Adsorption of Hexavalent Chromium from Aqueous Solutions by Chitosan/Chitosan Beads

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Abstract

Adsorption of hexavalent chromium from aqueous solutions by chitosan and chitosan beads has been studied through using batch adsorption techniques. The main objectives of this study are to investigate the hexavalent chromium from aqueous solutions by chitosan and chitosan beads, study the influence of pH, contact time, and initial chromium concentration. The results of this study showed that adsorption of hexavalent chromium by chitosan and chitosan beads observed at the medium pH. The maximum adsorption capacity of chromium absorption by chitosan and chitosan beads of pH 5. The adsorption of hexavalent chromium ions by two adsorbents observed that chitosan beads adsorbs more chromium ions as compared to chitosan. This obtained results showed that adsorption of hexavalent chromium ions by chitosan and chitosan beads reached to equilibrium after 90 min. The adsorption of chromium by chitosan and chitosan beads increased gradually at the higher initial chromium concentration at the constant amount of adsorbent. The obtained results showed that the adsorption of hexavalent chromium followed Langmuir isotherm equation for chitosan and also Freundlich equation for chitosan beads. In conclusion, both chitosan and chitosan beads can be employed as commercial adsorbents in the removal of hexavalent chromium from water and wastewater.

Keywords: chitosan, chitosan beads, adsorption, hexavalent chromium

Introduction

Chromium is one of heavy metals that has been a major interest in water and wastewater treatment. Chromium be able released to the environment through a large number of industrial operations, including metal, steel, iron, pigment, leather, and inorganic chemicals production. Chromium have two ions, trivalent chromium and hexavalent chromium. The hexavalent chromium more toxic than trivalent chromium[1]. The hexavalent chromium has been considered to be more hazardous due to its carcinogenic properties. This pollutants are mutagenic, carcinogenic, and teratogenic characteristics [2] on public, it become a serious health concern.

There are various methods to remove the hexavalent chromium including chemical precipitation, membrane technology, ion exchange, extraction, and electrolysis but these methods have high cost, reagent and energy requirements. Furthermore, these methods have incomplete metal removal and generation of toxic sludge or other waste products that require disposal and treatment[3]. In contrast, adsorption technique is one of the preferred methods for removal of heavy metals which high efficiency and low cost. Recently, the investigation on adsorption of heavy metals for water and wastewater treatment have been carried out for the effective removal using natural adsorbent.

This study concern to investigation the potentially of chitosan and chitosan beads for adsorbent to remove hexavalent chromium. Chitosan and chitosan bead have active site from hydroxyl and amine groups for physical and chemical adsorptions. Chitosan beads present a high adsorption capacity for removal of divalent lead on aqueous solution[4]. The chitosan beads are expected to be a good candidate for an excellent adsorbent of heavy metal ions in waste water stream[5].

This study focus on adsorption of hexavalent chromium from aqueous solutions by chitosan and chitosan beads has been studied through using batch adsorption techniques. The main objectives of this study are to investigate the hexavalent chromium from aqueous solutions by chitosan and chitosan beads, study the influence of pH, contact time, and initial chromium concentration.

Materials and Methods

Materials

Chitosan and chitosan beads prepared from natural chitin which enzyme and chemical extraction. The natural chitin extracted form Shrimp shells, that it was collected from waste of shrimp supplier at Yogyakarta. The deproteinization agent used papain which extracted from *Carica papaya* latex. Sodium hydrogen sulfite, sodium chloride, potassium dihydrogen phosphate, potassium hydrogen phosphate, phosphate acid, sulfuric acid, lactic acid, sodium hydroxide, methanol, chloroform, acetic acid, hydrochloric acid, diphenylcarbazide, potassium dichromate, and aceton purchased from Merck, Germany. All other chemicals and reagents were of analytical grade.

Preparation of Chitosan and Chitosan Beads

Preparation of chitosan and chitosan beads following the enzymatic and chemicals procedure[6]. Chitin was hydrolyzed by 30 % of papain on phosphate buffer solution at pH of 7, demineralized by lactic acid and depigmentation was done by chloroform, methanol and water. Preparation of

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chitosan by two stage deacetylation with 60 % w/v of sodium hydroxide solution. Chitosan was filtered and rinsed with distillate water, and finnally chitosan was dried at 65^oC for 24 hours. Chitosan was diluted on 5 % v/v of acetic acid solution and after that stirred for two hours. The chitosan solution was sprayed into petri dish containing 2 M of sodium hydroxide solution. The chitosan gel was separated and rinsed with distilled water to neutralize residual of sodium hydroxide. The chitosan gel was dried at 65^oC for 24 hours to obtained chitosan beads.

The Study on Adsorption of Hexavalent Chromium

A Stock solution of hexavalent chromium ions of 1000 mg/L was prepared by dissolving the potassium dichromate in distilled water. This stock solution was then diluted to obtain different concentrations. The adsorption of hexavalent chromium from aqueous solutions by chitosan and chitosan beads has been studied through using batch adsorption techniques. Batch adsorption experiments were performed in a 100 mL beaker and equilibrated using a magnetic stirrer. Twenty five milliliter of aliquots on these standard solutions were equilibrated with 100 mg of chitosan and chitosan beads. After filtration, the concentration of hexavalent chromium ion in the supernatant was analysed by using an UV-Vis spectrophotometer methods of coloured hexavalent chromium-1.1-diphenylcabazide complex[1].

The effect of chromium adsorption was studied in the pH range of 3 – 6. The pH of initial solution was adjusted to a pH value using phosphate buffer solution. Chitosan and chitosan beads were equilibrated at particular pH about 120 min and at 25 mg/L initial hexavalent chromium concentration. The effect of contact time, and initial chromium concentration was also studied to determine of the optimum conditions for adsorption of hexavalent chromium. The adsorption capacity was calculated based on the difference of hexavalent chromium concentration in an aqueous solution and the weight of the chitosan and chitosan beads as given below:

$$X = \frac{(C_o - C_a)V}{W}$$

X : adsorption capacity

C_o : initial of hexavalent chromium concentration (mg/L)

C_a : final or equilibrium of hexavalent chromium concentration (mg/L)

V : volume of hexavalent chromium solution (L)

W : weight of chitosan and chitosan beads (g)

Result and Discusion

The Effect of pH

Base on Figure 1. shows the effect of pH on the adsorption of hexavalent chromium by chitosan and chitosan beads. Generally, the capacity of adsorption hexavalent chromium onto chitosan bead more higher than chitosan. The difference porosity and structure chitosan beads be able increase the adsorption capacity of chromium on chitosan. The adsorption on the pH range of 2 – 5 increase significantly by chitosan and chitosan beads but on pH of 6 the adsorption decrease gradually. This data could be explained by the fact that a low pH, the amine groups in the chitosan and chitosan beads were easily protonated, which induced electrostatic repulsion of hexavalent chromium ions[4]. Furthermore, this condition existed a competition between protons and chromium ions for adsorption on active sites of the sorbents.

Figure 1. describes the optimum condition for adsorption of chromium ions on chitosan and chitosan beads at pH of 5, but the adsorption capacity decrease at a higher pH. The degree of dissociation of the hydroxides groups and the negative charge density on chitosan surface, respectively, resulted in a higher adsorption by the electrostatic interaction with chromium ions[4]. Therefore, hydrolysis of chromium ions become decreasing adsorption capacity. The interaction between the ions and amine or hydroxyl group on chitosan drop significantly. The adsorption of hexavalent chromium various as a function of pH with H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ and $CrO4^{2-}$ ions appear as dominant species[3].

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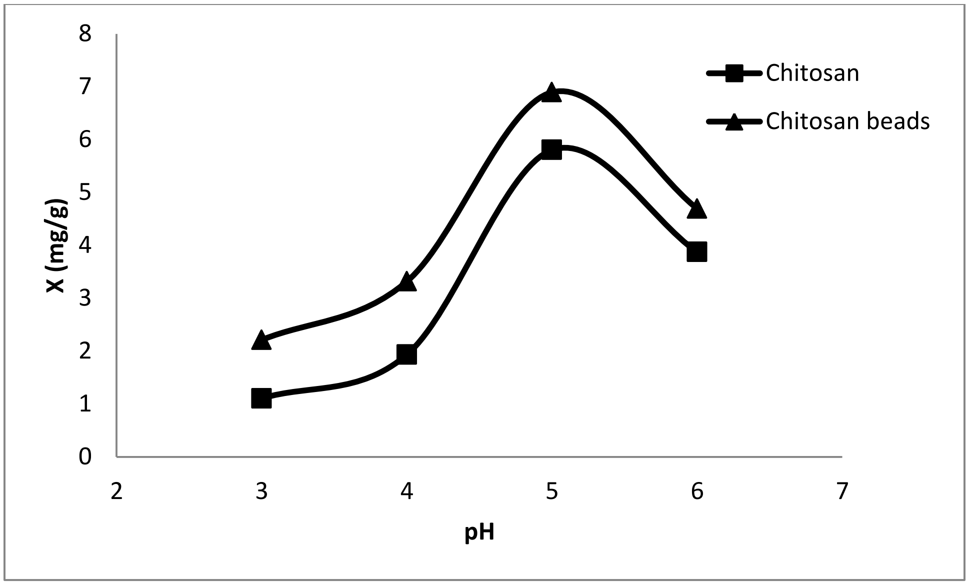

Figure 1. Effect of pH on hexavalent chromium adsorption onto chitosan and chitosan beads

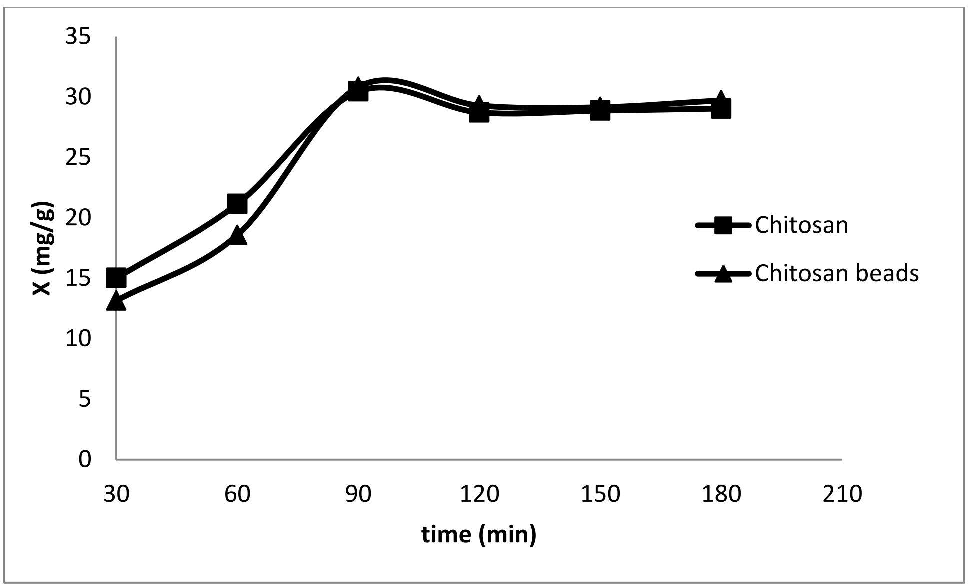

Figure 2. Effect of contact time on hexavalent chromium adsorption onto chitosan and chitosan beads

The effect of contact time on chromium adsorption

The influence of chromium in relation to the contact time between adsorbent and hexavalent chromium aqueous solution was determined. Figure 3 shows that the adsorption of chromium ions increased with contact time and equilibrium was achieved at about 120 min for chitosan and chitosan beads. The optimum contact time for adsorption of chromium ion was reached within 90 min and also the equilibrium concentration just over 120 min. Contact time is one of the effective factor in batch adsorption for removal heavy metal[3]. Base on this data, both chitosan and chitosan beads there are not difference the optimum contact time. The optimum adsorption capacity of chromium ions on chitosan become similar with interaction between chitosan beads and lead ions[4].

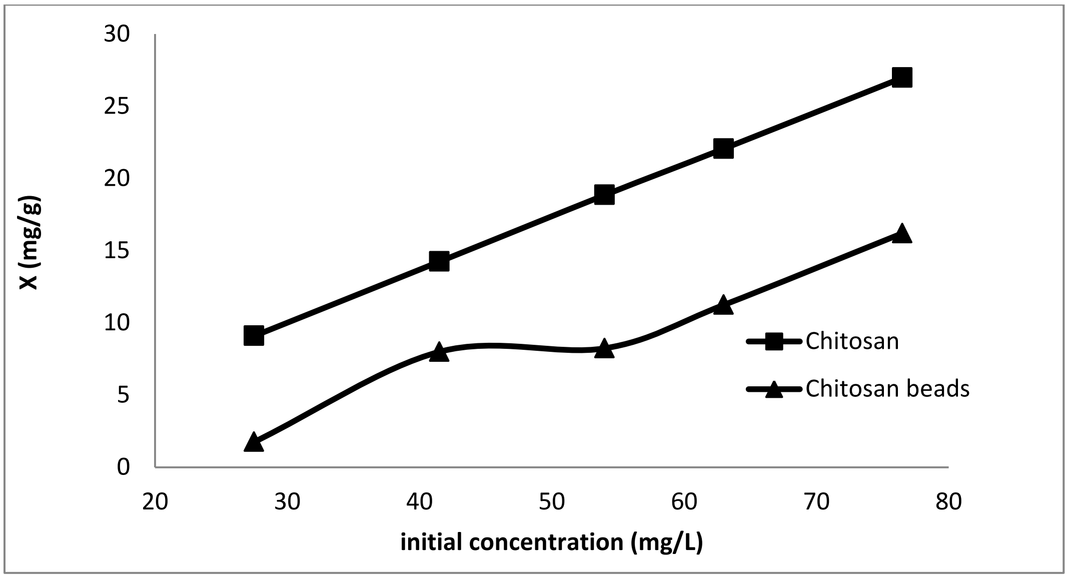

Figure 3. Effect of initial chromium concentration

The Effect of initial chromium concentration

Figure 3 presents the effect of initial concentration of chromium on adsorption process with chitosan and chitosan beads. The results describes that the effect of initial concentration increase significantly for adsorption capacity of chromium ions. The data shows that the adsorption capacity of chromium on chitosan more higher than chitosan beads. In contrast, the data of adsorption capacity for Figure 1 and Figure 2, chitosan beads have more higher adsorption capacity than chitosan.

Adsorption isotherms

Figure 4 shows the equilibrium isotherm for the adsorption of chromium ion onto chitosan and chitosan beads. According the data, the adsorption behaviours for this study described with the Langmuir and Freundlich adsorption equations.

Langmuir equation:

$$\frac{C_a}{X} = \frac{C_a}{X_{maks}} + \frac{1}{X_{maks}} b$$

C_a : the equilibrium or final concentration of chromium ions (mg/L)

X : the amount of chromium adsorbed per weight unit of adsorbent at equilibrium concentration (mg/g)

X_{max} : the maximum adsorption at monolayer coverage (mg/g)

b : the Langmuir adsorption equilibrium constant (L/mg)

Freundlich equation:

$$\ln X = \ln K_f + \frac{1}{n} \ln C_a$$

K_f : the Freundlich constant

n : the constant characterizing the affinity of the metals ions towards adsorbent per weight unit of adsorbent

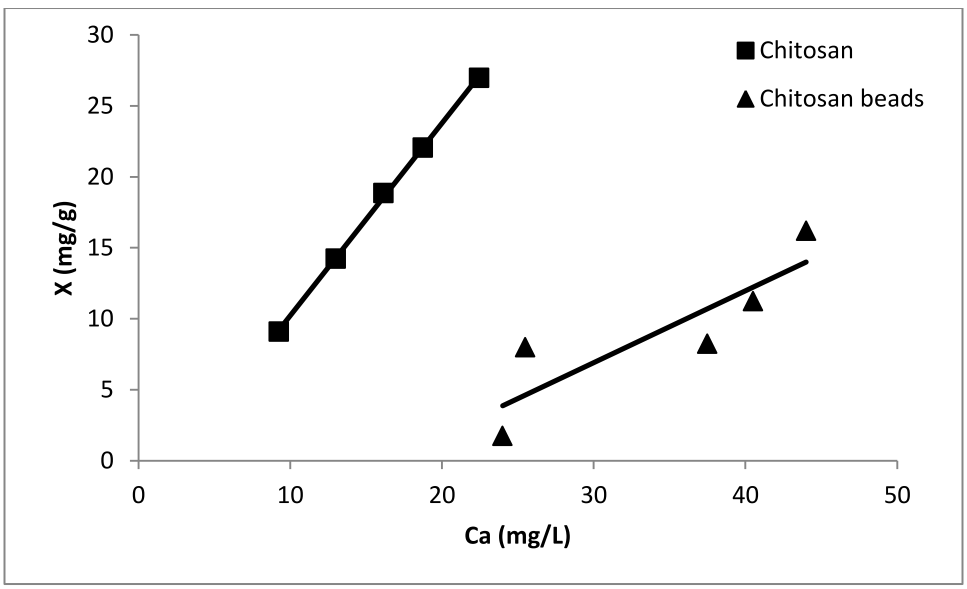

Figure 4. Adsorption isotherm of chromium ion onto chitosan and chitosan beads

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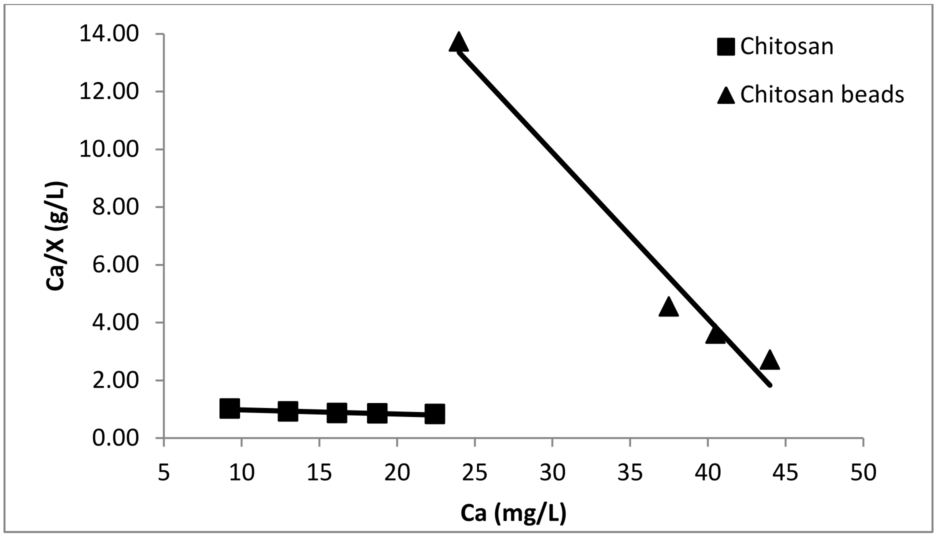

Figure 5. Linear model of Langmuir isotherm for chromium adsorption onto chitosan and chitosan beads

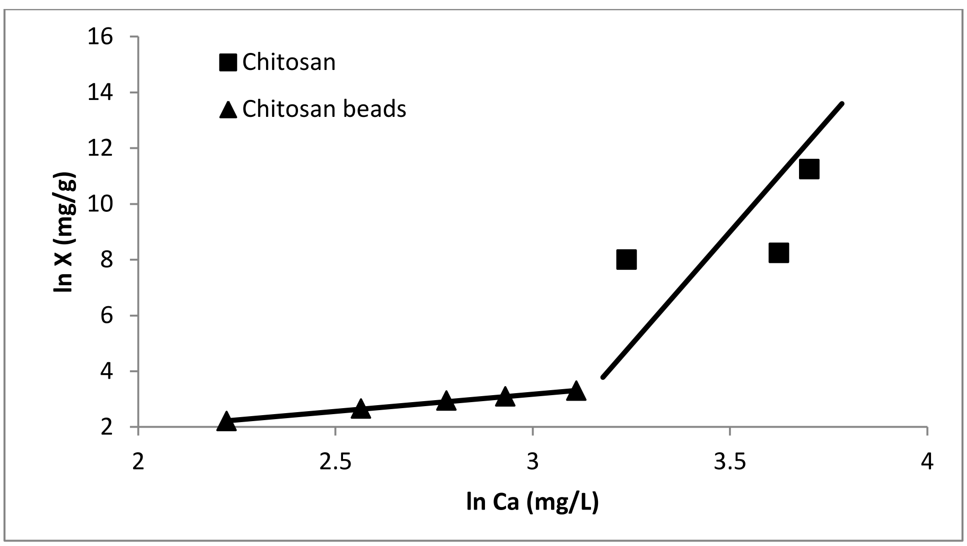

Figure 6. Linear model of Freundlich isotherm for chromium adsorption onto chitosan and chitosan beads

Base on Figure 5 and Figure 6, the values of the characteristic parameters includes the constant characterizing the affinity of the metals ions towards adsorbent per weight unit of adsorbent (n), the Freundlich constant (K_f), the maximum adsorption at monolayer coverage (X_{max}) and the Langmuir adsorption equilibrium constant were calculated. Table 1. presents the characteristic parameter for adsorption isotherms of hexavalent chromium ions by chitosan and chitosan beads.

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The results showed that the adsorption of hexavalent chromium by chitosan followed Langmuir isotherm equation, but the adsorption by chitosan beads similar with Freundlich equation. The data difference from adsorption of chromium by wheat brand and lead by chitosan beads, which adsorption equilibrium data are fitted much better to the Langmuir isotherm, compared to the Freundlich isotherm model[3,4]. The results followed the data for adsorption isotherms of divalent metal ions onto alginate-chitosan hybrid gel beads which followed Freundlich and or Langmuir equations[5].

Table 1. The Langmuir and Freundlich isotherm contants

Asorbents	Langmuir			Freundlich		
	X_{max} (mg/g)	b (L/mg)	R^2	K_f(mg/g)	n	R^2
Chitosan	72.993	81.131	0.849	47.698	0.062	0.729
Chitosan beads	1.735	47.173	0.974	0.5138	0.812	0.998

Conclusion

The results of this study showed that adsorption of hexavalent chromium by chitosan and chitosan beads observed at the medium pH. The maximum adsorption capacity of chromium absorption by chitosan and chitosan beads of pH 5. The adsorption of hexavalent chromium ions by two adsorbents observed that chitosan beads adsorbs more chromium ions as compared to chitosan. This obtained results showed that adsorption of hexavalent chromium ions by chitosan and chitosan beads reached to equilibrium after 90 min. The adsorption of chromium by chitosan and chitosan beads increased gradually at the higher initial chromium concentration at the constant amount of adsorbent. The obtained results showed that the adsorption of hexavalent chromium followed Langmuir isotherm equation for chitosan and also Freundlich equation for chitosan beads. In conclusion, both chitosan and chitosan beads can be employed as commercial adsorbents in the removal of hexavalent chromium from water and wastewater.

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