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ADSORPTION RATE CONSTANT AND CAPACITIES Of LEAD(II) REMOVAL FROM SYNTHETIC WASTEWATER USING CHITOSAN SILICA

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Abstract

The adsorption rate constant and capacities for the removal of Pb(II) from synthetic wastewater using chitosan silica were investigated. The adsorption kinetics model is used to determine the rate of adsorption is the order of the one nearing equilibrium and pseudo second-order. The results showed that the metal ion adsorption of Pb(II) reaches equilibrium at the 60 minute interaction by chitosan-silica bead. Adsorption kinetics model that is suitable for both the pseudo second-order rate constants. The adsorption followed the Langmuir and Freundlich isotherms but could best be approximated with the Langmuir model.

Key words: adsorption, Pb(II), chitosan silica

INTRODUCTION

Water is an essential matter to human and other living organisms. Water is polluted in many ways like effluents from leather and chemical industries, electroplating industries and dye industries. Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large-scale sector contains considerable amount of toxic metal ions (Bradbury, M. H., & Baeyens, B.,2002). These toxic metals ions are not only potential human health hazards but also to other life forms .Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, nickel, copper and aluminium poisoning: gastrointestinal (GI) disorders, diarrhoea, stomatitis, tremor, heamoglobinuria causing a rust–red colour to stool, ataxia, paralysis, vomiting and convulsion,depression, and pneumonia when volatile vapours and fumes are inhaled . Several methods have been used to purify the water like sedimentation, filtration, ultra filtration, precipitation, ion exchange, electro coagulation, electro dialysis, and reverse osmosis in cleaning wastewater .Hence, the disadvantages associated with traditional methods of heavy metal removal like incomplete metal removal, high energy requirement, generation of toxic sludge and other waste products have made it important to look of other cost-effective treatment methods(Chiou & Li, 2004) .Moreover, traditional methods of heavy metal removal are not so efficient when metals are present in concentrations less than 100mg/L. Hence, attention is being focused to the development of alternative methods of heavy metal removal like bioremediation. One of such processes is adsorption (Kalyani, S., et.al., 2009).Chitosan derivatives have been extensively investigated as adsorbents (Amit & Mika, 2009). Among them are chitosan derivatives containing nitrogen, phosphorus and sulfur as heteroatoms, and other derivatives such as chitosan crown ethers and chitosan ethylenediaminetetraacetic acid

(EDTA)/diethylenetriaminepentaacetic acid (DTPA) complexes (Varma, Deshpande, & Kennedy, 2004). Recently, chitosan composites have been developed to adsorb heavy metals and dyes from wastewater. Different kinds of substances have been used to form composite with chitosan such as montmorillonite (Wang &Wang, 2007), polyurethane (Won, Lee, Jeong, Min, & Lee, 2009), activated clay (Chang & Juang, 2004), bentonite (Wan Ngah, Ariff, & Hanafiah, 2010), poly vinyl alcohol, poly vinyl chloride, kaolinite (Zhu, Jiang,& Xiao, 2010), oil palm ash (Hameed, Hasan, & Ahmad, 2008) and perlite (Kalyani, Ajitha, Srinivasa, & Krishnaiah, 2005). In this research chitosan modified with silica, this composites have been proven to have better adsorption capacity and resistance to acidic environment.

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RESEARCH METHOD

Materials

Silica gel (100–200 mesh size); chitosan was supplied by IndoChem.,Indonesia. Glutaraldehyde was obtained from Shanghai Shengong Bioengineering Corp. All other chemicals used in the experiment were in analytical grade.

Preparation of chitosan - silica gel beads blend

Chitosan and glutaraldehide mixed solutions were prepared by dissolving 500 mg chitosan and glutaraldehid 5% in acetic acids solution. Ten grams silica gel (75–100 _m) was added into the solution and immersed overnight before drying in vacuum condition. The chitosancoated gel was suspended in dimethylsulphoxide (DMSO) and stirred vigorously in a flask. After dissipation, NaOH was added until pH reached above 10.0. The macrospores on the bead surface, filtered the solution. After thoroughly washed with pure water, the cross-linked matrix with some active aldehide groups was shaken in a 0.85M ammonia solution at 60 ◦C for 4 h. Then, the matrix was washed with purewater to remove the residual ammonia.

Adsorption Pb(II) in variation contact time

The kinetic experiments were carried out in a batch-type for using a 50-mL Erlenmeyer in shaker at room temperature. The volume of the solution of the reacting suspension was 10 mL, the initial Pb(II) ion concentration was 100 mg/L, the pH 5.0, and to each solution 10 mg chitosan-silica as added and then stirred continuously. At a selected time period, the sample was immediately filtered membrane filter and the concentration of Pb(II) remaining in the supernatant was analyzed using AAS. Sample and blank solutions were analyzed under the same condition. The amount Pb(II) sorbed was considered to the difference between the initial and the remaining amount of Pb(II) in the reacting solution. From the data obtained, the value of sorption and desorption rate constants were then calculated based on the assumption that the sorption obeyed. 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 capacity and energy

As much as 10 mg of chitosan-silica was interacted with and stirred in 10 mL of solu tions containing the various concentrations of 50, 100, 150, 200, 250, 300, 500, and 1000 mg/L Pb(II) for as long as 1 h. After separating the supernatants, the concentrations of Pb(II) in the supernatant were determined using AAS. Under the same condition with the sample solution, the blank solution was also analyzed. Based on the data obtained, the capacity (b) and equilibrium constant (K) of sorption was calculated based on the Langmuir isotherm sorption model, and the energy (E) of soprtion was then calculated from the equation of $E = RTlnK$

RESULT AND DISCUSSION

Preparation of the metal chelating support was performed in three steps consisting of chitosan coating, crosslinking, and metal chelating. The interaction mechanism of silica with chitosan has been described (Dewi, Rifa). The cross-linking by the glutaraldehide molecules could increase the stability of the coated chitosan layer. Some loss of the primary amino groups in cross-linking step could be recovered by amination of the residue aldehyde groups. BET analysis showed that specific surface area was 26.89m2/g and pore volume was 0.2063mLg−1 with macroporous structure (pore diameter ≥50 nm, 67.8%). The low pore volume might be ascribed to the special interconnected porous structure formed by the chitosan layer on the surface. Such porous surface might favor the accessibility for the target macromolecular binding. The SEM analysis showed that morphology chitosan-silica more porous so that this adsorbent has adsorption capacity more biger than chitosan flake

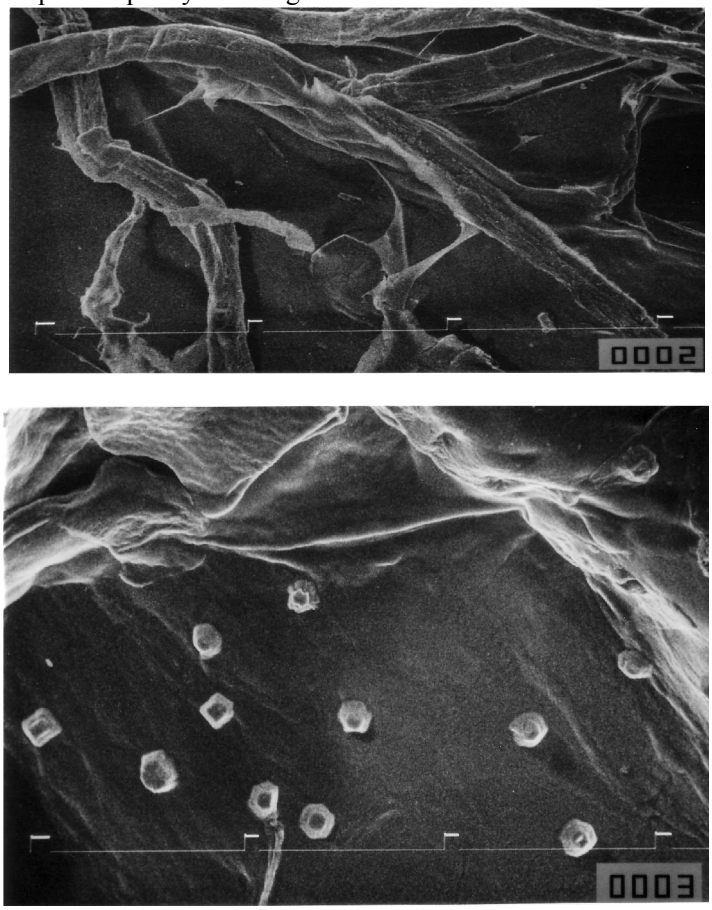

Fig. 1. SEM Chitosan –silica (a); Chitosan-silica-metal ion (b)

Kinetics

Figure 2 indicates the uptake of Pb(II) ions was increased as the contact time increases. The rapid removal of Pb(II) ion was noticed with the contact time variation from 30 to 240 mins, respectively. This is because at the early stage, more number of potentially active/vacant sites is available for adsorption. As the contact time increases maximum number of sites got adsorbed to the metal ions. Hence it is difficult for the metal ion to search for the very

fewer remaining sites. Therefore rate of adsorption decreases in the later. Hence 60 min was found to be an equilibrium adsorption time.

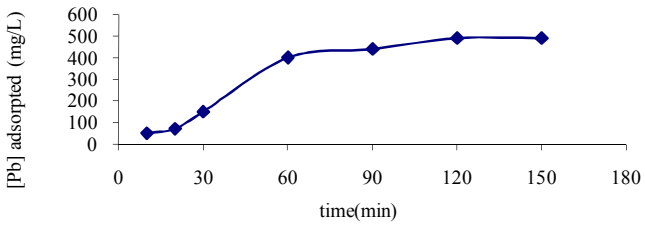

Fig 2. Effect interaction time on Pb(II) adsorption at chitosan silica

The analysis data with kinetic model showed in 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 Pb(II) metal ions tend followed kinetic model Kinetic pseudo-second order Ho.

Table 1 Adsorption rate constant and correlation coefficient for the adsorption of Pb(II) on chitosan-silica.

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-silica beads	5.1634	12.3109	0.7422	0.0631	8.0580	0.9192

Capacities and energy adsorption

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:

$$\frac{c}{m} = \frac{1}{bk} + \frac{b}{c} \qquad (1)$$

Freundlich isotherm model:

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

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. Fig 2 and 3 showed that adsorption Pb(II) on chitosan silica has different R^2, from two models isotherm showed that this adsorption tend followed Langmuir isotherm model.

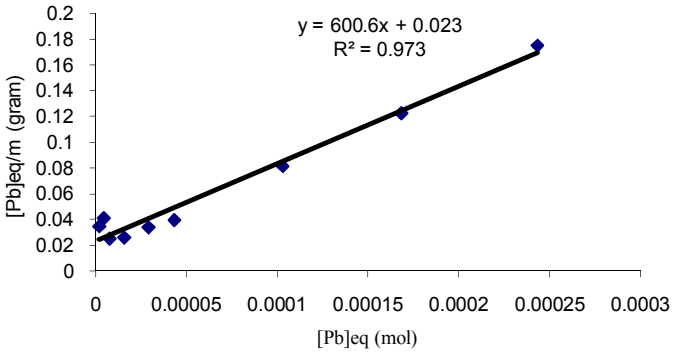

Fig 2. Linearitas Langmuir

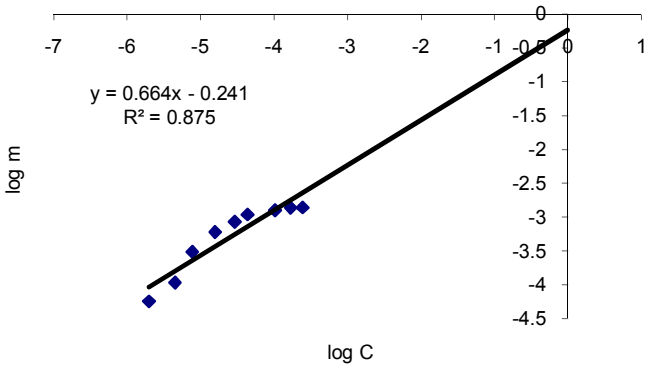

Fig 3. Linearitas Freunclich

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. Adsorption Pb(II) on chitosan silica. Adsorption capacity Pb(II) metal ion for the chitosan silica was 42.51 $.10^{-4}$ mole/g, involving energies of adsorption in a 25.04 kJ/mole.

CONCLUSION AND SUGGESTION

This study has created a composite chitosan and silica for adsorbent Pb(II).SEM characterization results show that chitosan silica has the greatest pore size. The adsorption capacity of chitosan-silica is equal 42.51 $.10^{-4}$ mole/g, involving energies of adsorption in a 25.04 kJ/mole with the adsorption rate following the pseudo second-order kinetics model.

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