abstract. A novel cellulose-based adsorbent was successfully prepared by radiation induced grafting of glycidyl methacrylate onto the surface of cellulose microspheres, followed by epoxy ring-opening reaction to introduce iminodiacetic acid disodium (IDA). The characterization of the obtained adsorbent was investigated in detail. To evaluate the adsorption performance of the novel adsorbent in comparison with commercial adsorbent D850, batch and column mode adsorption experiments against Cu(II) and Ni(II) were conducted. The equilibrium time for Cu(II) and Ni(II) were 20 and 30 min, which is much shorter than that of commercial adsorbent. The adsorption capacity of the adsorbent for Cu(II) and Ni(II) reached 96.90 and 111.11 mg/g, respectively. Applicability of the novel adsorbent on the actual wastewater generated from electroplating plants was also investigated. It was found that the novel adsorbent possessed a higher adsorption/desorption velocity and broadly similar adsorption capacity with the commercial adsorbent, signifying the effective adsorption performance of the developed grafted adsorbent.

1. Introduction
Metals with relatively atomic weights and high densities are generally defined as Heavy metals. These metals exposed to human and ecosystem will cause health issues in plants, animals and people. Hence, it is an environmental problem and worldwide concern [1]. In electroplating industries, large amount of wastewater are released from rinsed water of the electroplated process which equivalent to 20% of the chemicals [2]. Cu and Ni are widely found in the electroplating wastewater which exceeds the industrial effluent discharge limits stated by the Department of Environment. Then the heavy metal ions need to remove before being discharged [3].

Various technologies have been employed for removing heavy metals from polluted water bodies [1]. Adsorption is often used for the removal of low level heavy metal ions because of its efficiency, easy operation and the possibility of regeneration [4,5]. For the commercial adsorbents, the functional groups are mainly distributed in the matrix which makes the equilibrium time big longer due to ion diffusion. Directly introducing the functional groups onto the surface of a matrix is a method to solve the problem, which can increase the adsorption and desorption velocity [6].

Radiation-induced graft polymerization (RIGP) is often used to introduce desirable functional
group onto the polymer surface. This method has been widely employed to prepare various of adsorbents due to its advantages such as no initiator, high efficiency and no effect of substrate shape [7]. Cellulose is probably the most abundant organic compound on Earth. It has been widely studied for substrate due to its biodegradable hydrophilicity, good mechanical and thermal properties [8]. In this paper, a microcrystalline cellulose microspheres (MCC) based adsorbent was synthesized by RIGP for Cu (II) and Ni (II) removal. The adsorption performance of cellulose-based adsorbent towards Cu (II) and Ni (II) in electroplating wastewater was investigated. For comparison, the commercial adsorbent with same functional group was used for heavy metal ions removal in same condition.

2. Experimental

2.1. Materials
MCC microsphere (100-120 um) were supplied by Asahi Kasei Chemicals Corporation (Japan). Glycidyl methacrylate (GMA) and Tween 20 were bought from sinopharm chemical reagent Co., Ltd. Iminodiacetic acid disodium (IDA) was bought from Aladdin Chemical Co., Ltd. All reagents were analytical-grade chemicals and directly used as received. The commercial adsorbent D850 was supplied by Zhejiang Zhengguang Industrial Co., Ltd of China and washed by deionized water before used.

2.2. Preparation
Scheme 1 shows the preparation route of the cellulose based adsorbent. MCC microspheres were irradiated at dose of 30 kGy in the similar condition with that in [6]. After irradiation, the microsphere samples were put into the mixture solution of GMA and Tween 20 to react at 50°C for 2 h. Subsequently, the grafted microspheres (MCC-GMA) were separated and washed with deionized water, then dried at 50°C. The Grafting ratio (GR) calculated by mass increase of MCC microsphere before and after grafting, respectively. The MCC-GMA with GR of 230% was immersed into IDA solution for epoxy ring-open reaction. After opening-ring reaction, the resulted cellulose based adsorbent was obtained after washed and dried to a constant weight. The conversion rate calculated by mass increase was 42%.

2.3. Characterization
The FTIR spectra (FTIR-650 spectrometer) were performed in the transmittance mode with wavenumber ranging of 4000-400 cm⁻¹. The surface morphologies of the sample were observed by scanning electron microscope (Tescan, Vega3, Czech) at the accelerate voltage 10 kV.

2.4. Measurement of ion concentration
Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICP-AES-7510, SHIMADZU, Japan) was used to test the concentration of heavy metal ions. The concentration of anion ions were determined using Ion chromatograph (MagIC Net 883, Metrohm, Switzerland).

2.5. Batch adsorption experiments
0.1 g adsorbent was added in 100 mL, 10 mg/L ion aqueous solution with a 250 mL beaker. The
beaker was shaken by a shaker at 25°C. The adsorbed amount ($Q_t$) of total concentration of Cu (II) and Ni (II) ions adsorbed onto the adsorbents was calculated by equation (1):

$$Q_t = (C_0 - C_t) \times \frac{V}{m}$$

(1)

Where $C_0$ and $C_t$ were the concentration of Cu (II) or Ni (II) ions before and after adsorption, $V$ was the solution volume and $m$ was the mass of the adsorbent.

In the adsorption kinetics experiment, the pH was adjusted to 4. In the adsorption isotherms experiment, $C_0$ was ranged from 50 to 300 mg/L.

2.6. Column-mode adsorption

The column experiment was carried out with a volume 10 mL (7 cm×φ1.55 cm). The metal ion solution (10 mg/L) was pumped into the column at the flow rate 5 ml/min which corresponding to space velocity (SV) 30 h$^{-1}$. The bed volume (BV) was calculated as follows:

$$BV = \frac{V \times t}{NV}$$

(2)

where $V$ was the volume of the feed solution and $v$ was the flow rate.

After saturated adsorption, 1 mol/L HCl was used to regenerate the adsorbents at SV 10 h$^{-1}$.

3. Results and discussion

The shapes of the MCC, MCC-GMA and the as prepared cellulose adsorbent after IDA ring-open reaction (MGIDA) were all have a microsphere structure with a diameter of 100-500 um. The comparison of the physical properties between MGIDA and the commercial D850 were list in table 1.

| Adsorbent  | Matrix            | Functional group                  | color     | diameter (um) | water content (%) |
|------------|-------------------|-----------------------------------|-----------|---------------|------------------|
| MGIDA      | Cellulose         | Iminodiacetic acid disodium       | White     | 0.3-0.5       | (70-80)%         |
| D850       | Cross-linked polystyrene-divinyl benzene | Iminodiacetic acid disodium       | White     | 0.45-0.85     | (48-58)%         |

3.1. Characterization

The sample of MCC, MCC-GMA and MGIDA were characterized by FTIR spectroscopy shown in figure 1(a). As for cellulose, the O-H bending vibration frequencies at 1640 cm$^{-1}$ was attributed to micro amount of water. The absorption peak at 1060 cm$^{-1}$ was ascribed to the C-O bond stretching vibration in cellulose. Compared with cellulose, the adsorption bands of epoxide group at 840 cm$^{-1}$ and 907 cm$^{-1}$ and carbonyl group at 1730 cm$^{-1}$ appeared, which verified the grafting of GMA [9]. After ring-open reaction, a new peak appeared at 1598 cm$^{-1}$ assigned to N-H group, indicating the successful introduction of IDA. Moreover, the intensity of epoxy groups characteristic peaks of epoxy groups almost disappeared on account of the reaction between GMA and IDA.
Figure 1. IR (a) and TG (b) analysis of MCC, MCC-GMA, MGIDA and MGIDA-Cu samples. Figure 1(b) shows the TG curves of MCC, MCC-GMA and MGIDA. The thermal degradation curve of MCC and MCC-GMA is a one-stage process with decomposition temperature at 350°C. In contrast, the MGIDA curve shows two-step weight loss: first stage below 150°C attributed to the loss of water, and second stage in range of 250 to 500°C. In one word, these samples have good thermal stability.

Figure 2 shows the SEM morphologies of MCC (a), MCC-GMA (b), MGIDA (c) and MGIDA-Cu (d). It is found that there are smooth on the surface of MCC substrate. The surface became rough and their diameter became large due to GMA grafting and further ring-opening reaction.

3.2. Batch experiments

3.2.1. pH effect. Figure 3(a) shows the dependence of pH on Cu and Ni adsorption. At pH between 3 and 4, the maximum adsorption capacity was reached for the two adsorbents towards both Cu and Ni ions. So the origin Cu and Ni ion concentration at pH 4 was used for further batch and column adsorption test.

Figure 3. Effect of pH (a) and contact time (b) on Cu and Ni adsorption on MGIDA and D850 adsorbents: ion concentration 10 mg/L.

3.2.2. Adsorption kinetics. Figure 3(b) shows the contact time on Cu and Ni removal onto MGIDA and D850. The adsorbed amounts for the two adsorbent increased with increasing contact time. As for MGIDA, the equilibrium time of MGIDA for Cu(II) and Ni(II) were 20 and 30 mins, respectively. But D850 takes 120 and 120 mins to reach the equilibrium, which is a little big longer than that of MGIDA. This is because the functional groups are mainly distributed inside D850 and on the surface of MGIDA.

The pseudo-first-order and pseudo-second-order kinetic equations expressed by equations (3) and (4), respectively. The initial adsorption rate $h_0$ (mg/g/min) ($t \rightarrow 0$) can be calculated by equation (5).
In(q_e - q_t) = ln(q_e) - k_1 t \tag{3}
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}

h_0 = k_2 Q_e^2 \tag{5}

where, q_e (mg/g) and q_t (mg/g) were the amounts of Cu (II) and Ni (II) adsorbed per gram adsorbent at time t (min) and at equilibrium, respectively. k_1 and k_2 referred to rate constant for the pseudo-first-order and the pseudo-second-order model, respectively [10]. The calculated values are summarized in the table 2. The plots were well obeyed pseudo-second-order model by higher correlation coefficient (R^2), suggesting that there were chemical adsorptions process. The initial adsorption rate h_0 of MGIDA adsorbent for Cu (II) and Ni (II) were higher than that of D850 adsorbent, which also shows that MGIDA has higher adsorption velocity.

| Model                                      | Parameters        | MGIDA-Cu | MGIDA-Ni | D850-Cu | D850-Ni |
|--------------------------------------------|-------------------|----------|----------|---------|---------|
| pseudo-first-order kinetics                | k_1 (h^{-1})      | 0.1228   | 0.1832   | 0.0295  | 0.0523  |
|                                           | q_e (mg/g)        | 9.7077   | 9.8023   | 9.2789  | 9.7193  |
|                                           | R^2               | 0.9833   | 0.9841   | 0.9898  | 0.9763  |
| pseudo-second-order kinetics               | k_2 (g/(mg·min)) | 0.0242   | 0.0348   | 0.0022  | 0.0062  |
|                                           | q_e (mg/g)        | 10.0604  | 10.3306  | 12.1655 | 11.2360 |
|                                           | R^2               | 0.9958   | 0.9990   | 0.9903  | 0.9957  |
|                                           | h_0               | 2.4493   | 3.7106   | 0.3182  | 0.7791  |

Table 2. Parameters obtained from pseudo-first-order and pseudo-second-order kinetic of the MGIDA and D850.

Figure 4. Equilibrium studies of Cu and Ni ions adsorption; the inlet figure show the corresponding Langmuir model.
3.2.3. Adsorption isotherm. The isotherm studies are helpful to identify the distribution of Cu (II) and Ni (II) between the aqueous solution and the adsorbent. The isotherm curve for the adsorption of Cu (II) and Ni (II) were shown in figures 4(a)-4(d). Langmuir isotherm model and Freundlich isotherm model were employed to analysis the isotherm data.

The Langmuir isotherm equation was expressed by equation (6).

\[
\frac{C_e}{q_e} = \frac{C_n}{q_m} + \frac{1}{K_L q_m}
\]  

(6)

where \(C_e\) is the equilibrium concentration of metal ions (mg/L) in the solution after adsorption, \(q_e\) is the amount of metal ions per unit mass of adsorbent after adsorption (mg/g), \(q_m\) is the theoretical maximum adsorption capacity (mg/g) and \(K_L\) is the Langmuir constant (L/g). \(q_m\) and \(K_L\) were calculated from the slope and the intercept of the linear plot of \(C_e/q_e\) versus \(C_e\), as shown in the inset figure and listed in the table 3.

The equilibrium parameter \(R_L\) of Langmuir model for metal ions uptake were calculated from equation (7):

\[
R_L = 1/(1 + K_L C_0)
\]  

(7)

where \(K_L\) is a Langmuir constant and \(C_0\) is the initial concentration. The calculated \(R_L\) in this study are more than zero and less than unity (0 < \(R_L\) < 1), which reflects the favorable adsorption of Cu(II) and Ni (II) by the as prepared MGIDA adsorbent and the commercial adsorbent [11].

The Freundlich isotherm was applied to describe the adsorption for heterogeneous surface (multilayer adsorption). The Freundlich isotherm was expressed by equation (8) [12].

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]  

(8)

where, \(K_F\) and \(n\) are the Freundlich constant identified with the adsorption amounts and the adsorption intensity. Values of \(K_F\) and \(n\) were calculated from the slope and the intercept of the linear plot of \(\ln q_e\) versus \(\ln C_e\), and the calculated values are listed in the table 3. The degree of non-linearity between the dissolved ions concentrations and the adsorption was tended to from the heterogeneity factor \((1/n)\). In this adsorption process, \(n\) is greater than 1, which means that the uptake of the two adsorbent to Cu (II) and Ni (II) was favorableadsorption [12]. And the MGIDA adsorbent was especially favorable for Cu (II) than Ni (II) with the \(n\) value 108.8.

Table 3. Langmuir and Freundlich isotherm parameters and correlation coefficients for the adsorption of Cu (II) and Ni (II).

| Adsorbent | MGIDA-Cu | MGIDA-Ni | D850-Cu | D850-Ni |
|-----------|----------|----------|---------|---------|
| Langmuir  |          |          |         |         |
| \(q_m\) (mg/g) | 96.90    | 111.11   | 114.9   | 108.9   |
| \(K_L\)   | 4.9089   | 0.4556   | 0.2725  | 0.1850  |
| \(R^2\)   | 0.9999   | 0.9997   | 0.9985  | 0.99941 |
| Freundlich |          |          |         |         |
| \(K_F\) (mg·L\(^{-1}\)) | 92.8514  | 60.5573  | 64.7802 | 53.6778 |
| \(n\)     | 108.8139 | 9.7324   | 9.34579 | 7.5329  |
| \(R^2\)   | 0.9279   | 0.9778   | 0.9933  | 9.9251  |

3.3. Column test
The column test of MGIDA and D850 for individual Cu (II) than Ni (II) ions removal was performed separately. Figure 5(a) shows the breakthrough curves with Cu (II) than Ni (II) concentration of 10 mg/L at SV 30 h\(^{-1}\). All the curves show the similar characterization. At the beginning, there is almost no metal ion detected in the leakaged solution. The breakthrough of Cu (II) appeared at 2300 BV and
1500 BV for MGIDA and D850, respectively. The breakthrough of Ni (II) appeared at 1500 BV and 1000 BV for MGIDA and D850, respectively. After saturated adsorption, the adsorbent was regenerated by backwashing with HCl. As shown in the elution curve in figure 5(b), it needs 30 BV for completely elution of the Cu loaded on MGIDA adsorbent, but needs 40 BV for Cu loaded on D850. It needs 60 BV for completely elution of the Ni loaded on MGIDA adsorbent, but it is 100 BV for Ni loaded on D850. So the Cu (II) than Ni (II) adsorption of desorption efficiency are higher than commercial D850 adsorbent.

**Figure 5.** Breakthrough curve (a) and elution curve (b) of MGIDA and D850 adsorbents for Cu (II) and Ni (II) ions.

### 3.4. Actual electroplating wastewater treatment

Electroplating wastewater obtained from Sanyou electroplate plant (Sanyou Chemical Industries co., Ltd, Zhejiang Province) with pH 1.4 was filtrated and its pH was adjusted to 4 by NaOH, then filtration was done again to remove Fe (III). Table 4 shows the ion concentration of the solution before and after filtration to remove Fe (III). It can be seen that the two adsorbents cannot absorb the Ca and Ni with the co-existence ions of Ca and Fe at pH 1.4. The adsorbent have good adsorption to Fe (III) and Cu (II), and the MGIDA has better efficiency for Fe (III) and Cu (II) than D850. The concentration of Fe (III) decreased to a low value with pH 4 after filtration. MGIDA and D850 have higher adsorption efficiency to Cu and Ni ions at pH 4, which order is Cu > Ni. Figure A shows the anion ion concentration of the wastewater before and after adsorption for the wastewater with pH 1.4 and pH 4. It is noted that no obviously change before and after adsorption.

**Table 4.** The cation ion concentration before and after adsorption for the wastewater with pH 1.4 and pH 4.

|          | Ca      | Fe       | Ni       | Cu       |
|----------|---------|----------|----------|----------|
| pH=1.4   | Initial C₀ | 130.334  | 106.9845 | 54.00084 | 33.51061 |
|          | MGIDA adsorption | 126.730  | 57.30871 | 53.28075 | 9.974484 |
|          | D850 adsorption  | 130.118  | 72.70021 | 54.10571 | 23.02882 |
| pH= 4    | Initial C₀ | 125.489  | 15.89087 | 49.62494 | 29.64639 |
|          | MGIDA adsorption | 123.678  | 12.43454 | 23.03067 | 1.120146 |
|          | D850 adsorption  | 122.141  | 13.28408 | 26.31803 | 3.832458 |

The electroplating wastewater after filtration with pH 4 was through the adsorption column with the volume of 10 mL with SV 30 (flow rate: 300 mL/h). The ion concentration of Cu (II) and Ni (II) are 29.6 and 49.6 mg/L, respectively. As shown in figure 6(a) for the MGIDA adsorbent, Ni (II) curve reached breakthrough point quickly, Cu (II) curve reached breakthrough point at 400 BV. As for the
D850 adsorbent, Cu (II) and Ni (II) reached breakthrough point quickly in the beginning and reached equilibrium slowly. As shown in the elution curve in figure 6(b), the bed volumes were 2 and 4 BV to elute completely for the Ni (II) loaded MGIDA and D850 adsorbent, respectively. There were 5 and 8 BV to elute completely for the Cu (II) loaded MGIDA and D850 adsorbent, respectively. The results show that MGIDA adsorbent has higher desorption velocity than D850 adsorbent.

4. Conclusion
In the present study, an MGIDA adsorbent was successfully prepared by grafting GMA on cellulose using radiation induced grafting and further modification. The MGIDA had higher adsorption performance to Cu (II) and Ni (II). The Cu (II) and Ni (II) adsorption was well obeyed pseudo-second-order model. The MGIDA has higher adsorption velocity than commercial adsorbent D850. The adsorption capacity of Cu (II) reached 96.90 and 114.9 mg/g for the MGIDA and D850, respectively. The adsorption capacity for Ni (II) reached 111.11 and 108.90 mg/g for MGIDA and D850, respectively. Dynamic experiment for individual Cu (II) and Ni (II) revealed that Cu (II) and Ni (II) could be efficiently adsorbed by the adsorbent and fully desorbed using 1 mol/L HCl. The breakthrough for electroplating wastewater showed that all the adsorbents have higher adsorption capacity for Cu (II) than that for Ni (II). The novel adsorbent possessed a higher adsorption/desorption velocity and broadly similar adsorption capacity compared with commercial adsorbent D850, signifying the very effective adsorption performance of the developed grafted adsorbent.

Appendices

Figure A. The anion ion concentration before and after adsorption for the wastewater at pH 1.4 (a) and pH 4 (b).
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