Influence of pH on Cr(VI) ions removal from aqueous solutions using carboxymethyl cellulose-based hydrogel as adsorbent

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Abstract. The major problem in heavy metal pollution is that these metals are not biodegradable and accordingly accumulate in the bodies of living organisms, causing dangerous diseases and serious cell disorder. According to World Health Organization (WHO), the long term exposure of Cr(VI) levels of over 0.1 ppm causes respiratory problems, liver and kidney damage, and carcinogenicity. Due to its easy operation and of various cheap adsorbents development, adsorption has been proved to be efficient and most economically attractive technique and feasible to the removal of toxic heavy metal from wastewater. The study aimed to report the removal of Cr(VI) ions from aqueous solutions through adsorption process using carboxymethyl cellulose-graft-poly(acrylic acid) (CMC-g-PAA) hydrogel as adsorbent. Effect of pH was studied to remove hexavalent chromium. Graft copolymerization of poly(acrylic acid) onto carboxymethyl cellulose was carried out in the presence of benzoyl peroxide redox initiator and methylenbisacrylamide as crosslinker agent. Batch experiments were carried out to investigate the effects of initial pH. The adsorption of Cr(VI) ions as a function of pH was conducted in the initial pH range of 1 to 8. The results indicated that acidic pH strongly favored the adsorption. The optimum pH for adsorption of Cr(VI) ranged from 1 to 3, and the maximum uptake of Cr(VI) from the solution was 6.53 mg/g at pH 1 and 30°C. FTIR spectroscopy, SEM analyses were performed on the adsorbent before and after Cr(VI) binding. All analyses confirmed the complexation of Cr(VI) ions on the adsorbent.

1. Introduction
Heavy metals ion such as chromium, copper, lead, zinc, mercury, and cadmium are present in wastewater from various industries such as electroplating, tanning factories, steel works, wood preservation, plastic procession, metallurgical and mining activities, atomic power plants, dyes and pigments, chromate preparation, ceramic paints, and fertilizer industries [1-2]. The introduction of these harmful pollutants into aquatic systems is due to various industrial operations, which increase annually to cover the continuous needs from the rapid increase in the global population. The major problem in heavy metal pollution is that these metals are not biodegradable and accordingly accumulate in the bodies of living organisms, causing dangerous diseases and serious cell disorders. Among of the very complicated environmental pollution problem, the pollution of water resources with different agricultural and industrial effluent is a matter of great importance. According to World Health Organization (WHO), the long term exposure of Cr(VI) levels of over 0.1 ppm causes respiratory problems, liver and kidney damage, and carcinogenicity. Therefore it is necessary to treat effluents to reduce the Cr(VI) concentration in water and wastewater prior to its transport and cycling in environment [1].
Chromium species presence mainly in two different oxidation states in environmental water, namely Cr(VI) and Cr(III), of which possesses contrasting physiological effects. Cr(III) is considered as an essential trace element for the maintenance of an effective glucose, lipid, protein metabolism in mammals. On the other hand, Cr(VI) can be toxic for biological systems and cancerogenic in humans. Therefore speciation of Cr(VI) and Cr(III) is necessary to evaluate the toxicological behavior. Recently, chromium speciation was reported [4].

The removal of metal ions from aqueous solutions by adsorption depends on the solution pH since the acidity of the solution affects the ionization of the metal ions and concentration of the counter H⁺ ion of the surface groups. To maximize the removal of heavy metals by adsorbents, knowledge of an optimum pH is important [10].

When Cr(VI) comes in contact with organic substances or reducing agent (adsorbent), Cr(VI) is easily or spontaneously reduced to Cr(III) in an acidic medium due to its high redox potential value. The mechanism of Cr(VI) removal by cellulose adsorbent is an electrostatic attraction process in which Cr(VI) are present in the form of anions, such as HCrO₄⁻ and Cr₂O₇²⁻, while the surface of cellulose adsorbent has positive charges [1].

Techniques used for removal of heavy metal from polluted wastewater include chemical precipitation, ion exchange, adsorption, solvent extraction, flocculation, membrane separation, filtration, electrolysis and reverse osmosis. Due to its easy operation and of various cheap adsorbents development, adsorption has been proved to be efficient and most economically attractive technique and feasible to the removal of toxic heavy metal from wastewater [4-6].

Various adsorbent has been developed to remove heavy metal ions from aqueous solutions, such as clay, ion exchange resins, activated carbon, carbon nano-tubes, and metal oxides [1]. A variety of biomaterial have been exploited as adsorbent for the removal of Cr(VI) from industrial effluents [5-6]. Cellulose, the main constituent of plants, is the most abundant biomass in the world. However, the compact and inactive molecular structure of cellulose requires to be modified to improve is hydrophilicity as an adsorbent [7]. It is renewable, cheap, biodegradable, and can be chemically modified for enhancing its effectiveness by introduction of new functional groups. There is intensive research nowadays for the application of cellulosic material for hazardous contaminant adsorption from aqueous wastes. To date, the cellulose-based material are prepared by carboxymethylation, grafting and cross-linking [7]. Among of the cellulose-based materials, carboxymethyl cellulose (CMC) is a representative water-soluble cellulose derivative, biocompatible, nontoxic and low cost. CMC is used as an adsorbent for heavy metal and dye sorption from various wastewaters systems which have binding sites for divalent cations due to the presence of various functional group within its [2,7].

This paper aims to report the removal of chromium ions from aqueous solutions using carboxymethyl cellulose-acrylic acid graft hydrogel as adsorbent. Effect of pH has been studied to remove hexavalent chromium.

2. Experimental

2.1. Material

Potassium dichromate (K₂Cr₂O₇) analytical reagentgrade was used as a source of Cr(VI). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for pH adjustment. All chemicals were purchased from E-Merck Company Inc., German and were used without further purification. Deionized water was used in this work.

2.2. Method

2.2.1. Preparation of the adsorbent

The graft copolymer of CMC-g-PAA was synthesized by free radical and solution polymerization. CMC was dissolved in distilled water then stirred and purged by passing nitrogen gas. The solution was slowly heated up to desired temperature then added with benzoyl peroxide (BPO) initiator and methylenbisacrylamide (MBA) crosslinker agent. The reaction was continued until desired time and...
process of polymerization was completed. The hydrogel adsorbent was oven-dried, then purified by washing with distilled water and acetone [8].

2.2.2. Preparation of \( \text{Cr(VI)} \) solution

The stock of \( \text{Cr(VI)} \) ions solution at concentration of 1000 mg/L was prepared by using \( \text{K}_2\text{Cr}_2\text{O}_7 \) as a source of \( \text{Cr(VI)} \) ions. Experimental solutions of the desired concentrations were obtained by successive dilution. 0.5 M \( \text{NaOH} \) or 4 N \( \text{HNO}_3 \) was used for pH adjustment and controlled by pH meter [9].

2.2.3. Effect of pH

In this study, the pH on adsorption of \( \text{Cr(VI)} \) was varied of 1 – 8 at room temperature by shaking dry CMC-based hydrogel (100 mg) with \( \text{Cr(VI)} \) solution (100 mL, 10 mg/L) for 10 hrs at 300 rpm. \( \text{HCl} \) 4 N was applied to decrease the pH and \( \text{NaOH} \) 0.5M to increase pH. Absorbance of the standards and samples of chromium was recorded on atomic absorption spectrophotometer (Varian Type).

2.2.4. Adsorption

Adsorption was carried out in a 250 mL volumetric flask using 100 ml \( \text{Cr(VI)} \) ions solution. The flasks were placed on a Gallenkamp Orbital Incubator Shaker running at 100 rpm, 30°C for 10 hr. The amount of \( \text{Cr(VI)} \) adsorbed by the CMC-g-PAA hydrogel adsorbent \( (Q_e) \) and removal percentage \( (R\%) \) of \( \text{Cr(VI)} \) were calculated for each run by following equations,

\[
Q_e = \frac{(C_0-C_e)V}{W} \quad (1)
\]

\[
R\% = \frac{C_0-C_e}{C_0} \times 100 \quad (2)
\]

Where \( Q_e \) (mg/g) is the adsorption capacity, \( R \) (%) is removal percentage, \( C_0 \) (mg/L) is the initial concentration of \( \text{Cr(VI)} \), \( C_e \) (mg/L) is the equilibrium concentration of \( \text{Cr(VI)} \), \( V \) (L) is the volume of the solution of \( \text{Cr(VI)} \), \( W \) (g) is the weight of adsorbent added, and \( C_0 \) and \( C_e \) are initial and final respectively [11-12].

3. Result and discussion

3.1. Effect of pH

Result of the adsorption of \( \text{Cr(VI)} \) as a function of pH is shown in Figure 1. It shows that the adsorption of the cellulose adsorbent was highly pH dependent. \( \text{Cr(VI)} \) removal efficiency decreased with increasing the initial pH. The optimum pH for \( \text{Cr(VI)} \) removal was found at 1.0, and a maximum adsorption capacity of \( \text{Cr(VI)} \) 6.53 mg/g was obtained. About 21.5% removal was achieved at a pH of 2, which increases to about 64.3% at pH 1. The improved removal of Cr at low pH is probably due to reduction of hexavalent Cr to trivalent Cr [15].

At low pH:

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

At moderate pH:

\[
\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}
\]
At a lower pH (pH ≤ 3) value, Cr(VI) exist mainly is HCrO$_4^-$, CrO$_7^{2-}$, which have negative charge, while the surface of adsorbent is charged positively. The stable forms of chromium such as H$_2$CrO$_4$ and CrO$_3$ exist as polynuclear species at high Cr(VI) concentration, and hence the low pH value results in a higher percentage removal of Cr(VI). High adsorption at acidic pH condition could be explained by the chemical character of the chromium species and the adsorbent surface. In the acidic pH range (1 – 2), the prominent formation of the chromium are Cr$_2$O$_7^{2-}$, HCrO$_4^-$, and above pH 7 the primary stable species is CrO$_4^{2-}$. Therefore, at lower pH, Cr$_2$O$_7^{2-}$ and HCrO$_4^-$ were adsorbed onto the adsorbent, resulting in a high percentage of adsorption. At basic pH condition, the suppression of the hydrolysis of Cr(VI) may be the reason for the decreased adsorption [16]. At low pH, there is presence of a large number of H$^+$ ions, which in turn neutralizes the negatively charged adsorbent surface thereby reducing hindrance to diffusion of dichromate ion. It is anticipated that the effect of pH on adsorption is also governed by the development of an electric double layer on the adsorbent. The polarity of the double layer at the adsorbent surface may be the changed from positive to negative as the H$^+$ion concentration changes from acidic to basic with the increase of pH. It was found that at lower pH the system attain equilibrium faster and also the percentage of chromium adsorbed increased[15].

At pH ≥ 1.0, the adsorption efficiency of Cr(VI) decreases as pH increases. This may be explained on the basis of the lower extent protonated hydroxyl groups with rising pH or due to the dual competition between both the anions (CrO$_4^{2-}$ and OH$^-$) to be adsorbed on the surface of the adsorbent of which OH$^-$ predominant [1,3].

pH solution plays an important role during the adsorption process and affect the surface charge of cellulose adsorbent, the degree of ionization, and speciation of adsorbate. The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore the adsorption of other ions is affected by the pH of the solution [1,13].The pH of the aqueous solution affects the solubility of the metal ions, concentration of the counter ions on the functional groups on the sorbent and the degree of the ionization of the sorbent during the reaction. The active sites on the sorbent can either be protonated or deprotonated depending on the pH. Concurrently, the sorbent speciation in a solution also depends on the pH [14].

### 3.2 FTIR spectrum

Figure 2 shows the FT-IR spectrum of the CMC-g-PAA hydrogel adsorbent before and after adsorption of Cr(VI). The peak at 2920 cm$^{-1}$ and 2922 cm$^{-1}$ were due to the stretching vibration of aliphatic C-H. The peak at 1548 cm$^{-1}$ and 1544 cm$^{-1}$ was due to asymmetrical stretching vibration of COO$^-$ groups. Similar peak at 1398 cm$^{-1}$ and 1402 cm$^{-1}$ are assigned to symmetrical stretching vibration of
vibration of COO groups whereas peak appeared in 1017 cm\(^{-1}\) and 1021 cm\(^{-1}\) were attributed to the C-O-C stretching vibration[2].

![IR spectra of CMC-g-PAA hydrogel adsorbent (a) and Cr(VI) loaded adsorbent (b).](image)

Figure 2. IR spectra of CMC-g-PAA hydrogel adsorbent (a) and Cr(VI) loaded adsorbent (b).

To identify the possible functional groups on carboxymethyl cellulose adsorbent involved in the binding of Cr(VI), FTIR spectra were obtained before and after metal adsorption. If a ligand coordinates to a metal, the energy of the ligand material will most likely be perturbed leading ultimately to subtle shifts in the absorption peaks in the FTIR spectra. These FTIR absorption bands are usually shifted to lower or higher frequencies. Figure 2 shows the FTIR spectra of carboxymethyl cellulose adsorbent before and after Cr(VI) adsorption. There was a small shift of the ring vibration peak at 1706 cm\(^{-1}\), 1402 cm\(^{-1}\), 1171 cm\(^{-1}\), 1021 cm\(^{-1}\) in carboxymethyl cellulose adsorbent to 1702 cm\(^{-1}\), 1398 cm\(^{-1}\), 1164 cm\(^{-1}\), 1017 cm\(^{-1}\) for Cr(VI) loaded adsorbent [1].

3.3. SEM Image
SEM images of carboxymethyl cellulose adsorbent before and after adsorption are shown in Figure 3.

![SEM micrograph of CMC-g-PAA adsorbent before (a) and after (b) adsorption.](image)

Figure 3. SEM micrograph of CMC-g-PAA adsorbent before (a) and after (b) adsorption.

The SEM micrograph of hydrogel adsorbent showed fractured and rough surface morphology providing better adsorption sites. It can be observed that the surface of the adsorbent after adsorption changed, and the visible pores of the adsorbent had disappeared or had been filled up [1].

4. Conclusion
Current study concluded that the adsorption of Cr(VI) was pH dependent. The removal efficiency of adsorbent increased with the decreasing in pH. At pH of 1 about 64.3% Cr(VI) removal was possible. The present study showed that CMC-g-PAA hydrogel was effective adsorbent for Cr(VI) metal ions removal from aqueous solution. The adsorption of Cr(VI) ions was pH dependent. CMC-g-
PAA hydrogel was found to be a favourable adsorbent. Characterization with FTIR and SEM confirmed the binding of Cr(VI) onto the carboxymethyl cellulose adsorbent.

Acknowledgement
The authors gratefully acknowledge the Research Unit for Clean Technology-LIPI, Bandung, Indonesia, for providing financial support and facilities required to carry out this work.

References
[1] Chunxiang L, Sha Q, Wei L, Yifan L, Danhui L, Xiaojuan L, and Minghua L 2014 *BioResources*. (9) 4 6998-7017.
[2] Ali J Salim 2015 *Journal of Al-Nahrein University*. 18 (4) 40-48.
[3] Mack C, Wilhelmi B, Duncan J R, Burgess J E 2007 *Biotechnol. Adv.* 25264-271.
[4] Jun Dai, Ren F L, Tao C Y 2012 *Int. J. Environ. Res. Public Health*. 9 1757-1770.
[5] Li C, Zhang Y, Peng J, Wu H, Li J, Zhai M 2012 *Radiation Phy. and Chem.* 81 967-970.
[6] Abdel-Halim E S, and Al-Hoqbani A A 2015 *BioResources*. 10 (2) 3112-3130.
[7] Genlin Z, Lijuan Y, Hui D, Ping S 2013 School of Chemistry and Chemical Engineering, Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, China.
[8] Lik A, Nuri A, Agus H 2015 *Macromol. Symp.* 353178-184.
[9] Selvarani M, Prema P 2012 *Int. J. of Env. Scie.* 2(4).
[10] Sanna Hokkanen 2014 *Thesis, Lappeenranta University of Technology, Finland.*
[11] Jian H C, Hai T X, Hong X G, Guo P L, Wen W, Shi R H 2013 *J. of Hazardous Mat.* 285-294.
[12] Gad, H M H, Nabila A M 2014 *Int. J. of Adv. Scie. Tech. Res.* 4 (4) 184-201.
[13] Govindarajan C, Ramasubramaniam S, Gomathi T, Sudha P N 2011 *Archives of Appl. Scie. Res.* 3 (5):572-580.
[14] Abdul-Reheim M A R, Farag R, El-Saeed S M, and Abdel-Raouf M E 2015 *Res. J. of Pharmac. Biol. Chem. Scie.* 6 (6) 1197-1212.
[15] Verma A, Chakraborty S, Basu J K 2006 *Separation Purification Technol.* 50 336-341.
[16] Xuemei H, Huidong X, Hui L 2015 *World J. of Eng. Technol.* 3, 234-240.