# Synthesis of A Chelating Resin Chitosan-1,5-Diphenyl Carbazide and Characterization of Retention Toward Cr(Vi) Ions

Aman Sentosa Panggabean*[1], Subur P. Pasaribu[1], Dadan Hamdani[2], Nadira[1]

[1]Department of Chemistry-FMIPA, University of Mulawarman-Indonesia
[2]Department of Physic-FMIPA, University of Mulawarman-Indonesia
*amanspanggabean@yahoo.com

**Abstract**

Synthesis of the derivative chelating resin of chitosan-1,5-diphenyl carbazide (DPC), and characterization of retention for Cr(VI) ions has been carried out. Synthesis chitosan-DPC resin can be done by coupling reacts between diazonium ion from diazotation chitosan with DPC at temperature 1-3°C during 1 hour, the product of 70% yield was obtained. The optimal conditions to modified of chitosan-1,5-diphenylcarbazide microcapsules resin were 0.1 M $CaCl_2$ and 1% Na-alginate. Ca-alginate-chitosan-1,5-diphenylcarbazide microcapsule resin before and after interacted with Cr(VI) has characterization by using FT-IR spectroscopic, shows the spesific functional groups of the resin. Retention characteristic of resin was investigated for Cr(VI) ions. The optimal conditions for the analytical performance of resin with retention at pH 1, minimum contact time was 30 minutes, retention capacity was 1.7350 mg Cr(VI)/g microcapsule resin.

**Keywords :** Chitosan, alginate, Chelating resin, Diphenyl carbazide, Cr(VI).

## Introduction

Chromium occurs in nature at very low concentrations predominantly in two oxidation states, which differ significantly in their toxicity. While Cr(VI) is toxic and carcinogenic upon inhalation, Cr(III) is known to be an essential nutrient for humans supplied also in pharmaceutical products as a dietary supplement. Increasing production of Cr(VI), due to oxidation of Cr(III) in industrial plants or from its spontaneous oxidation in soils, may pose pollution problems to drinking and surface waters. (Paleologos et al., 2001). In recent years, the determination of chromium especially Cr(VI) is become very important in environmental samples. One technique of determining Cr(VI) developed in recent years is preconcentration technique based chelating resin, using a spectrophotometer detector.

Chelating resin basically is consisted of two components that are functional of chelating group and polymer matrix as supported. Nature of from both this components will determine usage and performance from a chelating resin. The selectivity will be determined by type chelating group, while capacities, mechanic strength and the chemistry resistance determined by supporter polymer type who applied (Saitoh, et al. 2007; Trochimczuk et al., 2004). This means that a chelating resin with certain characteristic can be synthesis by considering both the compiler components.

The strategy determines in preconcentration to apply chelating resin is how to incorporate chelating reactant into polymer supporter material (Bilba et al., 1998). Way of simple is through impregnation technique, but chelating resin yielded generally gives unfavourable performance because chelating group which only tied in physical to earn easily escapes again at the time of its use (Amran and Heimburger, 1996; Alexandratos and Smith, 2004). To solving problems explained above, hence chelating group shall tie chemically through covalent bond at polymer applied as supporter material (Prasada et al., 2004). The existing finite, chelating resin this type has not many checked more than anything else is commercial and still be classified as fine-chemicals.

Chitosan can be synthesized with deacetylation reaction by removal acetyl group ($COCH_3$) from chitin using alkali solution (Dutta et al, 2004). Pure chitosan is generally used as an absorbent for heavy metals in flakes and powder form. Adsorption ability of chitosan against heavy metals is strongly influenced by physical-chemical properties of chitosan. Chitosan which not cross-linked have an adsorption capacity is greater than the cross-linked chitosan, but the cross-linked chitosan have the physical endurance to acid better than not cross-linked chitosan (Wan Ngah, 2002). In recent years, the synthesis of chitosan have been carried out and modification of chitosan with the addition of side groups with the aim to analytical using such chelating resin against heavy metals contained in natural samples in trace concentrations (Katarina et al., 2005).

Based on above description this research has been synthesized chelating resin chitosan modified with the addition of 1,5-diphenyl carbazide (DPC) compound and modified into form of microcapsules in alginate salt which expected to be used as a microcapsule resin for retention of Cr(VI) ion. Chitosan obtained from chitin by deacetylation reaction from windu shrimp's (*Penaeus monodon*) shells with 60 % sodium hydroxide, and then DPC group is added as a chelating group to increase the retention capacity of the Cr(VI) ions.

**Experimental**

***Instrumentation***. A set of reflux system, three-neck flask, blender, sieve size of 100 mesh, filter paper, analytical balance, porcelain bowls, glass funnel, the volume pipettes, stopwatch, oven, hot plate with stirer, Spectronic 20 D+, Spectrophotometer FT-IR (Fourier Transform - Infra Red) Prestige 21-D., was used for all measurements.

***Reagents.*** All reagents were of analytical-reagent grade; sodium hydroxide, hydrochloric acid, sulfuric acid, nitrate acid, calcium chloride, acetic acid, ethanol, acetone, sodium nitrite, sodium alginate, 1,5-diphenyl carbazide, potassium bichromate, glacial acetic acid and aquabidest.

**Synthesis of Chitosan -1,5-diphenylcarbazide Resin**

2 g of chitosan added to 100 mL 1M HCl alternating with addition of 75 mL 1 M $NaNO_2$ until resin was azotated in the presence of iodine paper color change, by keeping the temperature between 1-3 °C. Then add dropwise 100 mL of 10% 1,5-diphenylcarbazide and stirred for 1 h with temperature between 1-3 °C and left for 24 h in the refrigerator. The mixture was then filtered and rinsed with destillated water until neutral pH and dried in oven at 60 °C (Panggabean et al., 2009)

**Production of Ca-Alginate-Chitosan-1,5- diphenylcarbazide Microcapsules Resin**

25 mL $CaCl_2$ solution prepared with various concentration of 0.1 - 1 M into each 100 mL glass beaker, then added 0.025 g Chitosan -1,5-diphenylcarbazide resin synthesis and stir until homogeneous with magnetic stirrer. 1% Na-alginate was added dropwise with a burette while stirring with a magnetic stirrer on to form of Ca-alginate-chitosan-1,5-diphenylcarbazide microcapsules, adjust the flow rate in the buret and the rotational speed of the magnetic stirrer and Ca-alginate-chitosan-1,5-diphenylcarbazide microencapsulated granules dried at room temperature for ± 24 hours. For the same steps, varied concentrations of Na-alginate 0.5 and 0.75% at the optimum concentration of $CaCl_2$ solution. Subsequently the dried resin microcapsules can be determined retention of the ion Cr(VI) (Panggabean et al., 2012).

**Characterization of Ca-Alginate-Chitosan-1,5- diphenylcarbazide Microcapsules Resin**

Microcapsule of resin before and after interacted with Cr(VI) has characterization by using FT-IR spectroscopic. The retention capabilities of chelating resin synthesis will be evaluated through a batch method are determining the optimum pH, minimum contact time, and retention of capacity. 0.05 g of Ca-alginate-chitosan-1,5-diphenylcarbazide microcapsule resin added 10 mL of standard metal ion Cr(VI) 1 mg/L, stirred and allowed 30 minutes, filtered. The amount of metal ions retented will be calculated by measuring the amount of residual determined by visible spectrophotometry at $\lambda$ = 540 nm. The data obtained can describe the character retention of the chelating resin synthesized.

ISBN: 978-979-96595-4-5 

## Results and Discussion

### Synthesis of Chitosan-1,5-diphenylcarbazide Resin

Synthesis of chitosan-1,5-diphenylcarbazide resin is done through the diazotation reaction. Diazotation is a way to change the amine group into a diazo group using concentrated acid solution (Panggabean, et al, 2009). In this process chitosan reacted with HCl 1 M and $NaNO_2$ 1 M alternately at 1-3 ° C until the resin azotated. Reaction temperature is maintained at below 3 °C because the reaction is highly exothermic. Hydrochloric acid is a strong acid which serves as a catalyst and forming chitosan chloride salt. $NaNO_2$ serves as forming nitrosonium ion together with HCl (Sykes, 1989) to produce diazonium salt. The mixture then reacted with 1,5- diphenyl carbazide 5 % dropwise and stirred for ± 1 hours at 1-3 °C. Diazonium salt is stable at low temperature (0-4 °C) and sensitive to light and can easily be damaged at ultraviolet wavelength and visible light (Panggabean, et al, 2009). Diazonium salt has coupling reaction with 1,5- diphenylcarbazide to produce chitosan- 1,5-diphenyl carbazide compound (**Figure 1**). The obtained Chitosan-1,5- diphenylcarbazide resin after diazotation is reddish brown with a yield of 39.43%.

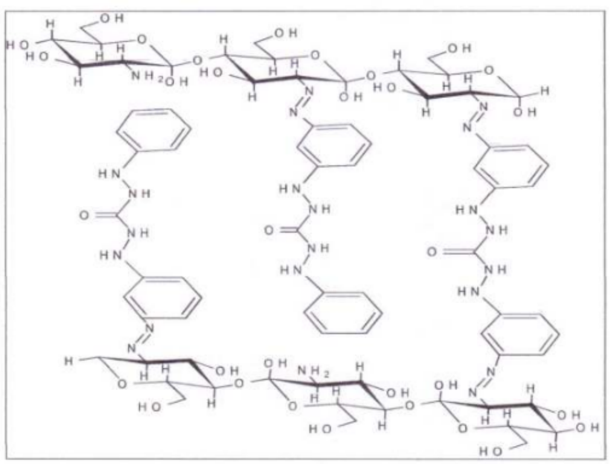

**Figure 1.** Structure of Chitosan-1,5-Diphenylcarbazide

### Production of Ca-Alginate-Chitosan-1,5- Diphenylcarbazide Microcapsule Resin

The production of Ca-alginate-chitosan-1,5- diphenylcarbazide microcapsules conducted by reacting the Na-alginate solution with chitosan resin-1,5-DPC in $CaCl_2$

ISBN: 978-979-96595-4-5 

solution. The formation of the microcapsules characterized by changes in the morphology of the original Na-alginate solution into Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule shaped gel sphere then Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule dried at room temperature. The concentration of $CaCl_2$ and Na-alginate solution be varied to obtain the microcapsules resin able to maximum retention of Cr(VI) ion.

On the variation of the concentration of $CaCl_2$ solution with a solution of 1% Na-alginate, the % retention of ions Cr(VI) are the most significant at concentrations of 0.1 M $CaCl_2$ solution is 84.60%, whereas the concentration of $CaCl_2$ solution 0.5 M and 1 M,% retention of the metal ions Cr(VI) is very small at just under 20% (**Figure 2**). This is because the form of the microcapsules at a concentration of 0.5 and 1 M $CaCl_2$ solution denser and less porous which in this case acts as a matrix Ca metal in metal uptake.

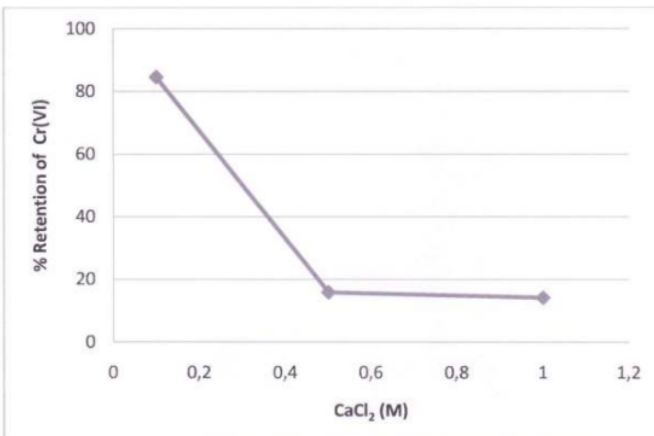


**Figure 2.** Effect of $CaCl_2$ concentration on making Ca-alginate-chitosan-1,5-diphenylcarbazide microcapsules

From the optimum concentration of $CaCl_2$, subsequently varied Na-alginate concentration of 0.5 and 0.75% respectively at remains 0.1 M $CaCl_2$, and measured the retention of the ions Cr(VI). Variations in the concentration of Na-alginate obtained results are best retention occurred in 0.75% Na-alginate with retention of 96.90% (**Figure 3**). However, because of the texture of the mixture is less well rounded in form microcapsules so feared ineffective in its application for preconcentration stage in minicolumn, then subsequently used for the manufacture of microcapsules composition of 1% Na-alginate which also has a high retention% was 90.20%.

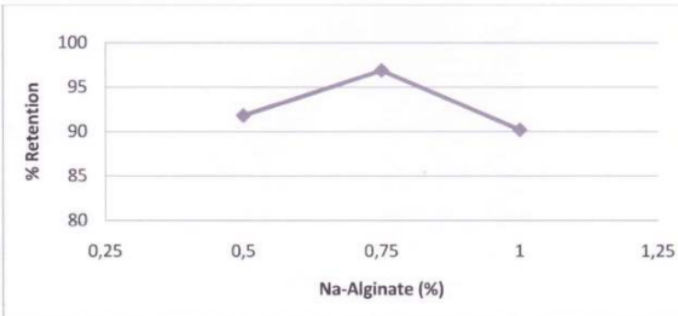


**Figure 3.** Effect of Na-Alginate Concentration on the Preparation of Ca-alginate-chitosan-1,5-diphenylcarbazide

**Analysis of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule**

Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule were analyzed by FTIR spectroscopy. Spectrum analysis of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule before interacted with Cr(VI) compared to the spectrum of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule that after interacted with Cr(VI) can be seen in **Figure 4** and **5**.

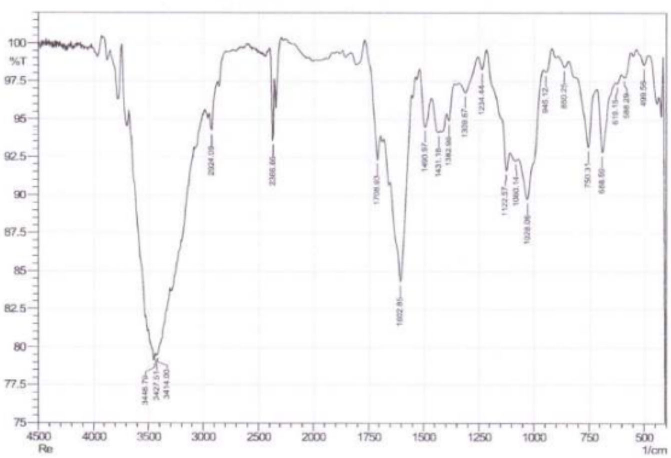


**Figure 4.** FTIR spectrum of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule

FTIR spectrum in **Figure 4** shows a broad absorption peaks at wave number 3446.79; 3427.51 and 3414.00 $cm^{-1}$ indicate typical absorption peak of O-H stretching vibration. Absorption peaks at wave number 2924.09 cm-1 is the CH stretching vibration of alkanes. Absorption peaks at wave number 1708.93 $cm^{-1}$ indicate typical absorption of stretching vibrations of carbonyl group (C=O) where is possibility of amide groups at 1.5 DPC and carboxylic acid salt of alginic. Absorption peaks at 1062.85 and 1490.97 $cm^{-1}$ is typical of the stretching vibration peak symmetry and asymmetry -N=N- groups that is likely to come from diazo bond between chitosan and 1.5-diphenylcarbazide or 1.5-difenilkarbazone. Absorption peaks at wave number 1028.06; 1080.14 and 1122.57 $cm^{-1}$ showed C-O stretching vibration from the compound chitosan and alginate. Absorption peaks at wave number 750.31 $cm^{-1}$, is typical absorption of stretching vibration of N-O (Silverstein, et al, 1986).

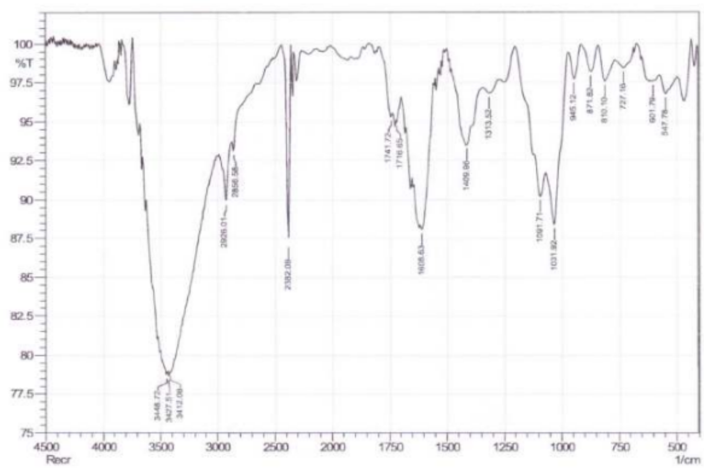


**Figure 5.** FTIR spectrum of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule + Cr(VI)

FTIR spectrum Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule has interacted with Cr(VI) (**Figure 5**), shows that most of the wave number has changed absorption intensity. It can be seen at 1741.72 and 1716.65 $cm^{-1}$ absorption peaks showed reduced uptake in group C=O and C-O followed by increased uptake in the wave number 1031.92 $cm^{-1}$. This is expected because there has been a change in the structure of 1.5-diphenylcarbazide to 1.5-diphenylcarbazone binds to Cr(VI). Intensity decrease also occurred in the -N=N- stretching vibration in wave numbers 1608.63 $cm^{-1}$ and also the NH- bending

**ISBN: 978-979-96595-4-5**

vibration at wavenumber 727.16 $cm^{-1}$, this may occur due to the interaction between the 1.5-diphenylcarbazone complexing with Cr(VI).

**Determination of Characteristic Retention of Microcapsules Resin**

In the process of Cr(VI) ion retention by Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule resin was carried out by batch method. That is by soaking the resin into Cr(VI) standard solution. The ability of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule resin in the retention of the metals Cr(VI) is obtained as a characteristic of the resin, which includes: optimum pH, minimum contact time, and retention capacity.

**Determination of optimum pH**

Determination of optimum pH microcapsules resin using a batch method or immersion is done by measurements the concentration of Cr(VI) with varying pH standard solution. 0.05 g microcapsules resin soaked for 30 min in 10 ml of 1 mg/L Cr(VI) standard solution so that can be determined the optimum pH Cr(VI) retented well.

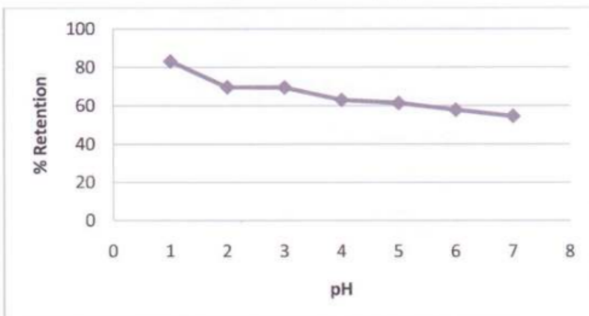


**Figure 6**. Determination of pH optimum

**Figure 6**. shows the microcapsule resin at pH 1, absorption has most favorable to the Cr(VI) ion is more than 80%. This is due to the pH stability of the complex formation occurs between DPC ligand with Cr(VI) ions which causes the metal ions can be maximum retented.

**Determination of the minimum contact time**

Determination of minimum contact time aims to find out how long it will need microcapsules resin in the retention of Cr(VI) ions well. At this stage of the research was done by 0.05 g of microcapsules resin into 10 ml of 1 mg/L Cr(VI) standard solution at the optimum pH 1 by varying the contact time from 1 - 120 min.

ISBN: 978-979-96595-4-5

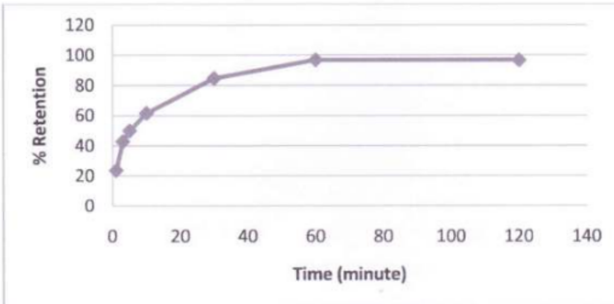


**Figure 7**. Determination of optimum contact time on the retention Cr(VI)

**Figure 7.** known that level of absorption of Cr(VI) is very fast at the beginning of the absorption process. This is caused by rapid diffusion and molecules absorption into contact to the external surface of resin. After the retention process is very fast. Cr(VI) retention rate gradually declined during the interval of time and reached equilibrium values. Where is this process due to the diffusion speed of Cr(VI) in the matrix of resin particles (Gong, 2010). From the calculation results showed minimum contact time required microcapsules resin to retent metal ions Cr(VI) is 30 minutes, where more than 80% of Cr(VI) ions has retented by resin and in the next minutes, the retention of Cr(VI) ions obtained is not much different.

**Determination of the retention capacity**

Retention capacity is a parameter that indicates the ability of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule resin to retent Cr(VI) ions. Determination of retention capacity is done by batch method, which is made of resin soaking 0.05 g of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule resin into 10 ml of Cr(VI) standard solution with pH 1 with various concentrations of Cr(VI) ions 1-15 mg/L, so it can be determined the ability of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule resin to retent Cr(VI) ions.

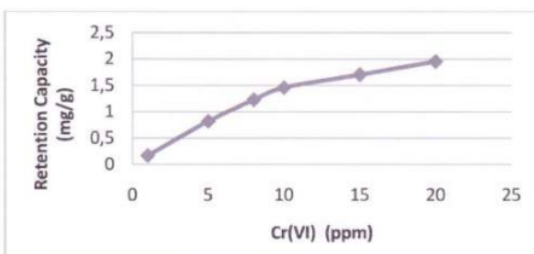


**Figure 8**. Determination Retention Capacity of microcapsule resin

**Figure 8**, relationships equation between Cr(VI) concentrations with many Cr(VI) ions retented by resin. By extrapolation method obtained two curves crossover point represents the value of the capacity retention of microcapsule resin. Where the two lines of equation $y = 0.117\ x + 0.113$ and $y = -0.110\ x + 3.260$ and the intersection between the two lines is the optimum retention capacity of Ca-Alginate-Chitosan-1,5-Diphenylcarbazide microcapsule resin was 1.7350 mg Cr(VI)/g resin. Where the results indicated that for every 1 g of resin microcapsule may retain 1.7350 mg Cr(VI).

**Conclusion**

Chitosan-1,5- Diphenylcarbazide resin compound can be synthesized and modified to became Ca-alginate-chitosan-1,5- Diphenylcarbazide microcapsule resin by reaction between Na-alginate solution with chitosan-1,5- Diphenylcarbazide resin in $CaCl_2$ solution. The optimal conditions were obtained by 0,1 M $CaCl_2$ and 1% Na-alginate. Characterization of Ca-alginate-chitosan-1,5-diphenylcarbazide microcapsule resin for Cr(VI) ion was indicated that optimal Cr(VI) ion retention at pH 1, minimum contact time 30 and retention capacity was 1.7350 mg Cr(VI)/gr microcapsule resin.

**Acknowledgement**

We thank to SIM-LITABMAS-DIKTI Jakarta for the *Penelitian Hibah Fundamental 2013* project for the financial support.

**References**

Alexandratos, S.D., and Smith, S.D. 2004. High Stability Solvent Impregnated Resins: Metal Ion Complexation as a Function of Time. *Solvent extraction and ion exchange*. **22(4)**, pp. 713–720.

Amran, M.B. and Heimburger, R. 1996. Arsenic speciation in marine organisms: from the analytical methodology to the constitution of reference materials. *Fresenius' J. Anal. Chem*. **354**, pp. 550-556.

Bilba, D., Bejan, D. and Tofan, L. 1998. Chelating sorbents in Inorganic Chemical Analysis. *Croatica Chemica Acta*. **71(1)**, pp. 155-178.

Dutta, P.K., Dutta, J. and Tripathi, V.P. 2004. Chitin and Chitosan: Chemistry, properties and applications. *Jounal of Scientific & Industrial Research*. Vol. **63**. pp 20-31.

Gong, R., Li, N., Cai, W., Lui, Y., and Jiang, J. 2010. α-ketoglutaric Acid-Modified Chitosan Resin as Sorbent for Enhancing Methylene Blue Remove from Aqueous Solutions. *Int. J. Environ. Res*., **4(1)**: pp. 27-32.

Katarina, R.S., Takayanagi, T., Oshima, M., and Motomizu, S. 2006. Synthesis of chitosan-based chelating resin and its application to the selective concentration and ultratrace determination of silver in enviromental water samples. *Anal. Chim. Acta*. **558**. pp. 246-253.

Panggabean, A.S., Amran, M.B. dan Pasaribu, S.P. 2009. Sintesis dan karakterisasi Resin Pengkhelat Polystyrene Divinylbenzene -1-(2-Pyridilazo) 2-napthol Serta Penggunaannya Dalam Modul Prakonsentrasi Ion Logam berat. *Laporan Penelitian Hibah Bersaing XV*, Lembaga Penelitian UNMUL. Samarinda.

Panggabean, A.S., Subur P. Pasaribu, dan Sari, I.Y.L. 2012. Prakonsentrasi ion Cu(II) Berbasis Mikrokapsul Ca-Alginat Secara off-Line Dengan Metode kolom. *Chemistry Progress*. **5(2)**. Hal. 70-76

Paleologos, E.K., Stalikas, C.D., Tzouwara-Karayanni, S.M., and Karayannis, M.I. 2001. Selective speciation of trace chromium through micelle-mediated preconcentration, coupled with micellar flow injection analysis–spectrofluorimetry. *Anal. Chim. Acta*. **436.** pp. 49–57.

Prasada, T.R., Praveen, R.S. and Daniel, S. 2004. Styrene-divinyl benzene copolymer: synthesis, caracterization, and their role in inorganic trace analysis. *Critical Reviews in Anal. Chem*. **34**, pp. 177-193.

Saitoh, T., Nakane, F., and Hiraide, M. 2007. Preparation of trioctylamine-impregnated polystyrene-divinylbenzene porous resins for the collection of precious metals from water. *Reactive & Functional Polymers*. **67**, pp. 247–252.

Silverstein, R.M., Bassler, G.C. dan Morril, T.C. 1986. Penyidikan Spektrometrik Senyawa Organik. Erlangga Jakarta.

Sykes, P. 1989. Penuntun Mekanisme Reaksi Kimia Organik. Gramedia. Jakarta.

Trochimczuk, A.W., Kabay, N., Arda, M. and Streat, M. 2004. Stabilization of solvent impregnated resins (SIRs) by coating with water soluble polymers and chemical crosslinking. *Reactive & Functional Polymers*. **59**, pp. 1–7.

Wan Ngah, W.S. 2002, Removal Copper (II) Ions from Aqueous Solution onto Chitosan and Cross-linked Chitosan Beads, *Reactive and Functional Polymers*, **50.** pp 181-190.

# Proceeding_The_2nd_ICICS_2013-22_sd_23_October_2013.pdf

ORIGINALITY REPORT

| 9% | 6% | 4% | 0% |
| --- | --- | --- | --- |
| SIMILARITY INDEX | INTERNET SOURCES | PUBLICATIONS | STUDENT PAPERS |

MATCH ALL SOURCES (ONLY SELECTED SOURCE PRINTED)

3%

★ www.researchgate.net

Internet Source

| | | | |
| --- | --- | --- | --- |
| Exclude quotes | Off | Exclude matches | Off |
| Exclude bibliography | On | | |