Original Paper

ADSORPTION OF Mg(II) ION FROM AQUEOUS SOLUTION ON CHITOSAN BEADS AND CHITOSAN POWDER

Sari Edi Cahyaningrum[1,], Narsito[2], Sri Juari Santoso[2] and Rudiana Agustini[1]*

Chemistry Department, Faculty of Mathematics and Natural Sciences
Surabaya State University, Surabaya
Chemistry Department, Faculty of Mathematics and Natural Sciences
Gadjah Mada University, Yogyakarta

ABSTRACT

A basic investigation on the removal of Mg(II) ion from aqueous solution by chitosan beads was conducted in a batch adsorption system. The influence of different experimental parameters; pH, agitation period and different concentration of Mg(II) ion was evaluated. A pH 7.0 was found to be an optimum pH for Mg(II) adsorption onto chitosan powder and chitosan beads. The Langmuir and Freundlich adsorption isotherm models were applied to describe the isotherms and isotherm constants for the adsorption of Mg(II) onto chitosan powder and chitosan beads. Results indicated that Mg(II) uptake could be described by the Langmuir adsorption model. The maximum adsorption capacities of Mg(II) ion onto chitosan powder and chitosan beads were 7.20 and 17.39 mol $g^{â*1}$, respectively. The rate of adsorption Mg(II) on chitosan powder and chitosan beads were $16.0.10^{-4}$ min^{-1} and $48.00 . 10^{-4}$ min^{-1}, respectively.

Keywords: Chitosan beads, Mg(II), Adsorption, chitosan powder

*Corresponding : phone : +62-031-8298761; E-mail: muhacahya@ yahoo.co.id

INTRODUCTION

An important source of water pollutants is industrial discharge water. Most industrial wastewaters are discharged directly into natural water systems without proper management process. Chemical precipitation, membrane separation, and adsorption are mayor techniques applied to minimize the metal content in waters (Cardenas, *et.al.,* 2001). Compared to the adsorption technique, chemical precipitation and reverse osmosis become inefficient, when metal ions are present in very small concentration. Moreover, membrane process includes reverse osmosis and electrodialysis is generally expensive in its application. For that reason, adsorption technique becomes promising alternative available. Adsorption is a physico-chemical technique which involves mass transfer between liquid and solid phase. This process can reduce chemical residues.

Various sorbent materials have already been applied to remove metal ions from waters. These include the utilization of bentonite (Ding, *et.al.,* 2002) and humic acid (Franco, *et al.,* 2002; Santoso, *et.al.,* 2007) exchange resins (Akzu, 2004) and invaluable materials such as tropical soil and diatomae earth. Some of those materials such as ion exchange resins are highly effective but expensive. In the contrary, other materials such as tropical soils, diatomeae earth, and bentonite are inexpensive but ineffective (Amesha and R Shit., 2006). Activated carbon and humic acids in peat soil seem to

very effective in removing metal ion, but these materials are readily soluble under high pH condition (Allen, S.J, *et.al.,* 2005).

Instead of the above adsorbent materials, we have recently synthesized chitosan beads and it was then applied as sorbent to metal ions. Our previous study revealed that compared to chitosan powder, this type of adsorbent has been proven to posses higher adsorption capacity for metal ion such as Cu(II) and Zn(II) (Cardenas, *et. al.,* 2001). In this study, the chitosan beads are investigated as adsorbent for Mg(II) ion. The performance of the adsorbent is evaluated based on the data of energy, capacity, and rate constant of adsorption.

MATERIALS AND METHODS

Materials

Reagents used in this study are analytical grade originally produced by E. Merck Co.Inc (Germany), and then tested and prepared in order to be suitable for real experiments. The prepared reagent consist of: (1) reagent for isolation of chitosan, i.e. 3.5% (w/v) NaOH, 1 M HCl and 50% (w/v) NaOH; (2) reagents for preparation of chitosan beads, i.e 1% acetic acid, NaOH and ethanol; (3) Stock solution of 1000 ppm Mg(II) from $MgCl_2$ crystal, (4) standard solutions for preparing standard curve for the determination of Mg(II) using atomic absorption spectrometer (AAS). Buffer solution at 4.0, 7.0, and 10.0 produced by Fischer Scientific Co for pH meter calibration.

Chitosan was prepared from shrimp (*Penaeus monodon*) shell through deproteination (removal of proteins from shrimp shell with NaOH solution), demineralization (removal of minerals from shrimp shell with HCl solution) followed by deacetylation (removal of acetyl functional groups from chitin with NaOH solution) processes according to the method of Hong *et. al.,*(1989). Chitosan beads are prepared by swelling the chitosan powder with acetic acid and then the chitosan gels are sprayed to NaOH solution.

Methods

Adsorption of Mg(II)
Effect of medium acidity

First, a series of 20 ml of Mg(II) 100 mg/l solutions was prepared and their acidity was adjusted to 3.0 until 8.0 by adding HCl or NaOH solutions. Into every Mg(II) solution, 100 mg of adsorbent was poured and then stirred for 2 h. After filtering through 0.45-μm membrane filter, the concentration of Mg(II) in the supernatant was analyzed by using atomic absorption spectrometry (AAS). Sample and blank solutions were analyzed under the same condition. The amount of Mg(II) adsorbed was considered to be the difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed.

Adsorption kinetics

The kinetics experiments were carried out using a batch type reactor using a 50-ml erlenmeyer in a water bath at 25± 0.01 ºC. The volume of adsorption medium was 20 ml, the initial metal ion concentration was 100 mg/l, the acidity was adjusted at pH 7.0; and each solution, 100 mg of adsorbent was added and then stirred continuously. At selected time the sample was immediately filtered through 0.45-μm membrane filter and the concentration of Mg(II) in the supernatant was analyzed by using atomic absorption spectrometry (AAS). The data obtained was then analyzed using two different adsorption kinetics models, i.e pseudo-second order Ho and first order reaching equilibrium proposed here.

Adsorption thermodynamics

The experiment were also conducted using a batch-type reactor using a 50-ml Erlenmeyer

in a water bath at 25 ± 0.01 ^{o}C. As much as of adsorbents was interacted with sample and stirred in 20 ml of solutions containing the various concentrations of Mg(II) at pH 7.0 for 2 h. After separating the supernatants, the concentration of Mg(II) in the supernatans was determined by AAS. The data obtained was then analyzed using Freundlich and Langmuir isotherm models.

RESULTS AND DISCUSSION

Effect of medium acidity

The acidity of the adsorption medium greatly affects the amount of adsorbed Mg(II) (**Fig.1**). Adsorption Mg(II) increased with increasing pH from 4.0 to 7.0. From 7.0 to lower acidity, the adsorption Mg(II) significantly decreased. The amount of sorbent Mg(II) was highly afected by medium acidity. With decreasing medium acidity from 4.0-7.0, the adsorbed Mg(II) on chitosan

beads and chitosan powder sharply increased and at low medium acidity (pH > 7.0), the adsorbed of Mg(II) again decreased rapidly. The similar pattern by profile of the sorbed Mg(II) on the chitosan beads and chitosan powder. The maximum adsorption Mg(II) on chitosan beads and chitosan powder were observed at pH around 7.0. Whereas the optimum pH of adsorption Cd(II) on chitosan beads was 4 (Iowe, 2005) and Pb(II) on chitin beads was 5 (Zhao, 2004). The increase of adsorption Mg(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 Mg(II) and H^+ in occupying the active sites on the adsorbents also decreased (Gotoh Takeshi and Matsushima. 2004). 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 Mg(II) occurred just at medium acidity in which Mg(II) started precipitating.
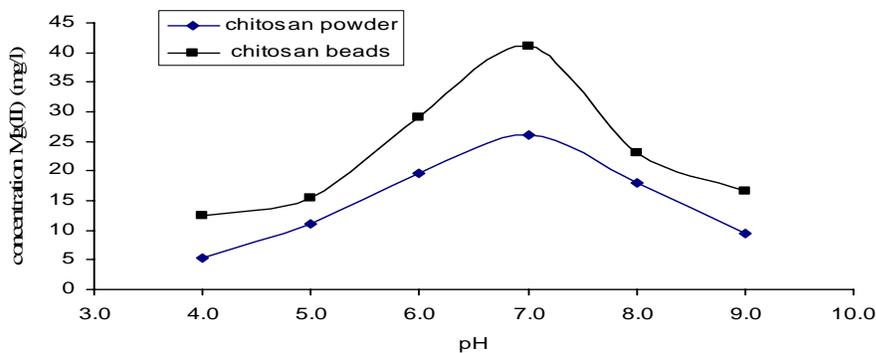
Fig.1 Effect of medium acidity on adsorption Mg (II) on adsorbent

Adsorption kinetics

Although the adsorption of Mg(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 Mg(II) on chitosan powder occurred at the 90 min, while that on chitosan beads at the 60 min.
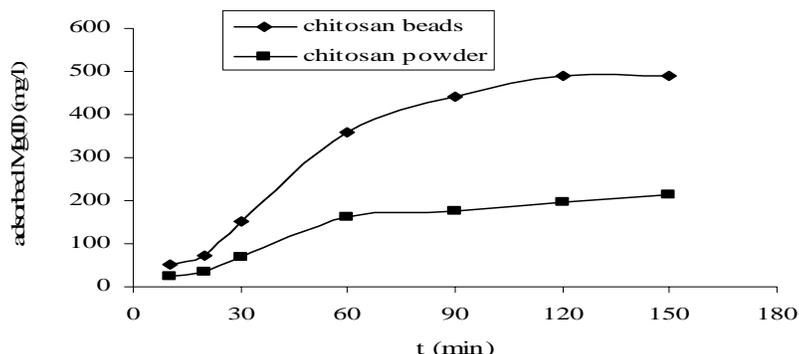
Fig.2. Effect of contact time on the adsorption of Mg(II) on chitosan powder and chitosan beads

Applying a kinetic model of first order adsorption reaching equilibrium with the mathematical expression as shown below (Santoso, S.J, *et.al.,* 2007), 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 (Santoso, S.J, *et.al.,* 2007) linear relationship between t/q_t and t was obtained with

correlation coefficient (R^2) = 0.9051and 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 posses lower correlation coefficient so that adsorption Mg(II) ion on chitosan powder and chitosan beads tend followed kinetic model of first order adsorption reaching equilibrium.

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} (min^{-1})	Q. (mol/L)$^{-1}$	R^2	h (mg g^{-1} min^{-1})	k_2' 10^{-4} (g mg^{-1}min^{-1})	R^2
Chitosan powder	1.60	5.49	0.9874	0.029	9.058	0.9051
Chitosan beads	4.80	22.96	0.9422	0.077	9.058	0.8789

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 1.6×10^{-3} for the adsorbent chitosan powder to 4.8×10^{-3} min^{-1} for adsorbent chitosan beads. The swelling process add 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.

Adsorption thermodynamics

The Langmuir and Freuchlich 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: $C/m = 1/bK + C/b$

Freundlich isotherm model:

$\log m = \log B + 1/n \log C$

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. The Langmuir isotherm is designed for monolayer adsorption of a species on a homogeneous surface with adsorption energy is the same for all active site regardless of the degree of coverage, while the Freundlich is for multilayer adsorption on heterogeneous surface with the frequency of sites associated with free energy of adsorption decrease exponentially with the increase of the free energy (Santoso, S. J, *et.al*. 2007). The Langmuir's adsorption capacity is representation of the capacity of nitrogen on the N acetyl group in adsorbing Mg(II), while the Freundlich's adsorption capacity of all possible sites in adsorbing Mg(II). The Langmuir's adsorption capacity may indicate the adsorption capacity of this $– NH_2$, while the Freundlich's adsorption capacity is a representative of the adsorption capacity of $- NH_2$ and other functional group all together.

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	K	E	R^2	B	n	R^2
	(10^{-4}mole/g)	$(mol/L)^{-1}$	(kJ/mol)		(10^2mol/g)		
Chitosan beads	17.39	6477.16	21.81	0.9835	7,60	1,87	0.9717
Chitosan powder	7.20	4605.50	21.04	0.9808	12,61	1,42	0.9565

CONCLUSION

The optimum pH of adsorption Mg(II) metal ion process on chitosan beads and chitosan powder was 7. The swollen of chitosan powder enhanced adsorption capacity of Mg(II) metal ion. Mg(II) metal ion uptake on chitosan beads and chitosan powder tend followed the Langmuir isotherm adsorption model. Adsorption capacity Mg(II) metal ion for the chitosan beads and chitosan powder were $17.39x10^{-4}$ mole/g and $7.20x10^{-4}$ mole/g, respectively. The adsorption of Mg(II) metal ion on chitosan powder and chitosan bead were called chemical adsorbed involving energies of adsorption in a range from 21.04 to 21.81 kJ/mole. Adsorption Mg(II) ion on chitosan beads and chitosan powder tend followed kinetic model of first order adsorption reaching equilibrium. Adsorption rate Mg(II) metal ion for the chitosan bead and chitosan powder were $4.80\ 10^{-3}$ (min^{-1}) and $1.60x10^{-3}$ (min^{-1}).

REFERENCES

Cardenas, G., Orlando, P., Edelio, T. (2001), Syntesis and Applications of Chitosan Mercaptanes as Heavy Metal Retention Agent. *Int. J. Biol. Macro.,* 28, 167-174.

Ding P, Huang., Liu K., Zeng W. 2002, Contribution to the Study of Complexes of Copper by Chitosan an Oligomer, *J.Polymer*.43.1267-1276.

Franco, L.O., Maia, R.C., Porto, A.L.2004, Heavy metal biosorption by chitin and chitosan isolated from *cunninghamella elegans*, *Brazilian J. Microbiol*, 35,243-247.

Santoso. S. J, Siswanto, D., Kurniawan, A, Rahmanto. W.H. 2007, Hybrid of Chitin and Humic Acid as High Performance Sorbent for Ni(II), *J.Surface Sci*. 4, 163.

Santoso, S. J, Siswanto, D., Sudiono, S., Sehol M. 2007, Synthesis and Utilization of Chitin -Humic Acid Hybrid as Sorbent for Cr(III), *J.Surface Sci*. 4, 161
.

Aksu, Z. 2005. Application of Biosorption for the Removal of organic pollutans . A review. *Process Biochem*. 40.997-1026.

Amesha and R Shitty. 2006, Metal Anion Removal from Wastewater Using Chitosan in Polimer Enhanced Diafiltration System. *Int. J. Biol. Macro., 43*, 467-474

Allen, S.J.Gan,Q and Matthews. 2005. Kinetic Modeling of the Adsorption of Basic Dyes by Kudzu. *J.Colloid. Inter. Sci* 286. 101-109

Benavente, Marta and Ru Lig .2008, Improving the proprties of Chitosan as Suport for the Covalent Multipoint Immobilization of Chymotripsin. *Biomacromolecules*.9(8) 2170-2179.

Gotoh Takeshi and Matsushima. 2004, Preparation of Alginate–Chitosan Hybrid Gel Beads and Adsorpstion of Divalent Metal Ion, *Chemosphere*., 55, 135-140.

Hong Meyers, S.P.1989, Crawfish Chitosan as a Coagulant in Recovery of Organic Compounds from Seafood Processing Steam, *J. Agric. Food. Chem*., 37, 580-583.

Zhou Dao and Zhang Lina. 2004, Cellulosa/chitin beads for adsorption Heavy metal, *Water Res*., 38.2846-2850.

Guibal., Milot, C., Tobin, J.M., 2004. Interactions of Metal Ions with Chitosan Based Sorbent. *Review Separation and Purification Tech*. 38. 43-74

Iowe J.C., Ogunewe , Abia., 2005, Competitive Adsorption Zn(II), Cd(II) and Pb(II) Ions from Aqueous and Non Aqueous Solution. *J.African Biotechnol* 4.10.1113-1116