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Adsorption of Cu(II) and Ni(II) by pelletized biopolymer

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Abstract

Chitosan and Ca-alginate, derivatives of biopolymer, were separately prepared from crab chitin and algin in pellet form for adsorption of Cu(II) and Ni(II) from aqueous solutions. The capability of these biopolymers was also investigated to remove copper and nickel from aqueous solutions in an immobilization system, along with a comparison made of these biopolymers with other adsorbents. Additionally, the feasibility of alginate/chitosan in pellets to remove nickel ion and nickel cyanide complex from polluted water was investigated. Stabilizing chitosan physically in an alginate support medium was deemed possible, by means of which both free metal and metal cyanide ions could be removed from aqueous solutions in an engineering system. However, the crosslinking reaction during immobilization would result in blocking of some adsorption sites.

Keywords: Chitosan; Cu(II); Adsorption; Biopolymer; Immobilization

1. Introduction

Heavy metals at low concentrations are difficult to remove. Chemical precipitation, reverse osmosis, and other available methods become inefficient when heavy metal contaminants are present at trace concentrations in a large volume of solution. Adsorption is one of few alternatives available in such a situation. The use of adsorbents, e.g., activated carbon, low cost industrial products, and microbial materials, has received extensive attention [1]. All of these technologies have their inherent advantages and limitations. For instance, activated carbon still requires complexing agents to improve performance in removing inorganic matters. Ion-exchange resins are effective but expensive. Among various adsorbents, biosorbents are attracting an increasing amount of interest for its capability to prepare polymers as effective scavengers of heavy metals [2]. This process is based on the binding of metal ions by the

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biopolymer to various functional groups. Chelating groups contributed by the natural biopolymers include amino and hydroxyl groups in chitosan [3] and the carboxyl group in alginate [4]. Chitosan prepared from crab chitin has been widely studied to adsorb heavy metal (Hg, Pb, Zn, Cd, Cr) [5–7], but not widely applied in wastewater treatment. In this work, two biopolymers in pellets, i.e., chitosan/alginate and calcium-alginate, are developed to remove dissolved metal ions and metal cyanide complexes from aqueous solutions. The primary objectives of this work involve evaluating the capability of these biopolymers to remove copper and nickel from aqueous solutions in an immobilization system, as well as making a comparison with commercial ion-exchange resin and other adsorbents. Additionally, an investigation is undertaken regarding the effect of deacetylation, pH, and particle size on the metal binding by powdered chitosan and the feasibility of pelletized alginate/chitosan to remove nickel ion and nickel cyanide complex from aqueous solutions.

2. Experimental

2.1. Materials

Chitin isolated from a crab shell was crushed to a powder form. Chitosan was prepared by deacetylating chitin with NaOH (45%, w/w) at 100 °C for three treatment periods (20, 120, and 360 min). Following that, the product was cleaned several times by deionized water until the pH value of the chitosan suspension reached 7, and dried at 80 °C for 48 h. The optimal duration of deacetylation was 20 min based on tests of Cu(II) adsorption. The sheet of deacetylated chitin was then crushed to powdered form sieved through various meshes to obtain the powder of the required particle size.

Calcium-alginate beads were prepared from sodium alginate (2% w/w, Hayashi Ltd.) which was dropped into $CaCl_2$ solution (4%) through the tip of a transfer pipette, and hardened in $CaCl_2$ solution for 12 h. The mean diameter of the beads was 2.05 mm.

The chitosan beads were stable in alkaline and neutral solutions, but dissolved readily in acid solution. In order to make their use feasible in an engineering system, the chitosan powder was immobilized with Ca alginate. Immobilization was performed by external gelatin as follows: chitosan (1 g, 140/200 mesh) was mixed into the alginate solution (2% w/v) with a magnetic stirrer. The alginate/chitosan suspension was dropped into a solution of $CaCl_2$ (4%) in which the alginate gelled as pellets, and hardened in $CaCl_2$ solution for 12 h. The mean diameter of pellet was 3.10 mm.

Following preparation, these three adsorbents were further purified through washing with distilled water several times to remove impurities from the surface, and then stored at 4 °C until use.

2.2. Metal adsorption experiments

Equilibrium isotherms for adsorption of Cu(II) on the biopolymer were measured in a batch mode. Initial Cu(II) concentrations in the range 5×10^{-6}–10^{-4} M, i.e. all less than the solubility limit set by the solution of pH 5, were used to screen the binding capacity of chitosan powder, Ca-alginate bead, and alginate–chitosan (AL-CHI) bead. Chitosan powders were divided into 40/80 meshes, 100/140 meshes, and 140/200 meshes, which corresponded to 0.177–0.420, 0.105–0.149, and 0.074–0.105 mm, respectively. The biopolymer (5 mg) on a dry weight basis was mixed with the Cu(II) solution (100 ml) in a reciprocating shaker at 150 rpm for 24 h at 25 °C. To determine the effect of pH on adsorption, the pH of the Ni(II) solution was adjusted with one unit increment in pH within the range of 2–10, and the initial concentration of free metal and metal complex was 5×10^{-5} *M*. Biopolymer (0.02 g/100 ml) on a dry weight basis was applied in each batch. The ionic strength in those experiments was controlled with $NaClO_4$. After 24 h to attain equilibrium, the biopolymer was removed by filtration through a membrane filter (0.45 μm, Millipore), and filtrates were analyzed for residual metal concentration with an atomic absorption spectrophotometer (Hitachi Z-8100).

Kinetic tests on interactions between metal ions and pelletized biopolymer were performed with a well-mixed reactor (1 l). To facilitate comparison of results, all experiments were conducted at a pH value close to 5 as possible. The initial metal concentration was 5×10^{-5} *M* and the ionic strength was 10^{-2} *M* added as $NaClO_4$. Biopolymer (0.1 g on a dry weight basis) as pellets was added to a sample (500 ml) to initiate adsorption. A sample (1.5 ml) was withdrawn periodically and filtered through a membrane filter (0.45 μm), and filtrates were analysed for residual metal concentration with atomic absorption spectrophotometer. The sampling and filtering by hand for each time interval required 4 s of retention period. Therefore, the exact time scale should be $t = 2 \pm s$. The total volume of samples withdrawn from the batch reactor was about 19.5 ml for each run, i.e., 3.9% of the sample was lost when the kinetic experiment was completed.

3. Results and discussion

3.1. Metal selectivity

A series of experiments have been performed to apprehend the capabilities of chitosan and Ca-alginate in removing six metal ions. The results shown in Table 1 indicate that chitosan exhibits a highest binding capacity for Cu(II) and Hg(II), which is consistent with Coughlin's and Mitani Tomuyo's work [8]. This table also reveals that Ca^{2+} has been released from chitosan during metals adsorption. With examples of Cu(II) and Ni(II), however, the amounts of Ca^{2+} release are 538 μmol/g and 750 mol/g corresponding to 265 and 41 μmol/g of amounts of Cu(II) and Ni(II) adsorption, respectively. This fact implies that Ca^{2+} release is not a feature of metal adsorption. Hence, Ca ions released from chitosan may exchange with H^+ ions in the solution [9]. Table 2 indicates that Ca-alginate is comparatively more effective in the removal of Hg(II), Cu(II), and Pb(II) than Ni(II) and Cd(II), i.e., similar to the result reported by Seki [10]. These results also indicate that Ca-alginate fails to adsorb Ca^{2+} ions but it releases more Ca^{2+} ions during metal(II)

Table 1
The capabilities of chitosan in adsorbing various metal ions

Metal	Co (mol/l)	Q (μmol/g)	Release of Ca (μmol/g)
Cu	5.47×10^{-5}	265	538
Cd	5.03×10^{-5}	76	800
Ni	4.96×10^{-5}	41	750
Pb	4.93×10^{-5}	79	638
Hg	5.22×10^{-5}	257	850
Ca	4.92×10^{-5}	−556[a]	556

Experimental conditions
Chitosan: Alkaline treatment time = 20 min, particle size = 140/200 mesh; dosage = 0.02 g dry wt./100 ml.
Ionic strength: 0.01 *M* $NaClO_4$.
Final pH: 5.
[a] Desorption.

adsorption. This knowledge suggests that the mechanism of Ca-alginate interacting with metals is different from that of chitosan. Metal ions have chelated with the carboxyl or hydroxyl groups in the Ca-alginate by replacing Ca ions as well as with the amino and hydroxyl groups in the chitosan. In the following experiment, Cu(II) is selected as a model metal to evaluate the feasibility of pelletized biopolymer for metal removal.

3.2. Deacetylation effect

Chitosan was prepared by deacetylating chitin with NaOH (45%, w/w) at 100 °C. The degree of deacetylation has been quantified by Toei and Kohara [11] and degree of deacetylation increased with the treatment time. Deacetylation can remove

Table 2
The capabilities of Ca-alginate in adsorbing various metal ions

Metal	Co (mol/l)	Q (μmol/g)	Release of Ca (μmol/g)
Cu	4.98×10^{-5}	248	432
Cd	5.10×10^{-5}	138	317
Ni	5.17×10^{-5}	179	308
Pb	5.04×10^{-5}	247	455
Hg	4.95×10^{-5}	247	461
Ca	4.98×10^{-5}	−275[a]	275

Experimental conditions
Ca-alginate: Particle size = 2.05 mm; dosage = 0.02 g dry wt./100 ml.
Ionic strength: 0.01 *M* $NaClO_4$.
Final pH: 5.
[a] Desorption.

the acetyl groups from the structure and leave bare amino groups ($-NH_2$) on the structure. These free amine groups are then available for the binding of heavy metal. The results of Cu(II) and Cd(II) adsorption corresponding to the degree of deacetylation are summarized in Table 3. This table indicates that the longer treatment time is in favor with Cd(II) adsorption but not with Cu(II). Functional groups containing oxygen possess a higher Cu(II) affinity than those containing nitrogen. Inversely, functional groups containing nitrogen possess a higher Cd(II) affinity [12]. Therefore, the increase of N-groups in the chitosan having underwent the deacetylation results in the decrease of Cu(II) adsorption. Moreover, the time for alkali treatment is determined to be 20 min in light of economic and engineering considerations.

3.3. *Effect of particle size*

According to the preliminary test, using a N_2-BET meter failed to measure surface area of powder chitosan because the chitosan structure was destroyed due to high temperature of degassing operation in the BET measurement. Instead, the chitosan powder was sieved into three groups with different size ranges, which provides an alternative way to compare the adsorption capacity. Equilibrium isotherms of Cu(II)–chitosan system with particles of these sizes are presented in Fig. 1. Also shown in this figure, are the experimental data fitted to the Langmuir equation by means of a nonlinear regression (NLR) program in an iterative calculation to obtain the maximum adsorption capacities.

Experimental results show that the number of adsorption sites per unit mass increases with decreasing particle size, which is consistent with Coughlin's work. Chitosan can be considered as a microporous material. When chitosan is at ambient temperature, the thermal motion of chain segments is restricted [13]. After chitosan is crushed into a smaller particle, adsorption sites on the chitosan chain are increasingly opened and available to bind metals.

Table 3
The adsorption capabilities of Cu(II) and Cd(II) corresponding to the alkaline treatment time

Treatment time (min)	Adsorption capabilities (μmol/g)	
	Cu	Cd
0	46	17
20	265	76
120	262	79
360	258	84

Experimental conditions
Initial conc: Cu(II), 5.41×10^{-5}; Cd(II), 5.18×10^{-5}.
Chitosan: Particle size = 140/200 mesh; dosage = 0.02 g dry wt./100 ml.
Ionic strength: 0.01 *M* $NaClO_4$.
Final pH: 5.

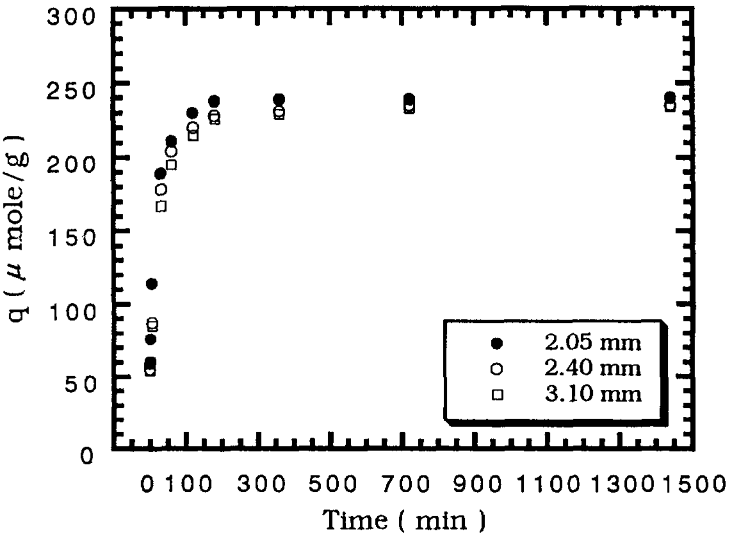

Fig. 1. The effect of particle size on adsorption isotherm of Cu(II) binding onto chitosan powder with 0.005 g-dry weight/100 ml at $pH_f = 5.0$.

3.4. Adsorption kinetics

The rates of Cu(II) adsorption by different sizes of Ca-alginate beads and alginate–chitosan beads of varied sizes have been determined in this work to observe the effect of particle size on the adsorption rate. Batch experiments show that adsorption, including film diffusion, pore diffusion, and chemical binding, requires one day to attain equilibrium (Fig. 2). Metal uptake by pellets may be expected to fol-

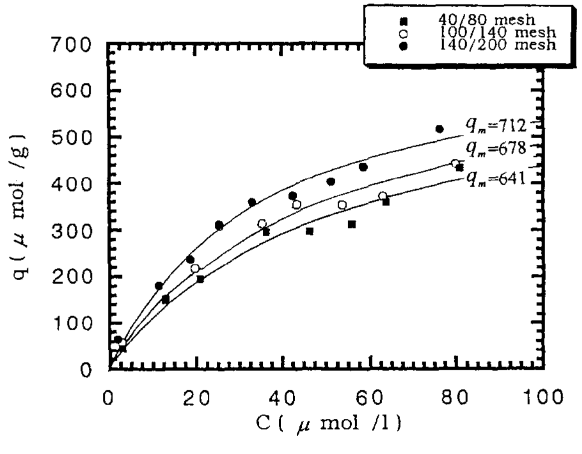

Fig. 2. The comparison of the rate of Cu(II) adsorption with different sizes of Ca-alginate beads at $pH_f = 5.0$ and $I = 0.01$ M $NaClO_4$.

Table 4
Overall diffusion coefficient, k_a, and r^2 obtained from the analysis of the parabolic diffusion law for Ca-alginate and AL-CH bead

Adsorbent	k_a	r^2
Ca-alginate (2.05 mm)	0.0728	0.989
Ca-alginate (2.40 mm)	0.0676	0.989
Ca-alginate (3.10 mm)	0.0634	0.988
AL-CH (3.10 mm)	0.0646	0.992

low two-step kinetics. The extrapellet association (surface binding) occurs first and does so rapidly. Further metal uptake may be controlled by diffusion through the pellet pores. The rate-limiting step is diffusion inside the alginate beads [14]. The adsorption behavior has been analyzed according to the parabolic equation for diffusion:

$$\frac{q}{q^*} = k\sqrt{t} + \text{constant},$$

where q is the quantity of Cu(II) adsorbed at time t, q^* is the amount of Cu(II) adsorbed at equilibrium, and k is the overall diffusion coefficient.

Despite the initial stage of extrapellet association, the uptake of Cu(II) by the alginate beads and AL-CH beads within the intermediate stage ($C/C^* = 0.2$–0.8) correlates sufficiently with the parabolic model of diffusion. The diffusion coefficients are listed in Table 4. The results indicate that Cu(II) adsorption on alginate beads attains equilibrium in 5 h; the calculated overall diffusion coefficient k increases with decreasing size of the pellet. Alginate beads of one kind, having the same size (3.1 mm) as AL-CH beads, have a value of k similar to that of AL-CH beads. The similarity reveals that the particle size rather than the composition has a significant effect on the rate of adsorption of Cu(II).

3.5. Adsorption isotherm

A biopolymer removes heavy metals from solutions as functions of pH value and metal concentration in a manner analogous to various adsorbents. Fig. 3 illustrates the Cu(II) adsorption isotherm of three kinds of biopolymers, i.e., chitosan, alginate, and alginate–chitosan (AL-CH, line B) beads and the amount of maximum Cu(II) adsorption. This figure reveals that an affinity series following the order: alginate (999 μmol/g) > alginate–chitosan (794 μmol/g) > chitosan (712 μmol/g). The theoretic Cu(II) adsorption isotherm for a 1:1 AL-CH bead is shown as Line A, and its maximum adsorption capacity is calculated to be 856 mol/g from the mathematics average of two corresponding maximum adsorption capacity, that is (999 + 712)/2. However, the experimental result of this capacity for AL-CH bead is 794 mol/g. The immobilization of chitosan by alginate obviously results in a decrease by 62 μmol/g of the Cu(II)-binding capacity. This phenomenon implies two possibilities: (i) Positively charged amino groups on chitosan interact with negatively charged carboxyl

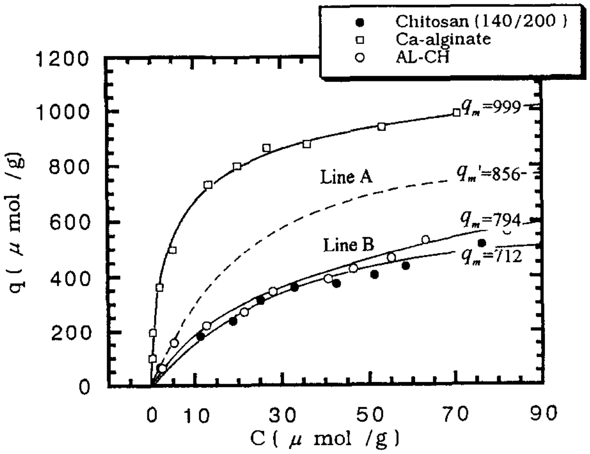

Fig. 3. Adsorption isotherm of Cu(II) binding onto chitosan powder, Ca-alginate bead, and alginate–chitosan bead.

groups of Ca-alginate during immobilization, thereby resulting in blocking of adsorption sites to decrease the number of available sites for metal binding; some adsorption sites have been blocked. (ii) Immobilization of chitosan onto alginate bead results in that the exposed surface of pellet is the lower affinity chitosan.

3.6. Comparison with other adsorbents

Cu(II) adsorption isotherms of several adsorbents at pH 5 and the same background electrolyte are shown in Fig. 4. The metal-binding capacity of a natural

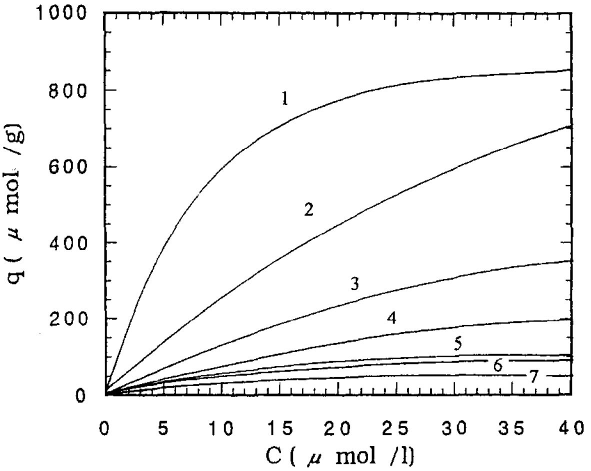

Fig. 4. The comparison of Cu(II) adsorption isotherms with various adsorbents at $pH_f = 5.0$ and $I = 0.05$ or 0.01 M $NaClO_4$. Adsorbents including (1) Ca-alginate, (2) ion exchanger, (3) chitosan, (4) fungus [15], (5) crab shell [16], (6) algae [17], and (7) activated carbon [18].

Table 5
The effect of CN^- on Ni(II) removal by chitosan and Ca-alginate

CN/Ni(II)	Ni^{+2} (% of Ni(II))	$NiCN^+$ (% of Ni(II))	$Ni(CN)_4^{-2}$ (% of Ni(II))	$NiH(CN)_4^-$ (% of Ni(II))	$NiH_2(CN)_4$ (% of Ni(II))	Adsorption by	
						Chitosan (% of Ni(II))	Ca-alginate
0	100	0	0	0	0	18	57
2	30	18	5	31	16	23	30
4	19	14	8	48	10	25	7

Experimental conditions
Initial Ni(II) conc. = $5.19*10^{-5}$ *M*.
Ionic strength = 0.01 *M* $NaClO_4$.
Final pH = 5.0.
Temperature = 25 °C.

Stability constant
$[HCN]/[H^+][CN^-] = 10^{9.2}$, $[NiH_2(CN)_4]/[Ni^{+2}][H^+]^2[CN^-]^4 = 10^{41.4}$.
$[NiCN^+]/[Ni^{+2}][CN^-] = 10^{7.7}$, $[NiH_3(CN)_4^+]/[Ni^{+2}][H^+]^3[CN^-]^4 = 10^{44.0}$.
$[Ni(CN)_4^{-2}]/[Ni^{+2}][CN^-]^4 = 10^{30.9}$, $[NiOH^+]/[Ni^{+2}][OH^-] = 10^{4.1}$.
$[NiH(CN)_4^-]/[Ni^{+2}][H^+][CN^-]^4 = 10^{36.7}$, $[Ni(OH)_2]/[Ni^{+2}][OH^-]^2 = 10^9$.
$[Ni(OH)_3^-]/[Ni^{+2}][OH^-]^3 = 10^{12}$.

biopolymer is comparable with that of other biosorbents and conventional solids such as activated carbon. Three biopolymer adsorbents, i.e., chitosan powder (d = 0.074–0.105 mm), Ca-alginate bead (d = 2.05 mm), and alginate–chitosan bead (d = 3.10 mm), are included in this figure. Ion-exchange resin (q_m = 1325 μmol/g) exhibits a higher capacity of Cu(II)-binding than Ca-alginate (q_m = 999) and other adsorbents. However, the Langmuir binding constant related to energy of Ca-alginate bead is 0.235, which is of an order higher than that of chitosan (k = 0.031) and resin (k = 0.024). We can conclude that Ca-alginate exhibits a clear advantage in Cu(II) removal as compared with other adsorbents. Extracted biopolymers from natural materials generally compare favorably with biosorbent (including crab shell, fungi, and algae) in Cu(II) binding. This fact indicates that the binding of Cu(II) by the various solids adsorbents from diluted waters follows the order: Ca-alginate > ion exchange resin (Amberlite IR-120)chitosan (0.074–0.105 mm)fungus (Aspergillus oryzae) > crab shell > algae (S. quadricauda) > activated carbon (Nuchar SA).

3.7. Cyanide effect

Wastewater from an electroplating plant generally contains free metal ions, free cyanide ions and complex ions. If cyanide is present in the form of nickel-cyanide complex, the conventional alkali-chlorine method would fail to oxidize cyanide. A combined cation/anion exchange resin can hopefully solve the problem of coexistence of Ni^{2+} and $Ni(CN)_4^{2-}$ in water. Therefore, cyanide complex ion is chosen as model complex in this study.

When cyanide ion exists in the metal solution, several reactions occur to form metal cyanide complexes. Ni(II) can form a strong complex with CN^-, predominately as either $Ni(CN)_4^{2-}$ or $NiH(CN)_4^-$. In the presence of cyanide and nickel with the molar ratio of 2:1 at pH 5, 36% of total Ni(II) presents as $Ni(CN)_4^{2-}$ and $NiH(CN)_4^-$ in the solution. However, this molar ratio increases to 4:1, in which

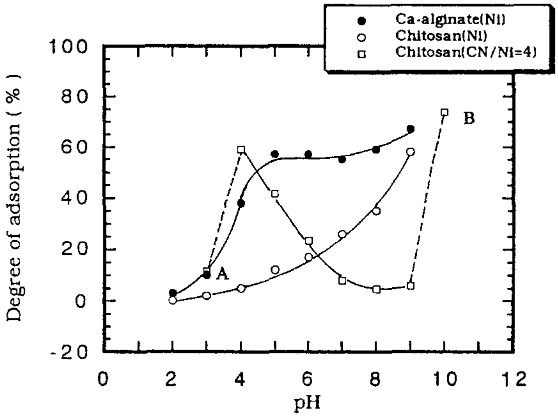

Fig. 5. The pH effect on the Ni(II) removal by chitosan and Ca-alginate. Initial concentration of Ni(II) = 4.98×10^{-5} M; solid conc. = 0.02 g-dry weight/100 ml.

56% of total Ni(II) is present in the same form. The increase of cyanide fraction in the Ni(II) solution results in the decrease of free nickel ion, thereby increasing the concentration of nickel-cyanide complex. The effect of CN^- on Ni(II) removal by chitosan and Ca-alginate is presented in Table 5. This table clearly indicates that an increase in the fraction of nickel-cyanide complex anion from 0% to 36% and from 36% to 56%, would subsequently result in a decrease in the Ni(II) binding capacity of Ca-alginate by 27% and 23%, respectively. These phenomena occur because the major part of the functional groups on Ca-alginate brings a negative charge (COO^- or O^-) at pH 5, thereby resulting in a repulsive force when Ni(II) complex anions approach. Other than Ca-alginate, the Ni(II) binding capacity of chitosan increased with the fraction of nickel-cyanide complex anion. This result would imply that the nickel cyanide complex anion exhibits favorable binding onto chitosan. The reason for this favorable binding is that the affinity of the amino group for $Ni(CN)_4^{2-}$ and $NiH(CN)_4^-$ on chitosan is greater than Ni^{2+}.

3.8. *Effect of pH*

A combined cation/anion exchange resin can hopefully solve the problem of coexistence of Ni^{2+} and $Ni(CN)_4^{2-}$ in water. Therefore, an AL-CH adsorbent is developed for this purpose. The feasibility of an AL-CH bead for a diverse of pH requires consideration with respect to the variation of pH of electroplating wastewater. Fig. 5 depicts the effect of pH on nickel adsorption by Ca-alginate and chitosan, and on nickel cyanide ions by chitosan. The trend of the effect on removal of nickel ions by chitosan is similar to that by Ca-alginate. That is, the amount of Ni^{2+}

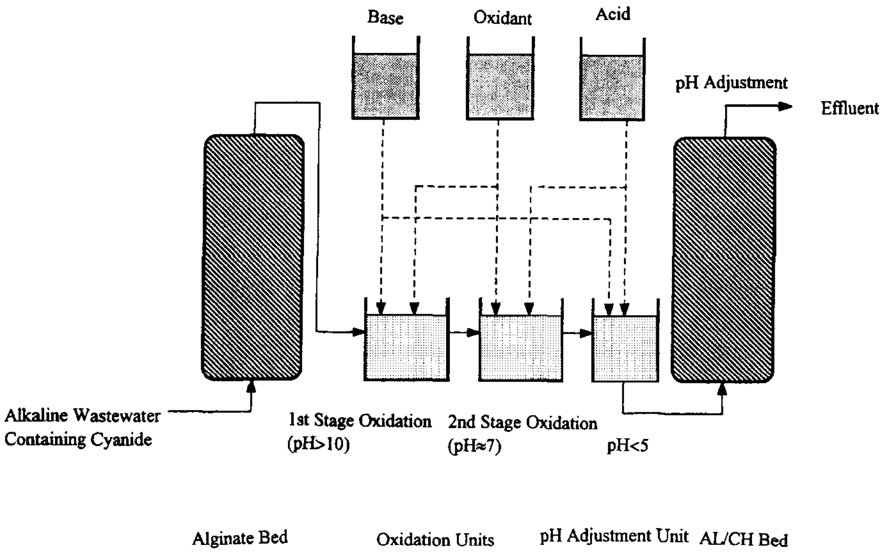

Fig. 6. The proposed flow-chart included biopolymer adsorption beds for treating wastewater containing cyanide.

adsorption increases with an increasing pH value. This figure indicates that the amount of Ni^{2+} adsorption by Ca-alginate increases abruptly above pH 3, and later reaches a plateau at pH 5. According to the acidic constant of the carboxyl group on Ca-alginate ($pK_a = 2.96$) [19], Ni^{2+} adsorption by Ca-alginate may be effected by ionization of carboxyl groups that serve as the binding site. This same figure reveals that adsorption of nickel cyanide ion by chitosan is strong in the acidic condition, and becomes weaker as pH is increased. Point A in this figure denotes that dissolution of chitosan powder occurs under extremely acidic condition (pH 3); in addition, point B denotes Ni(II) precipitation because of the formation of $Ni(OH)_{2(s)}$ above pH 9.

As the high pH is the favorable condition for the heavy metal adsorption by the Ca-alginate and the AL-CH beads, and acidic condition is favorable to the metal–complex adsorption by the AL-CH beads, it is recommended that a combination of alginate bed, two oxidation units with respective high pH and neutral pH operations, pH adjustment unit, and AL-CH bed is suitable to treat wastewater containing cyanide. The proposed flow chart is schematically shown in Fig. 6.

4. Conclusion

Ion exchange resins can compete with Ca-alginate in cost, but the cost of preparation of chitosan is greater. Apart from the advantage of reusing the waste, however, chitosan has the capability of adsorbing either metal ions or metal complex ion at the same time. In conclusion, the adsorption of metal ion by Ca-alginate is superior to that by chitosan. Therefore, a Ca-alginate bead is deemed feasible for application as an adsorbent to remove metal ions from polluted water. The combination of chitosan with alginate is effective for heavy metal removal from industrial wastewater containing cyanide in an engineering system. In alkaline conditions, chitosan and Ca-alginate exhibit a strong cation-exchange behavior to remove metal ions from industrial wastewater. In acidic conditions, chitosan causes anion exchange sites to be made available to bind the nickel-cyanide anion. Therefore, an AL-CH exchange column with pH adjustment may be developed to replace the conventional process for cyanide wastewater. That approach is effective in solving the problem of metal cyanide ion in polluted waters.

The density of adsorption sites on chitosan increased with decreasing particle size. Chitosan is effective in binding both metal ions from alkaline waters and metal-cyanide anion from acidic waters; however, Ca-alginate is effective only in adsorbing metal ion from alkaline waters. Hence, metal-cyanide anion exhibits favorable binding onto chitosan rather than onto Ca-alginate. Stabilizing chitosan physically in an alginate support medium to form the pellet is deemed possible, and is also feasible for removing both metal ions and metal-cyanide ions from water in an engineering system. However, the crosslinking reaction during immobilization results in blocking of adsorption sites. This pellet, the AL-CH bead, possesses a combined cation/anion exchange capacity, which can simply solve the problem of cyanide wastewater containing nickel.

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