Cross-linking of succinate-grafted chitosan and its effect on the capability to adsorb Pb(II) ion

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**Abstract.** The aim of this research was to improve the adsorption capacity of chitosan by modification of the chitosan using various cross-linking agents and followed by grafting using succinate anhydride. Succinate anhydride was grafted into chitosan that had been cross-linked using ethylene glycol di-glycidyl ether (EGDE), diethylene glycol diglycidyl ether (DEGDE) and bisphenol Adiglycidyl ether (BADGE) on the hydroxyl group of chitosan to yield Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc, respectively. Modified chitosans were analyzed using FTIR and TG-DTA and then applied as adsorbents for Pb(II) ion. Adsorption was carried out in batch condition with a variation of solution pH, contact time, and concentration of Pb(II) in the solution. Adsorption of Pb(II) ion reached optimum condition at pH 5 and contact time of 120 minutes. Adsorption of Pb(II) ion on all of the adsorbents fit well the pseudo-second order kinetic equation. Adsorption capacities of Pb(II) on Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc were 0.333, 0.388 and 0.898 mmolg\(^-1\), respectively, which mean that the adsorption of Chit-BADGE-Suc was the highest and followed by Chit-DEGDE-Suc and Chit-EGDE-Suc.

**1. Introduction**

Contamination of water resources by heavy metals ion becomes serious problem for public health and the environment. Heavy metals ion are considered toxic owing to their non-biodegradability and accumulation in living organism [1]. Lead (Pb(II)) is one of the industrial pollutants. The sources of lead pollution are the wastewater from processing industries engaged in metal electroplating, paints, lead storage battery, pigment and electronic. Lead is toxic metal that is harmful if inhaled or swallowed. It has both acute and chronic effects on human being, as it may cause anemia, nervous system problems, high blood pressure, kidney damage, and headache. Hence, it necessary to remove this element completely from industrial wastewater before discharge into natural water systems [2, 3].

There are many methods to remove lead from wastewater include ion exchange, reverse osmosis, chemical precipitation, solvent extraction, electroflotation, coagulation, and adsorption. Biosorption of lead is promising alternative method due to high removal ability, high selectivity, easy handling and low operating cost [4]. Biomaterial such as agricultural waste, fungal or bacterial biomass, alginate, chitin, and chitosan are prospective adsorbent due to biodegradability, non-toxic and low cost [5].

Chitosan is a product of the partial N-deacetylation of chitin, which has several desirable properties like biodegradability, hydrophilicity, antibacterial and non-toxicity [6-7]. The presence of a large number of functional groups such as amino (NH\(_2\)) and hydroxyl groups (OH) allow chitosan to have a...
high adsorption capacity for metal ions[8-9]. Chitosan is poor acidic resistance and mechanical strength. Therefore, it is necessary to improve the chemical resistance of chitosan to apply it as an adsorbent [1]. Attempts were made to improve the chemical stabilities chitosan in acid condition through chemical cross-linking with cross-linking agents such as glutaraldehyde (GLA), epichlorohydrin (ECH), and ethylene glycol diglycidyl ether (EGDE) [1,4,10-13].

Cross-linking agents prefer to react with the amine groups instead of the hydroxyl groups in chitosan and consequently the adsorption capacity of the cross-linked chitosan is reduced. The primary amine groups of chitosan are known to be the main chelating sites for many types of heavy metal ions [14]. Chitosan cross-linked enhance the resistance of chitosan against acid and alkali medium [15]. Li and Bai (2005) [16] reported a new cross-linking method that protected the amine groups in chitosan using formaldehyde before the cross-linking reaction and subsequently releases the protected amine groups after the cross-linking reaction. Oshita et al. (2008) [10] used benzaldehyde as protecting agent.

Adsorption capacity and selectivity of modified chitosan can be increased by grafting functional groups on chitosan cross-linked. Amine groups can be reacted with an aldehyde, alkyl halide, epoxide and anhydrate groups. Many works were done to graft other functional groups to chitosan such as phenylarsonic acid [18], EDTA[19], 3,4-dihydroxy benzoic acid [20] and carboxylic acid [21].

In this paper, chitosan was modified by cross-linking using three cross-linkers namely: EGDE, DEGDE, and BADGE. All of the cross-linkers are bifunctional reagent having two epoxide groups. Epoxide groups can be reacted with amine and hydroxyl groups. The structure of the cross-linkers is shown on figure 1.

![Figure 1. The structure of cross-linkers were used: EGDE (A), DEGDE (B) and BADGE (C)](image)

Cross-linked chitosans were then grafted using succinate anhydride on their amine groups. Grafting succinate anhydride will produce carbonyl and carboxylate groups in addition to hydroxyl and amine groups. These succinate-grafted materials were used as adsorbed for Pb(II) ions. The effect of pH solution, adsorption kinetic and adsorption isotherm have been studied.

**2. Methods**

2.1. Material.
Chitosan flakes (DD>75), EGDE, DEGDE, and BADGE, were obtained from Sigma-Aldrich Germany. Dioxane, benzaldehyde, ethanol absolute, NaOH pellet, HCl 37%, dimethyl sulfoxide, succinate anhydride, HNO$_3$ 65% and Pb(NO$_3$)$_2$ were obtained from E Merck Germany and distilled water obtained from Gadjah Mada University.
2.2. Instrument.
Instruments used in this study are consisted of reflux apparatus, analytical balance (Metler AE 100), hot plate and stirrer, filter Buchner, oven (Heraeus), thermometer, magnetic bar, shaker (MarusInstrument), pH meters (TOA-DKK HM-30R), FTIR(Shimadzu, Prestige-21), Thermoanalysis TG-DTA (ThermoplusEvoRigaku, T 8120), and Atomic absorption spectrophotometer (AAS) (Perkin Elmer Model 3110).

2.3. Adsorbent preparation.
Cross-linked chitosan was synthesized using a procedure that was reported by Oshita et al. (2008)[10]. Chitosan (5.0 g) was suspended in 50 mL of ethanol, added 20 mL benzaldehyde and stirred for overnight. The solution was filtered using Whatman filter paper and washed using ethanol and water to remove unreacted benzaldehyde to obtain benzaldehyde-protected chitosan (Chit-Ben). The obtained Chit-Ben was put in a round flask containing 75 mL of dioxane and then added 10 mL of 1 M NaOH and 5.3 g EGDE or DEGDE (6.7 g) or BADGE (5.3 g). The mixture was refluxed for 6 hours add the existing solid was separated and then washed with ethanol and distilled water until neutral pH to obtain cross-linked chitosans. Benzaldehyde was released from the amine group of cross-linked chitosan by stirring it in 0.5 M HCl (200 mL) for 15 hours, and this process was done twice. Cross-linked chitosans were washed with ethanol and water to remove any remaining benzaldehyde and cross-linkers. Cross-linked chitosans were grafted using succinate anhydride according to the procedure reported by Yan et al. (2006) [22]. Cross-linked chitosans we resuspended in 100 mL DMSO, then added 7.7250 g succinate anhydride and stirred for 24 hours in 60 ºC. The mixture was neutralized using acetic acid and washed with water and ethanol until neutral. The mixture was dried in the oven to obtain Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc. Chitosan and its derivative were analyzed by FTIR using KBr pellet method on wave numbers 400-4000 cm$^{-1}$. TG-DTA was done at a temperature between 30-600 ºC in an air atmosphere with increasing temperature rate of 10 ºC per second.

2.4. Influence of pH solution.
Batch experiments were carried out using 15.0 mg adsorbent, added bottle containing 25 mL of Pb(II) solution (150 mg L$^{-1}$). The solution was agitated using shaker at 40 rpm for 1200 min. The pH solution was adjusted with a solution of 0.1 M HNO$_3$ or 0.1 M NaOH. The solution was filtered using Whatman filter paper and the concentration of Pb(II) was analyzed using AAS. The adsorbed Pb(II) on adsorbent was calculated using equation (1).

\[
Q = [(C_o - C_e)V]/(m)
\]

where Q is the amount of Pb(II) adsorbed on a gram adsorbent (mmol g$^{-1}$). $C_o$ dan $C_e$ is the initial and final concentration Pb(II) in the solution (mmol L$^{-1}$), V is the volume of metal solution (mL), and m is the weight of the adsorbent used (g).

2.5. Kinetic study.
The kinetic study was carried out using 15.0 mg adsorbent in 25 mL of Pb(II) at pH 5 with initial concentration 150 mg L$^{-1}$. Solutions were agitated using shaker at 40 rpm at predetermined time intervals 5-1200 min. The solution was filtered using Whatman filter paper to separate adsorbent and filtrate. The concentration of Pb(II) in filtrate was analyzed using AAS.

2.6. Adsorption isotherms.
Adsorption isotherms were studied using 15.0 mg adsorbent in 25 mL of Pb(II) at pH 5 in variations initial concentration 25-500 mg L$^{-1}$. Solutions were agitated using shaker at 40 rpm for 20 hours. Solutions were filtered using Whatman filter paper and the concentration of Pb(II) in the filtrate was analyzed using AAS.
3. Result and Discussion

The cross-linking grafted-chitosan with succinate anhydride. Chitosan cross-linked were done on hydroxyl groups using EGDE, DEGDE and BADGE as cross-linker. On the other hand, grafting Grafted succinate anhydride on chitosan cross-linked were done on amine groups. Chitosan cross-linked and grafted were analyzed using FTIR and TG-DTA.

3.1. FTIR spectroscopy.

FTIR spectra of chitosan, Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit-BADGE-Suc was shown in figure 2. The FTIR spectrum of chitosan exhibits a strong peak at 3335 cm\(^{-1}\) which can be assigned to stretching vibration of O-H and N-H groups. The peak at 2868 cm\(^{-1}\) indicates C-H stretching vibration of –CH and CH\(_2\). The peak at 1635 cm\(^{-1}\) is the characteristic vibration of C=O from amide that is overlap with N-H vibration from amine group at 1592 cm\(^{-1}\). The band at 1381 cm\(^{-1}\) indicates deformation of asymmetry –CH\(_3\) and bending vibration CH. The broadband at 1080 is skeletal vibration involving C-O stretching that is characteristic of chitosan’s saccharide structure \cite{23, 24}. The FTIR spectra of Chit-EGDE-Suc and Chit-DEGDE-Suc showed new peaks at 1726 cm\(^{-1}\) and 1558 cm\(^{-1}\) from grafting succinate (C=O vibration from carboxylic and C=O amide). The peak at 1101 cm\(^{-1}\) become stronger due to increasing amount of C-O groups from EGDE or DEGDE. Spectrum Chit-BADGE-Suc exhibits new peaks at 835 cm\(^{-1}\) and 1510 cm\(^{-1}\) because of benzene groups in BADGE \cite{25-26}.

3.2. Thermal analysis.

Thermal properties of Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc were studied thermal properties at temperature 30 to 600 °C and the result of TG-DTA thermogram shown in figure 3. TG-DTA of modified chitosans showed the fourth stages of degradation. For thermogram of Chit-EGDE-Suc, the first stage was at temperature 40 to 110 °C with a weight reduction of 8%. This peak was an endothermic reaction due to releasing adsorbed water. The second stages were an exothermic reaction at 190 to 274 °C with a weight reduction of 31% due to initial degradation of adsorbent, especially functional groups attached to the main chain of chitosan such as hydroxyl, amine and carboxylate groups. The third stages were an exothermic reaction at 274 to 356 °C and weight loss of 33% due to decomposition of main chains of chitosan and cross-linked. The last stages were exothermic degradation and weight loss of 27% due to continued degradation at a temperature above 400 °C and produced water, carbon dioxide, and other small gas compounds \cite{27, 15}.

![Figure 2. Spectrum FTIR of Chitosan, Chit-EGDE-Suc, Chit-DEGDE-Suc dan Chit-BADGE-Suc.](image-url)
Figure 3. Thermogram TG-DTA of Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit- BADGE-Suc.

Thermogram of Chit-DEGDE-Suc showed similarly curve as Chit-EGDE-Suc but in the third stages, the energy that released higher because DEGDE structure heavier than EGDE. Thermogram of Chit-BADGE-Suc showed the high exothermic reaction at 500 °C due to degradation of cross-linked. BADGE have two benzene rings that its decomposition occurs at the high temperature.

3.3. Effect of pH on sorption of Pb(II).

The pH of the sorption medium is an important parameter in adsorption processes. In this study, the effect of pH was carried out in the pH range 1.0-6.0 to ensure to the solubility of metal ions. The effect of pH on adsorption of Pb(II) on Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit-BADGE-Suc were shown on figure 4. The adsorption of Pb(II) ion was highly dependent on the pH because pH can affect the solubility of the metal ions and at the same time influence the ionization state of the functional groups on the adsorbent. In the lower pH, adsorption ability of adsorbent is very low since more proton are available, and functional groups are protonated. Active sites on adsorbent are amine group (pKa 6.2) and carboxylate group (pKa 4.6) [6,17,28]. The positive charge of functional groups exerts a high electrostatic repulsive force, which prevent Pb(II) ion from approaching the adsorbent surface. At around pH 4 and 5, the inhibitory effect of H⁺ decrease, which led to an increase in the Pb(II) adsorption. When pH > 6, precipitation of lead hydroxide occurs. As a result, the maximum uptake of Pb(II) ions takes place at pH 5. Adsorption ability of Chit-BADGE-Suc at each pH was higher than Chit-EGDEE-Suc and Chit-DEGDE-Suc, this is may be due to the presence of benzene ring which has a high affinity toward Pb(II) by π bounding [28].
3.4. Adsorption is kinetic.
To investigate the mechanism of Pb(II) adsorption and to identify the rate-determining step, the pseudo first-order, and pseudo second-order equations were applied to analyze the kinetic data. The profile of time contact effect on adsorption of Pb(II) was displayed in figure 5. In the initial, adsorption capacity increased quickly due to all of active site in the adsorbent fully empty. Equilibrium times was reached 80 min, and beyond, this time, no change in adsorption occurred.

The pseudo-first-order equation (Ho) is given by eq.(2) [30]

\[
\ln(q_e - q_t) = \ln(q_e) - k_1 t
\]  

(2)

where \( q_e \) and \( q_t \) are the adsorption capacities (mmol g\(^{-1}\)) at equilibrium and at time \( t \) (min), respectively, and \( k_1 \) is the rate constant of the first-order adsorption (min\(^{-1}\)).

Figure 4. Effect of pH on the adsorption capacity of Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit- BADGE-Suc for Pb(II) ions.

Figure 5. Effect of contact time on the adsorption capacity of Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit- BADGE-Suc for Pb(II) ions.
The pseudo-second-order kinetic models (Ho) was illustrated as eq.(3) [30]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
\]

(3)

Where \( k_2 \) (g mmol\(^{-1}\) min\(^{-1}\)) is the rate constant of adsorption.

The parameters obtained from the pseudo first-order model, and pseudo second order model is shown in Table 1. The adsorption Pb(II) using Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc did not fit the pseudo-first-order equation, owing to its low correlation coefficient value (\( R^2 \)): 0.356, 0.127 and 0.961, respectively. The third modified chitosan follows the pseudo second-order equation, given by its high \( R^2 \) value: 0.944, 0.996 and 0.998, respectively. The pseudo-second-order assumes that chemisorption is the rate-determining step of the adsorption process. It is suggested that the overall of Pb(II) adsorption process be controlled by the chemical attachment and not by mass transport. The adsorption mechanism may involve valency forces through sharing of an electron between Pb(II) and adsorbent [29].

3.5. Adsorption Isotherm.

The effect of concentration of Pb(II) ions on the adsorption by Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc, is shown in figure 6. The result indicated that the adsorption of Pb(II) ions increased with the increasing concentration of Pb(II) in the initial stage and then relatively constant with the increasing concentration. This was due to the fixed total active sites in the adsorbent, and the adsorption amounts would reach a state of saturation.

The experimental data were analyzed by Langmuir and Freundlich adsorption isotherm. Langmuir adsorption isotherm based on the monolayer adsorption on the active sites. The Langmuir adsorption isotherm can be expressed in the linear form as follows [31]:

\[
\frac{C_e}{q_e} = \frac{1}{bK} + \frac{1}{b}C_e
\]

(4)

Where \( q_e \) is capacity adsorption in the equilibrium (mmolg\(^{-1}\)), \( C_e \) is the equilibrium concentration of metal in the solution (mmoll\(^{-1}\)), \( b \) is adsorption capacity maximum (mmolg\(^{-1}\)), \( K \) is Langmuir constant (L mol\(^{-1}\)).

Freundlich isotherm assumed multiple layer adsorption with uniform energy and can be expressed as eq.(5) [30]

\[
\log m = \log K_f + \frac{1}{n} \log C_e
\]

(5)

where \( m \) is amount of Pb(II) ion adsorbed (mmolg\(^{-1}\)), \( K_f \) (L mol\(^{-1}\)) is the Freundlich constant related to adsorption capacity, and \( n \) is the Freundlich constant related to adsorption intensity.
Table 1. Kinetic parameters for Pb(II) on Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc

| Adsorbent       | Pseudo-first-order | Pseudo-second-order |
|-----------------|--------------------|---------------------|
|                 | K(min⁻¹)          | R²                  | K (g mmol⁻¹ min⁻¹) | R²    |
| Chit-EGDE-Suc   | 1.7×10⁻²          | 0.356              | 3.1×10⁻³          | 0.944 |
| Chit-DEGDE-Suc  | 2.3×10⁻⁴          | 0.127              | 3.8×10⁻²          | 0.996 |
| Chit-BADGE-Suc  | 1.6×10⁻²          | 0.961              | 4.3×10⁻³          | 0.998 |

Table 2. Langmuir and Freundlich parameter for adsorption isotherm Pb(II) on Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit-BADGE-Suc

| Adsorbent       | Langmuir             | Freundlich          |
|-----------------|----------------------|---------------------|
|                 | b (mmol g⁻¹) (L mmol⁻¹) | R² | Rₐ     | N   | Kᵢ (mmol g⁻¹) | R²    |
| Chit-EGDE-Suc   | 0.333                | 1.442               | 0.957       | 0.841-0.221 | 2.042 | 0.185       | 0.921 |
| Chit-DEGDE-Suc  | 0.388                | 2.363               | 0.974       | 0.777-0.217 | 2.488 | 0.251       | 0.983 |
| Chit-BADGE-Suc  | 0.898                | 2.634               | 0.962       | 0.907-0.159 | 2.053 | 0.621       | 0.933 |

Figure 6. Effect of initial concentration on the adsorption of Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc for Pb(II) ions.

The parameters of Langmuir adsorption isotherm and Freundlich adsorption isotherm of Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc for Pb(II) are shown in Table 2. The coefficient correlation (R²) value of Langmuir and Freundlich adsorption isotherm are similar. Pb(II) ion can be bound on hydroxyl, amine or carboxylate simultaneously.

The adsorption capacity of Pb(II) on Chit-EGDE-Suc, Chit-DEGDE-Suc and Chit-BADGE-Suc are 0.333, 0.388 and 0.898 mmol g⁻¹, respectively. Adsorbent Chit-BADGE-Suc has the highest capacity of Pb(II) ions because cross-linker BADGE has benzene groups that are rich with an electron. The benzene ring binds Pb(II) ion through π electrons on its ring. The adsorption capacity of Pb(II) ions on Chit-DEGDE-Suc is higher than Chit-EGDE-Suc because cross-linker DEGDE is longer than EGDE. The longer cross-linker made space between chains of chitosan increase, so it is easier for the active site to bind Pb(II) ion.
Langmuir parameter ($R_L$) is used to predict the favorability of adsorption process. The ($R_L$) was calculated from the following equation using Langmuir constant (6) [32]:

$$R_L = \frac{1}{1+KC_0} \tag{6}$$

where $K$ is the Langmuir constant (L mmol$^{-1}$) and $C_0$ is the initial concentration Pb(II) ion (mmol L$^{-1}$). It is considered to be unfavorable ($R_L > 1$), linear ($R_L = 1.0$), favorable ($1 > R_L > 0$) and unfavorable ($R_L = 0$). The $R_L$ values for adsorption Pb(II) on Chit-EGDE-Suc, Chit-DEGDE-Suc, and Chit-BADGE-Suc were in the range $1 > R_L > 0$, indicating that the adsorption process was favorable.

4. Conclusion
In this study, we observed that cross-linking and grafting chitosan produced material that was chemically stable at low pH value, allowing its use in the acidic solution. Type of cross-linker influenced capacity adsorption of Pb(II). Chit-BADGE-Suc showed the highest capacity adsorption of Pb(II) due to its benzene ring that bind Pb(II) ion effectively. The adsorption was influenced by some parameters such as the pH of solution, contact time and initial Pb(II) concentration.

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References
[1] Meneghetti E, Baroni P, Vieira R S, da Silva MGC, and Beppu M 2010 Mater. Res. 1389.
[2] Hussain M A, Salleh A, and Milow P 2009 Am. J. Biochem & Biotech. 5 75.
[3] Jiang W, Su H, Huo H and Tan T 2010 Appl. Biochem. Biotechnol. 160 467.
[4] Vieira R S, Guibal E, Silva E A and Beppu M 2007 Adsorption 13 603.
[5] Copello G J, Varela F, Vivot M and Diaz L E 2008 Bioresour. Technol. 99 6538.
[6] Guibal E 2004 Sep. Purif. Technol. 38 43.
[7] Hasan S, Krishnaiah A, Ghosh T K, Viswanath D S, Boddu V M, and Smith E D 2006 Ind. Eng. Chem. Res. 45 5066.
[8] Mello KGPC, Bernusso L C, Pitombo R N M and Polakiewicz B 2006 Braz. Arch. Biol. Tech. 49 665.
[9] Miretzky P, and Cirelli A F 2009 J. Hazard. Matter. 167 10.
[10] Oshita K, Takayanagi T, Oshima M and Motomizu S 2007 Anal. Sci. 23 1431.
[11] Vieira R S and Beppu M 2005 Adsorption 11 731.
[12] Sigh A, Narvi S, Dutta P K and Pandey N D 2006 Bull. Mater. Sci. 29 233.
[13] Oliveira B F, Santana M H A and Re M E 2005 Braz. J. Chem. Eng. 22 353.
[14] Ngah W S W, Endud C S and Mayanar M 2002 React. Funct. Polym. 50 181.
[15] Leach J B, Wolinsky J B, Stone P J and Wong J Y, 2005 Acta Biomater. 1 155.
[16] Li N and Bai R 2005 Ind. Eng. Chem. Res. 44, 669.
[17] Mourya V K, Inamdar N N and Tiwari A, 2010 Adv. Mat. Lett. 1 11.
[18] Oshita K, Seo K, Sabarudin A, Oshima M, Takayanagi T and Motomizu S 2008 Anal. Bioanal. Chem. 390 1927.
[19] Katarina R S, Takayanagi T, Oshita K, Oshima M, and Motomizu S 2008 Anal. Sci. 24 1537.
[20] Sabarudin A, Noguchi O, Oshima M, Higuchi K, and Motomizu S 2007 Microchim. Acta, 159 341.
[21] Ladenslager M J, Schiffman J D and Schauer C L 2008 Biomacromol. 92682.
[22] Yan C, Chen D, Gu D, Hu H, Zhao X and Qiao M 2006 Yakugaku Zasshi 126 789.
[23] Dong Y, Xu C, Wang J, Wang M, Wu Y and Ruan Y 2001 Sci. In China B. 44216.
[24] Van de Velde Kand Kiekens P 2004 Carbohydr. Polym. 58 409.
[25] Zhang J, Zhang Y, Li R and Pan Q 2012 Ind. J., of Chem. Technol. 19 161.
[26] Chan Z, Ping Q, Zhang H and Shen J 2003 Eur. Polym. J. 39 1629.
[27] Jiao T F, Zhou J, Zhou J X, Gao L H, Xing Y Y and Li X H 2011 Iranian Polym. J. 20 123.
[28] Reddy A S and Sastry G N 2005 J. Phys. Chem. A. 109 8893.
[29] Bunting J W and Thong K 1971 Canadian J. Chem. 48 1654.
[30] Ho Y S and McKay G 1999 Process. Biochem. 34 451.
[31] Erosa M S D, Medina T T S, Mendoza R N, Rodriguez M A and Guibal E 2011 Hydrometallurgy 61 157.
[32] Dalida P M I, Mariano A F V, Futalan C M, Kan C, Tsai W and Wan M 2011 Desalination 275 154.