Supporting Information

Aniline Grafted Chitosan: Adsorption and Fluorescence Behavior Study toward Cu(II) Ions

Authors: Bahareh Vafakish and Lee D. Wilson*

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan, S7N 5C9, Canada

*Correspondence: lee.wilson@usask.ca, Tel.: +1-306-966-2961; Fax: +1-306-966-4730

Fig S1: Proposed chemical structure of CS-Ac-An. R is the acetyl group.







 Table S1: Elemental analysis results by the EDX technique

Element	Series	[wt.%]
Carbon	K-series	59.24
Oxygen	K-series	8.154
Sulfur	K-series	4.596
Copper	K-series	17.75
Nitrogen	K-series	10.25

Table S2: Curve fitting results of XPS analysis for C1s, N1s, O1s and Cu 2p before and after copper adsorption

Peak	Suggested attribution	BE (eV) before adsorption	BE (eV) after adsorption
C 1s	C=C	283.24	283.31
	C-C	284.80	284.83
	C-O, C-N	286.29	286.38
	Cu(II)-π system	-	287.29
N 1 <i>s</i>	-NH2	396.82	396.85
	-NH3+	397.41	397.42
	-N-Cu(II)	-	399.05
O 1 <i>s</i>	O-C	529.81	529.87
	О-Н	530.48	530.50
Cu 2 <i>p</i>	2 <i>p</i> _{3/2}	-	931.02
	Satellite	-	940.04
	2 <i>p</i> 1/2	-	951.02
	Satellite	-	960.04

Figure S3: Proposed structure of adsorbed copper with η =6, sandwiched between two arene ring



Table S3: Langmuir Fitting Parameters for Cu (II) uptake with CS and CS-Ac-An

CS				CS-Ac-A	N n
Q _m (mg g ⁻¹)	K _L (L g ⁻¹)	Adj-R ²	Q _m (mg g ⁻¹)	$K_L (L g^{-1})$	Adj-R ²
5.7	9.1	0.746	138.1	5.8	0.959

Adsorbent	Adsorption capacity (mg g ⁻¹)	Reference
Polystyrene-supported chitosan	99.8	54
Chitosan in prawn shell	17.1	20
Chitosan-coated sand	8.18	51
Magnetic carboxymethyl chitosan nanoparticles	232	55
Tripolyphosphate crosslinked chitosan beads	15.6	44
Chitosan-derived Schiff bases	32.5	22
Chitosan	4.7	52
Formaldehyde cross-linked modified chitosan- thioglyceraldehyde Schiff's base	76	53
Chitosan-coated mesoporous microspheres of calcium silicate hydrate	425	50
Porous poly(L-lactic acid) (PLLA)-Chitosan	112	56
Aniline grafted chitosan	106.5	This study

Table S4: Comparison of the adsorption capacity (Q_m) of different adsorbents for Cu(II)

Fig S4: (a) Effect of temperature on Cu(II) adsorption from 288 to 308K at ambient pH and temperature. Cu(II) concentration: 100 ppm, contact time: 24 h,(b) Plot of Ln K_e versus 1/T for the determination of Δ H° and Δ S° using the vant' Hoff equation (eq 5)



 Table S5:
 Thermodynamic Parameters

Temp (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)	R ²
288	-1.07	19.6	72.2	0.994
298	-1.88			
308	-2.52			

Table S6: PFO and PSO Fitting Parameters

Pseudo First Order (PFO)			Pse	udo Second Order	(PSO)
$Q_t(mg g^{-1})$	$k_1(\min^{-1})$	\mathbb{R}^2	$Q_t (mg g^{-1})$	$k_2(g \text{ mol}^{-1} \min^{-1})$	R ²
28.3	8.56×10^{-3}	0.973	35.3	3.89×10^{-3}	0.982

Table S7: Rate (k_i) values with the unit of (mg/g.min^{1/2})

20 ppm		50 ppm		100 ppm	
k_1	<i>k</i> ₂	k_1	<i>k</i> ₂	k_l	k_2
1.71	0.303	0.450	0.489	0.142	0.714

Fig S5: Regeneration cycles for CS-Ac-An loaded with Cu(II). Adsorption cycle condition: copper ion concentration: 100 ppm, contact time: 24 h, adsorbent dosage: 5 mg. Desorption cycle condition: EDTA solution: 0.01 M, contact time 3 h.



Figure S6: UV-Vis Spectra of CS-Ac-An $(1g L^{-1})$ in 2% acetic acid from 250-550 nm in the presence of various concentration of Cu(II) ion



Figure S7: Fluorescence emission spectra of CS-Ac-An at different excitation wavelength

