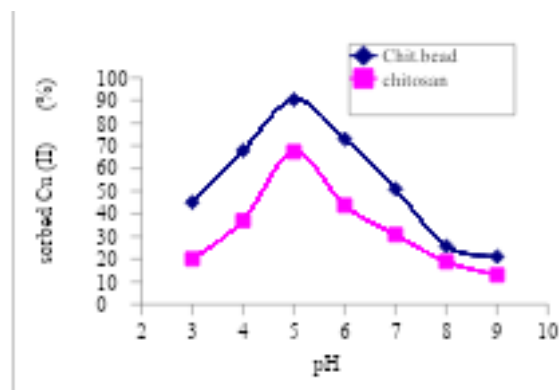


highly affected by medium acidity. With decreasing medium acidity from 4.0-7.0, the adsorbed Cu(II) on chitosan beads and chitosan powder sharply increased and at low medium acidity ($\text{pH} > 7.0$), the adsorbed of Cu(II) again decreased rapidly. The similar pattern by profile of the sorbed Cu(II) on the chitosan beads and chitosan powder. The maximum adsorption Cu(II) On chitosan beads and chitosan powder were observed at pH around 7.0.



Gambar 1. Effect of medium acidity on adsorption Cu(II) on chitosan and chitosan beads

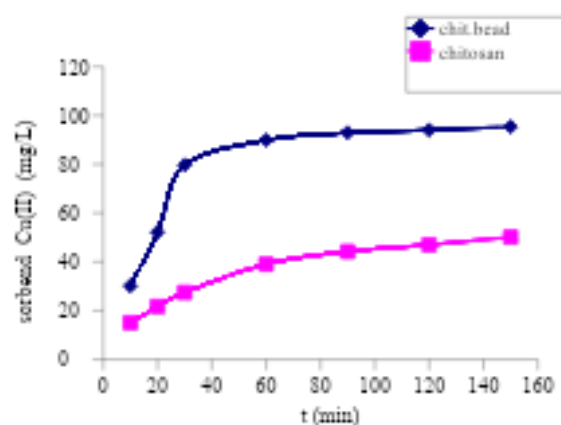
Whereas the optimum pH of adsorption Cd(II) on chitosan beads was 4 [14] and Pb(II) on chitin beads was 5 [12]. The increase of adsorption Cu(II) on chitosan beads and chitosan powder from pH 4.0 to 7.0 must be caused by the decrease of the amount of H^+ in the medium, and therefore, the competition between Cu(II) and H^+ in occupying the active sites on the adsorbents also decreased [10]. At pH higher than 7, the adsorption competed with the precipitation, and the proportion of precipitation and adsorption became relatively the same at 9.0. As a result, the maximum adsorption of Cu(II) occurred just at medium acidity in which Cu(II) started precipitating.

Adsorption kinetics

Although the adsorption of Cu(II) on both chitosan powder and chitosan beads was initially rapid and then slower, the swelling of Chitosan powder became chitosan beads enhanced the adsorption rate (Fig.2). The rapid adsorption for Cu(II) on chitosan powder occurred at the 90 min, while that on chitosan beads at the 60 min.

Applying a kinetic model of first order adsorption reaching equilibrium with the mathematical expression as shown below [5], linear relationship between $\ln(C_{A0}/C_A)C_A$ and t/C_A was obtained with correlation coefficient (R^2) = 0.9874 and 0.9422 for adsorbent of chitosan powder and chitosan beads, while that applying a kinetic pseudo-second order Ho with the mathematical expression as shown below [5] linear relationship between t/q_t and t was obtained with correlation coefficient (R^2) = 0.9051 and 0.8789 for adsorbent of chitosan powder and chitosan beads, respectively (Table 1). That compared to kinetic model of first order adsorption reaching equilibrium, this type of kinetic model has been proven to possess lower correlation coefficient so that adsorption Cu(II) ion on chitosan powder and chitosan beads tend followed kinetic model of first order adsorption reaching equilibrium.

As can be predicted from Fig.2 that the swelling of chitosan powder may enhance the adsorption rate. This prediction was confirmed, i.e the adsorption rate constant (k_1) increased 3.0 times, from $1.6 \cdot 10^{-3}$ for the adsorbent chitosan powder to $4.8 \cdot 10^{-3} \text{ min}^{-1}$ for adsorbent chitosan beads. The swelling process adds the amount of active site suitable for adsorption of metal ion especially for relatively hard metal cations. But the active site must compete with water in attracting the hard cation.



Gambar 2. Effect of contact time on the adsorption of Cu(II) on chitosan powder and chitosan beads

Table 1. Adsorption rate constant and correlation coefficient for the adsorption of Mg(II) on chitosan powder and chitosan beads

Adsorbent	Kinetic model of first order adsorption reaching equilibrium			Kinetic pseudo-second order Ho		
	k_1 $10^{-3} (\text{min}^{-1})$	Q_e $(\text{mol/L})^{-1}$	R^2	h $(\text{mg g}^{-1} \text{min}^{-1})$	k_2' $10^{-4} (\text{g mg}^{-1} \text{min}^{-1})$	R^2
Chitosan powder	1.60	5.49	0.987	0.029	9.058	0.905
Chitosan beads	4.80	22.96	4	0.077	9.058	1
			0.942			0.878
			2			9

Adsorption thermodynamics

The Langmuir and Freundlich isotherm adsorption model with the mathematical expression given below was used to determine the capacity (b) and equilibrium constant (K) of adsorption, and energy (E) adsorption was then calculated

Langmuir isotherm model:

$$\frac{c}{m} = \frac{1}{bK} + \frac{c}{b} \quad (1)$$

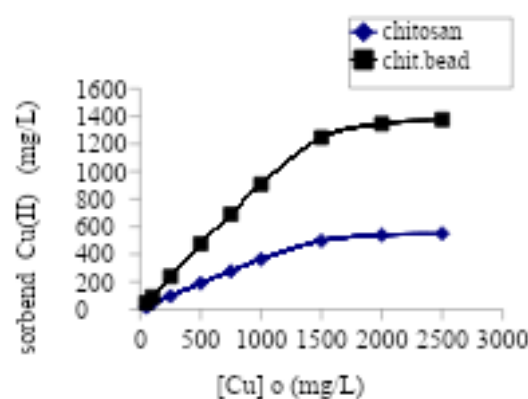
Freundlich isotherm model:

$$\log \log m = \log \log B + \frac{1}{n} \log C \quad (2)$$

where C, the equilibrium concentration in solution; b, Langmuir's adsorption capacity; K, adsorption affinity; m metal adsorbed per g adsorbent at equilibrium; B, Freundlich's adsorption capacity and n, constants.

The application of the two models resulted in the adsorption parameters as shown in Table 2. As occur for adsorption rate constant, the swelling of chitosan powder enhanced the adsorption capacity. exponentially with the increase of the free energy [5]. The Langmuir's adsorption capacity is representation of the capacity of nitrogen on the N acetyl group in adsorbing

Cu(II), while the Freundlich's adsorption capacity of all possible sites in adsorbing Cu(II). The Langmuir's adsorption capacity may indicate the adsorption capacity of this – NH₂, while the Freundlich's adsorption capacity is a representative of the adsorption capacity of -NH₂ and other functional group all together.



Gambar 3. Effect of concentration on adsorption Cu(II) on chitosan and chitosan bead

Table 2. Adsorption capacity (b), Energy (E), and Adsorption affinity (K) obtained from Langmuir isotherm as well as Adsorption capacity (B) obtained from Freundlich isotherm for Mg(II) on Chitosan powder and chitosan beads

Adsorbent	Langmuir				Freundlich		
	b (10^{-4}mole/g)	K $(\text{mol/L})^{-1}$	E (kJ/mol)	R^2	B (10^2mol/g)	n	R^2

Chitosan beads	17.39	6477.16	21.81	0.983	7,60	1,87	0.971
Chitosan powder	7.20	4605.50	21.04	5	12,61	1,42	7
				0.980			0.956
				8			5

KESIMPULAN

Kesimpulan dari penelitian ini adalah..... Adsorption Cu(II) ion on chitosan beads and chitosan powder tend followed kinetic model of first order adsorption reaching equilibrium. Adsorption rate Cu(II) metal ion for the chitosan bead and chitosan powder were $4.80 \cdot 10^{-3} \text{ (min}^{-1} \text{)}$ and $1.60 \cdot 10^{-3} \text{ (min}^{-1} \text{)}$.

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