# The Adsorption of Cr(VI) Ions Using Chitosan-Alumina Adsorbent

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## ABSTRACT

Chitosan as adsorbent has been used widely, however it was not effective yet for metal ions adsorption in industrial scale. In acidic condition, chitosan's active site tends to decrease. This drawback can was solved by coating of chitosan active site on alumina. This paper discloses to overcome that limitation. The charateristic of the active side was analysed by FTIR spectrometry toward vibration N-H group at 1679.15 cm<sup>-1</sup>, C=O group of oxalate at 1703.30 cm<sup>-1</sup>, and Al-O group of alumina at 924.07 cm<sup>-1</sup>. The adsorption capacity of the developed adsorbent was tester to adsorb Cr(VI) ions under various of pH value such as 1, 2, 3, 4, 5, 6, and 7. The contact time affect toward the adsorption was also reported in 20, 30, 400 500, and 600 ppm) was also studied. Chromium (VI) was measured using spectronic-20. Adsorption capacity was obtained at 66.90 mg/g under optimum conditions pH 2, and contact time 60 minute, respectively.

Key word: Adsorption, Chitosan-Alumina Adsorbent, Cr(VI) ions

### **INTRODUCTION**

Disposing of waste-contained heavy metals into environment becomes a major issue on the accumulation of water pollution. This affects increasing of organism-contained a polluted heavy metal such as on marine biota, coral, and some family of algae or sea weeds. Tragically, a high consumption of this polluted seafood sources by human is an important issue for human health [1]

Chromium metal polluted a water environment for example was reported because of the leaching and or a water disposal contained a toxic and water soluble of Cr(VI) from electroplating industry. This species is able to penetrate to human cell wall and is reduced by cell forms a toxic Cr(III). This was reported able to damage the DNA of cell and caused a cell mutation and also initiate a cell cancer [2]. Theoretically the method to reduce heavy metal pollution in environment is by filtration, chemical precipitation, ion exchange, adsorption, and by membrane system. The common method applied is adsorption due to easily to undertake, simple, and efficient in some certain conditions. This method is also applied for a dilute concentration of heavy metal, and easily to be regenerated. Some biomaterials such as moss [3], green tea leave [4], coconut fibrous shell [5], and also non biomaterial sources such as perlite, peat soils, and mud was reported their application for adsorption some heavy metals in waste water.

According to Ngah and Liang [6] beside those reported common adsorbent, chitosan was isolated from shrimps shell was able to be used as adsorbent after deacetylation process. Other biological sources of chitosan were reported such as mollusk shell, clamshell and some fungi species [7]. Chitosan can also be used as emulsifier and coagulant. A high chemical reactivity of chitosan indicate its ability as polyeletrolite cations, ion exchange, and also as potential adsorbent for heavy-metal polutants, organic compounds and dye from industrial waste water [1,8]. However application in industrial-scale still requires a lot effort study due to sensitivity to acidic conditions. A high acidic condition can promote protonation and decreased the adsorption capacity.

Hanung (2004) [9] modified a chitosan as its N-carboxymethyl chitosan (NCMC) which able to adsorp lead 6.038 mg/g in 60 min shaking time. Another report by Boddu and Smith (2002) [10], that modification of chitosan with  $\alpha$ -alumina as adsorbent for Cr(VI) indicated 154 mg/g capacity at pH 4 with initial Cr(VI) concentration 800 ppm. This paper reports recent investigation on modification of chitosan following Boddu and Smith (2002) [10] using alumina as supporting material. This paper is also reports effectiveness of the modified chitosan to adsorb Cr(VI), including optimum condition for adsorption, and its capacity.

## EXPERIMENTAL

## Chemicals and instrument analysis

All chemicals used has pro-analytical or synthetic grade, and were used as bought from the manufacturer, except as mentioned. Chitosan was prepared according to Sofana (2003) [11], alumina anhydrous 8-14 mesh (Wako), potassium chromate (Merck), dehydrated of oxalic acid (Merck), diphenylcarbazide (Sigma), sodium hydroxide (Smart Lab), nitric acid (Smart Lab), hydrochloric acid (Smart Lab), and distilled water.

Instruments applied during research include FTIR spectrometer (Jasco FTIR 5300) and sample was measured as a mixture on KBr plate, UV-Vis spectrometer (Shimadzu spectronic 20), analytical balance (Metler AE 166), pH meter (Inolab), mechanical shaker (Edmund Buhler BC 25), and ovens (local brands).

## **Preparation of Chitosan**

Chitosan (5.0 g) in glass beaker was added gently oxalic acid (100 mL, 10%). This mixture was heated with stirring at 40 to 50 °C until the gel was formed. Then, the afforded gel was collected and colled to room temperature, and the product was analysed using FTIR spectrometer.

### **Preparation of Alumina**

Alumina (75.0 g) was dried in oven at 110  $^{\circ}$ C for 2 h until provided a constant weight. The dried alumina (50.0 g) was added in beaker glass, poured with oxalic acid (100 mL, 10%) and stirred for 9 h at room temperature. This mixture was further decanted, filltered, washed with aquades. The solid precipitate of alumina-treated with oxalic acid was dried in oven for 12 h at 70  $^{\circ}$ C, and the product was analysed using FTIR spectrometer.

## First coating of chitosan-alumina adsorbent

Gel of chitosan (43.36 g) was added water (100 mL) in glass beaker and heated at 40-50 °C. Then, it was gently added suspency of alumina-treated with oxalic acid (50.0 g) in water. This mixture was stirred until homogene and left at room temperature. This product was decanted and filtered with Buchner funnel. The resulted filtrate was washed with a quabidest, and dried in oven for 12 h at 55  $^{\circ}$ C.

## Second coating of chitosan-alumina adsorbent

The disolved product from first coating chitosan-alumina adsorbent (43.46 g) in aquades (100 mL) was stirred for 4 h at room temperature, and decanted. The filtrate was discarded, and the precipitate afforded was added with sodium hydroxide (125 mL, 1.0 M) and stirred for 30 min. Then, this mixture was left at room temperature, decanted, filterred and eashed with aquabides (250 mL). The precipitate was dried in oven 55 °C for 4 h to afford the product as white solid (66.26 g), and it was analysed its functional groupds using FTIR spectrometer and analysed the degree of deacetylation. This product was applied for further used as a chitosan-alumina adsorbent.

## **Determinantion of pH optimum adsorption**

A 10 mL of Cr(VI) solution (100 ppm) in beaker glass was adjusted to pH 1 by addition solution of sodium hydroxide (0.1 M) or hydrochloric acid (0.1 M). This solution was diluted quantitatively until 25 mL and was added chitosan-alumina adsorbent (0.1 g). This mixture was then shaked with mechanical shaker at 125 rpm for 60 min. The mixture was filtered and the filtrate afforded was measured using spectrometer to determine Cr(VI) concentration. Using similar procedure was undertaken process with different pH conditions i.e. 2, 3, 4, 5, 6, and 7.

### **Determination of contact time adsorption**

Ten mL of solution Cr(VI) (100 ppm) was adjusted to pH 2 by addition a solution of sodium hydroxide (0.1 M) or hydrochloric acid (0.1 M). This solution was adjusted to 25 mL of total volume by addition of aquades. Then, it was placed in glass beaker, and added with chitosan-alumina adsorbent (0.1 g). This mixture was shaked with mehanical shaker at 125 rpm for 60 min, and filterred. The resulted filtrate was measured using spectrometer to determine Cr(VI) concentration. Using similar procedure was undertaken determination of contact time adsorption with variation shaking for 10, 20, 30, 40, 50, and 80 min, respectively.

### **Determination of adsorption capacity**

A 25 mL solution of Cr(VI) (100 ppm) was adjusted to pH 2 by addition solution of sodium hydroxide (0.1 M) or hydrochloric acid (0.1 M), and poured on 100 mL-glass beaker. Then, it was added chitosan-alumina adsorbent (0.1 g), and shaked under mechaninal shaker at 125 rpm for 60 min. The mixture afforded was filterred, and the filtrate was analysed using spectrometer to detemine Cr(VI) concentration. Using similar procedure was performed treatment with differ variation of chitosan-alumina adsorbent i.e. 200, 300, 400, 500, and 600 ppm respectively.

## **RESULTS AND DISCUSSION**

## Preparation of chitosan-alumina adsorbent Preparation of chitosan gel

Chitosan was dissolved in 10% solution of oxalic acid, and heated to afford complete solution. Then, this was left for a while until a clear-brown gel was formed. This process was aimed to swell and activate the chitosan structure. Chitosan is one of polysaccharide contains

D-glucosamine structure, and also contain starch as a granule. Interaction of chitosan with oxalic acid able to absorp water molecule and affect its structure swollen up, however the degree of swelling was limited. Heating process in 40-55 °C is proved able to increase chitosan granule.

The observed process during gel formation was initiated by changing the color of suspency from a clear during heating. The translation of chitosan solution was followed with swelling its granule. The kinetics energy of water molecules increases over heating and stronger than interaction between chitosan molecules. This affects the reducing hydrogen bonding or hydrogen interaction of chitosan molecule in granule. On the other hand, over heating process the oxalic acid kinetic energy increases and much higher than interaction between chitosan molecule in granule. This causes the oxalic acid molecule easily penetrate, enter the granule and bind inside the chitosan granule system.

The presence of hydroxyl groups in chitosan structure promotes the swelling by adsorption of water molecules, and also increase viscocity of the system due to carboxylic groups from the outside penetrate inside of the granule before suspency was heated. During gel formation of chitosan was also observed color changing from a clear brown to white during cooling, and reaction of chitosan with oxalic acid was presented in Figure 1.



Figure 1. Schematic reaction of chitosan and oxalic acid

## **Preparation of alumina**

The drying of alumina in 110 °C over 2 h was aimed to reduce water contents. Meanwhile activation was performed with addition of oxalic acid. This process formed a ring structure from complex of alumina(III) oxalate as a white powder. The reaction was schematically presented in Figure 2.



Figure 2. Reaction of alumina and oxalic acid

### Coating of chitosan in alumina

Figure 3 presents chitosan-alumina reaction. This is a coating process which is aimed to provide more chitosan structure sitting in alumina pores, and to afford its structure more hindered and stable when exposed in low pH. The amino group (NH<sub>2</sub>) of chitosan as active side is also more supported by alumina and not directed facing inside of the alumina. As result can increase number of site active in pores.

The journal homepage www.jpacr.ub.ac.id ISSN : 2302 - 4690 Choosing of alumina as a solid supporting material for chitosan adsorbent considers its pores size, and have a fine structure. And also, the numbers of side actives of chitosan in alumina pores can be developed and increased by coating with other material or recoating, recoating of chitosan-alumina with a half-part of chitosan.



Figure 3. Schematic formation of chitosan-alumina adsorbent

## Characterization of chitosan-alumina adsorbent

Chitosan was applied as adsorbent isolated from chitin. This was deacetylated using 50% of sodium hydroxide solution. In practice, chitin and chitosan can be determined according to their solubility in acetic acid. Polymer of chitin is not soluble in a dilute of acetic acid solution. During preparation, a depigmentation of shrimp shell powder is chitin polymers, and the soluble product in a dilute acetic acid of the resulted polymer after deacetylation step is chitosan [12]. The degree of deactylation of chitosan can be calculated spectrometrically using infra red spectrometer. The result gives 86.97 *dd* according to Wood Kellog Method (equation 1). The higher the value of *dd*, the purer of the isolated chitosan was afforded.

$$dd = 98.03 - \left[ 34.68 x \left( \frac{absorbancy on N - H amide}{absorbancy on C - H methylene} \right) \right]$$
(1)

Where dd = degree of deacetylation; 98.03 is the highest value of deacetylated chitosan; and 34.68 is the lowest value of deacetylated chitosan.



Figure 4. Infrared spectra of chitosan, alumina, and a chitosan-alumina adsorbent

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Characterisation of functional group of chitosan side active was undertaken using infrared spectrometry. Changing the infrared spectra was indicated from chitosan, alumina, and chitosan-alumina adsorbent (Figure 4). Tabulation of the functional groups and band absorption was presented in Table 1.

Functional groups*	Alumina		Chitosan		Chitosan-Alumina	
					Adsorbent	
	Peak	$v (cm^{-1})$	Peak	$v (cm^{-1})$	Peak	$v (cm^{-1})$
O-H	1	3458.68	1	3422.03	1	3466.39
=С-Н	-	-	2	2939.78	2	2928.21
C=O	-	-	4	1633.85	4	1703.30
N-H (amine)	-	-	5	1541.26	5	1679.15
N-H (amide)	-	-	6	1448.67	6	1429.38
C-H metal	-	-	-	-	-	-
C-N (amine)	-	-	7	1032.01	-	-
Al-O	3	985.07	-	-	7	924.07
A second in set $D = f [12]$						

**Table 1.** Tabulation of the main peaks FTIR spectra of alumina, chitosan, and chitosan-alumina adsorbent

\*According to Ref. [13]

According to infrared spectra interpretation (Table 1), indicated that chitosan-alumina adsorbent was afforded. A mixture bands reveal the interaction of chitosan and alumina. The presence of C=O of oxalate in chitosan-alumina recorded at 1703.30 cm<sup>-1</sup> (peak 4), bending vibration of N-H amine from chitosan at 1579.15 cm<sup>-1</sup> (peak 5), and Al-O band of alumina in 924.07 cm<sup>-1</sup> (peak 7) was also observed. Band from KBr was also showed between 2400 and 2200 cm<sup>-1</sup> [14]. Band for alumina in 2361.08 cm<sup>-1</sup> (peak 2), peak 3 on chitosan, and peak 3 on chitosan-alumina (2359.15 cm<sup>-1</sup>) was a characteristic band from KBr.

A literature result from Boddu and Smith (2002) [10] reported the character of chitosan-alumina adsorbent according to Brunauer Emmett Teller (BET) theory had surface area 105.2 m<sup>2</sup>/g, pore volume 0.187 cm<sup>3</sup>/g, and pore diameter 71.2 A<sup>o</sup> as a white powder. However for this result, we have no report.

## Adsorption of Cr(VI) by chitosan-alumina adsorbent Detemination of pH optimum

Optimation of pH conditions during adsorption of Cr(VI) by chitosan-alumina adsorbent was performed using variation of pH from 1 to 7. The maximum adsorption of Cr(VI) on conditioned pH was defined as its pH optimum adsorption. The result was reported in Figure 5.

The adsorption of Cr(VI) increases from pH 1 to 2. This was predicted because protonation of the amino groups of chitosan-alumina adsorbent occur, and afforded ammonium ions which able to neutralize the negative charge in the alumina-sides. This condition probably can promote more interaction between adsorbent and chromium (VI) metal which presences as  $HCrO_4^-$  or  $CrO_4^-$ . This interaction occurs as an electrostatic interaction [15]. Meanwhile, position at pH 2 was determined as optimum adsorption, because the number of Cr(VI) adsorbed by chitosan-alumina adsorbent in equilibrium, and the number of Cr(VI) adsorbed after pH 2 was decrease steadily by increasing pH value. This condition also increases the presence of hydroxyl groups (-OH), and compete with  $Cr_2O_4^{=}$  to interact with adsorbent.



**Figure 5**. Adsorption of Cr(VI) using **Figure 6**. Mechanism of chromium(VI) chitosan-alumina adsorbent in various pH adsorption value

The high pH means decreasing of proton number and lowering interaction of amino group with proton. As an affect, the ionic interaction between adsorbent and  $Cr_2O_4^{=}$  decreasing. This also affects on alumina, where active side on alumina persist in negative charge, and can distract ionic interaction with  $Cr_2O_4^{=}$ . The influence of pH on adsorption process is a complicated interaction, acidity pH solution can changing the adsorbent's surface properties, molecular properties of the adsorbant and solution composition. Schematic of mechanism is showed in Figure 6.

Statistical analysis with error margin 5% gave  $F_{calc.}$  253.8262 and the  $F_{table}$  recorded 7.19 (error margin 5%). This analysis indicated variation of pH solution significantly affect Cr(VI) adsorption. The BNT test also gave a significant difference value during treatment from pH 1 until 7, and adsorption efficiency recorded at pH 2 with 91.85% of adsorbed Cr(VI).

#### **Determination contact time optimum for adsorption**

Determination of contact time adsorption was undertaken at pH 2 with variation on shaking time from 10 to 80 minute. This was aimed to find out minimum time to adsorb a maximum of Cr(VI) by developed adsorbent. The result is displayed in Figure 7.

Contact time affects on Cr(VI) adsorption. The adsorbed of Cr(VI) increases from 20 to 60 minute, and it decreases from 60 to 80 minute adsorption. It was predicted that during 20 until 60 minute adsorption process, the number of adsorbed Cr(VI) in adsorbent was not in equal number with it in a solution. But, equilibrium has occured after 60 to 80 minute adsorption. Further BNT statistical analysis (error margin 5%) gave  $F_{calc.}$  82.5164 while  $F_{table}$  7.19 for contact time between 20 and 60 minute. It means during this interval significantly affect the number of Cr(VI) adsorption. However, contact time between 60 and 80 minute was not gave a significant difference on statistical analysis, and means equilibrium was occur. From this result, it was also recorded that optimum contact time is achieved at 60 minute adsorption with 87.06% of Cr(VI) is adsorbed.



**Figure 7**. The effect of contact time toward the adsorption activity of Cr(VI) of developed chitosan-alumina adsorbent

**Figure 8.** Correlation of the increasing Cr(VI) concentration toward adsorption capacity of developed adsrobent

## **Determination of adsorption capacity**

The adsorption capacity of developed chitosan-alumina adsorbent was study by applying the variation of Cr(VI) concentration (100, 200, 300, 400, 500 and 600 ppm), using pH optimum 2 and 60 minute contact time. The result is presented in Figure 8.

The number of Cr(VI) adsorbed increase with increasing initial Cr(VI) concentration from 100 to 300 ppm. During this condition, transfer of Cr(VI) from the solution to the adsorbent surface occur sharply, and remain its concentration level on the solution equilibrium to its adsorbed. Statistical analysis also gave significant difference value. The  $F_{calc.}$  gave 8019.79 with 5% of error margin while  $F_{table}$  3.02. Conversely, at initial concentration above 300 ppm, 400-600 ppm indicates steady adsorption, and statistical analysis also did not give significant difference value. This result can be summarized that adsorption capacity of the developed chitosan-alumina adsorbent was achieved in 66.90 mg/g with initial concentration 300 ppm. This number is smaller that that reported by Boddu et al. with 154 mg/g under pH 4 and 60 minute contact time using alumina as supporting material [10].

## CONCLUSION

The infrared spectra give a conformed functional group of the developed chitosanalumina adsorbent at 1703.30 cm<sup>-1</sup> (C=O) from oxalate, 1679.15 cm<sup>-1</sup> band due to bending vibration of N-H amino group of chitosan, and also vibration band Al-O of alumina at 924.07 cm<sup>-1</sup>. and also the optimum pH 2 and 60 minute contact time with adsorption capacity 66.90 mg/g was afforded.

## REFERENCES

- [1]. Marganof P., Potensi Limbah Udang Sebagai Penyerap Logam Berat Timbal, Kadmium dan Tembaga di Perairan. *Jurnal Program Pasca Sarjana (S3)*, **2003**, 12 (2), 172-184.
- [2]. Casteen, T. G. Qualitative and Instrumental Analysis of Enviromentally Significant Elements, **1993**, John Wiley and Sons Inc., London.
- [3]. Low, K. S., C. K. Lee, and S. G. Tan, Environ. Technol., 1997, 18 (4), 449-454.
- [4]. Tee, Tan Wee, and Abd Rahman Majid Khan, *Environ. Technol.*, **1988**, 9 (11), 1223-1232.
- [5]. Munaf, E. dan Zein, R. Jurnal Kimia Andalas, 1999. 5 (1), 10-14.

- [6]. Wan Ngah, W. S., and K. H. Liang. Ind. Eng. Chem. Res., 1999, 38 (4), 1411-1414.
- [7]. Yang, Tony C., and Robert R. Zall, Ind. Eng. Chem.: Prod. Res. Dev., 1984, 23 (1), 168-172.
- [8]. Pradip Kumar Dutta, Joydeep Dutta, and V. S. Tripathi, J. Sci. Ind. Res., 2004, 63, 20-31.
- [9]. Hanung, H. Perbandingan Keefektifan Adsorben Pb (II) pada Adsorben Kitosan dan N-Karboksimetilkitosan. Skripsi (undergraduate thesis), Jurusan Kimia Fakultas MIPA Universitas Brawijaya. Malang, 2004.
- [10]. Veeram Boddu, Krishnaiah Abburi, Jonathan L. Talbott, and Edgard Smith, *Environ. Sci. Technol.* **2003**, 37, 4449-4456.
- [11]. Sofana, I, Sintesis *N*-karboksimetilkitosan melalui hidrogenasi, *Skripsi (undergraduate thesis)*, Jurusan Kimia, Universitas Brawijaya, Malang, **2003**.
- [12]. Budi Prasetyo, Totok Adiarto, and Djudjuk Sukandiati, Pengaruh Lama Pemanasan dan Konsentrasi NaOH Terhadap Sifat Mekanik Membran Kitosan. *Kumpulan Makalah* seminar Nasional Kimia XVI. Yogyakarta. 14 April 2005.
- [13]. Hardjono Sastrohamidjojo, Dasar-Dasar Spektroskopi. 2<sup>nd</sup> edition, **2001**. Liberty. Yogjakarta, p 12.
- [14]. Nyquist R. A. and Kagel R. O., Infrared spectra of inorganic compounds (3800–45 cm<sup>-1</sup>), **1971**, Academic Press Inc., New York.
- [15]. Maiqun, Fu, Journal of Sichuan University (Engineering Science Edition), 1997, 1 (5), 8-13.