MODULATION AND APPLICATION OF CHITOSAL TO ADSORB LEAD (Pb^{2+}) IN WASTEWATER

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ABSTRACT. – Modulation and application of chitosal to adsorb lead (Pb^{2+}) in waterwaste. One of methods to eliminate metals from water is the use of adsorption. Chitosal is a material with a biological origin and was chosen for this study. The material was extracted from shrimp shells. The final product of the extraction progress was chitosal gel with a diameter of 3.5 mm, 97% of purity and good solubility in 1% CH_3COOH solution. Three adsorption columns were built with PVC plastic. Two experiments at lead concentration 6.98 mg/l and 15.7 mg/l were carried out with the flow from the top down, at different water retention times of 15 minutes, 30 minutes, 45 minutes, 60 minutes, 90 minutes, and 120 minutes. The results showed that at lead concentrations of 6.98 mg/l we did not find the optimum water retention time. However, in the second experiment with lead concentration of 15.7 mg/l we determined the optimal water retention time was 60 minutes for column h1 and the lead adsorption efficiency achieved was 30.44%; column h2, h3 were the same time (90 minutes) and the lead adsorption efficiency reached 44.71%; and 52.87% respectively.

Keywords: Chitosal; Pb^{2+}; Adsorption; Lead pollution.

1. INTRODUCTION

Water is a precious natural resource, an indispensable factor for life. However in some places, the surface water is badly Pb^{2+} polluted, which leads to the harmful influence on the people's health. Protection of the environment, aquatic ecosystem and landscape basin river system is one of key programs of the developing countries for Water Resources Management now. Over the years there have been a number of attempts to prevent environmental pollution. These included measures to deal with the metals in water solutions that are of interest in such matters including chemical precipitation, redox, mechanical filtration, ion exchange, nanotechnology (Nhung, 2007), using osmotic membranes, adsorption (Rashed, 2001), biological methods and biotransformation by the metabolism of microorganisms (Kieu, 2013). However, these methods were performed in many

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different ways and at different Pb^{2+} concentrations. Some methods were limited by cost and its efficiency.

Adsorption by biological materials is a new technique and has practical significance to separate metals or compounds from the water. Among the polymers that derive from animals, is Chitin-chitosal, a kind of polysaccharide that is present in the shell of species of crustaceans. Chitin is found in abundance in shrimp shells (33%) so they are abundant sources of raw materials for the production of chitosan (Luong, 2004). Chitin is a straight chain polysaccharide, with linear structure which consists of N-acetyl-glucosamine joined by β-1, 4-glucoside links. Chitosan is derived from chitin, it is formed by a chemical reaction with chitin deacetyl, when the chitin is processed with alkali at high temperature (120°C) in solution. The result is that acetyl groups will be removed and decomposed into chitosal (Attila and Pavlath, 1996).

NH_2 groups and OH groups are present in the structure of chitosan. This is the position that chitosan can link metal ions in water (Kiet, 2010). Chitosan molecules can coagulate a huge amount of anion waste in solution, forming scum. Chitosan mixture can eliminate metal in drinking water**.** This experiment evaluated chitosal modulation from shrimp shells and designed adsorption PVC (Polyvinyl clorua) columns to treatment Pb^{2+} in water at different water retention times and different Pb^{2+} concentrations. Our experimental aim was to identify the highest adsorption efficiency at the optimal water retention time.

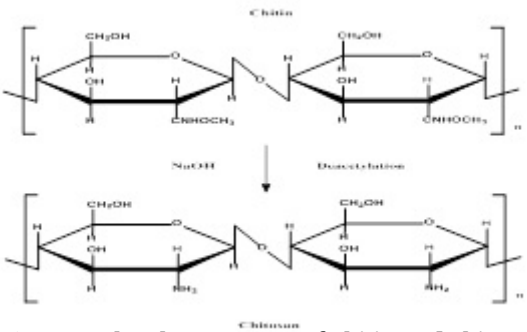

Fig. 1. ***Molecular structure of chitin and chitosal***

2. METHODS

Chitosal was extracted from shrimp shells and then modulated into chitosal gel particles with solid form around 3.5mm diameter. The adsorbed columns were made with PVC material. Pb^{2+} was prepared at concentrations ranging from 5-40mg/l. Adsorption capacity was assessed by the height of the different chitosal columns at different water retention time with the initial pH value was 7.79. The efficiency of lead adsorption for each experiment was calculated.

2.1. Parameters of filtration columns

The parameters of filtration columns are: diameter PVC columns D= 40mm; height of the PVC columns: H=600mm; height of the Chitosal: h_3= 300mm; h_2=200mm; h_1=100mm; height of the water columns: L_3=200mm; L_2=300mm; L_1=400mm; surface area of the PVC columns: Acolumn = $\Pi x D^2/4$ (Table 1); the volume of chitosal in the adsorption column: Vcolumn = Acolumn*h (Table 1); the volume of the chitosal porosity in the adsorption column Vr = Vcolumn* the chitosal porosity (Table 1); Q (flow)= Vr/t (water retention time) (Table 2); load on

the surface water recharge = Q/Acolumn (Table 2); the porosity of chitosal particle layer is determined by putting chitosal gel particles into a 1 liter beaker. Water was added to the 1 liter mark. The amount of water added is the porosity of chitosal particles layer. The porosity of the chitosal particle layer was 45% (Table 1).

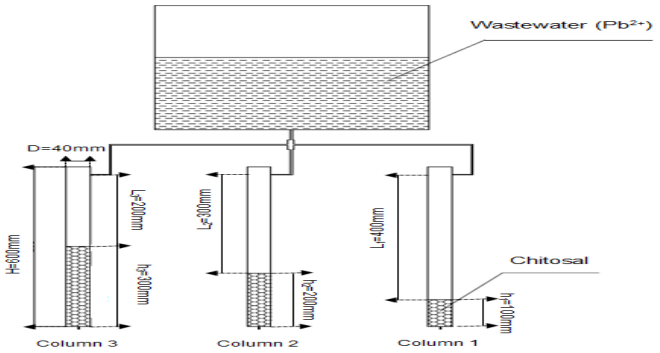

Fig. 2. ***Filtration columns model***

The experiments were performed with 3 filtering columns with design parameters as above, corresponding to 3 heights of chitosal (h_3 = 300 mm and h_2 = 200 mm, h_1 = 100mm). The experiments were conducted with concentration of lead of 6,98mg/l; 15,7mg/l at room temperature. Lead was determined by atomic absorption spectroscopy (AAS). Experiments were conducted with the flow from the top down at the water retention times: 15 minutes, 30 minutes, 45 minutes, 60 minutes, 90 minutes, 120 minutes. The input water flowed into the adsorption column from the top of the column and the output water was ejected from a tap at the bottom of the column. We conducted experiments with many discharge rates, and adjusted the water level in the column so that it was maintained at a constant position.

2.2. Modulation and determine the structure of chitosan

Shrimp shells after removal of inorganic salts, proteins and impurities were used to obtain chitin. Chitin after deacetyl produced chitosal which was then dissolved in 1% CH_3COOH. Purity of chitosal was determined by its solubility in this 1% solution. The molecular structure of chitosal was determined by infrared spectroscopy FTIR.

3. RESULTS

3.1 Modulation Chitin and Chitosal

Shrimp shells were purchased at Can Tho Biochemical Company and consisted of: Chitin 27.2%, protein 23%, 45.16% mineralization, water and other substances 3.64%. Shrimp shells were washed and sun dried. The shrimp shells were then soaked in a solution of HCl 3.5% at room temperature combined with stirring to accelerate the process of mineral removal for 1.5 hours and finally washed again with distilled water.

Removal of minerals andprotein and color bleaching of shrimp shells were performed according to the process in figure 3 to obtain chitin (Fig.4). The chitin deacetyl we obtained was white chitosal gel, odorless, small size, and homogenous (Fig. 5). Then, chitosal gel was dissolved with 2.5% glutaraldehyde solution for 24

hours to avoid chitosal gel by dissolving in an acid environment. We obtained cross-linking-yellow chitosal gel, odorless, 3.5mm diameter, round shape with many voids inside (Fig. 6).

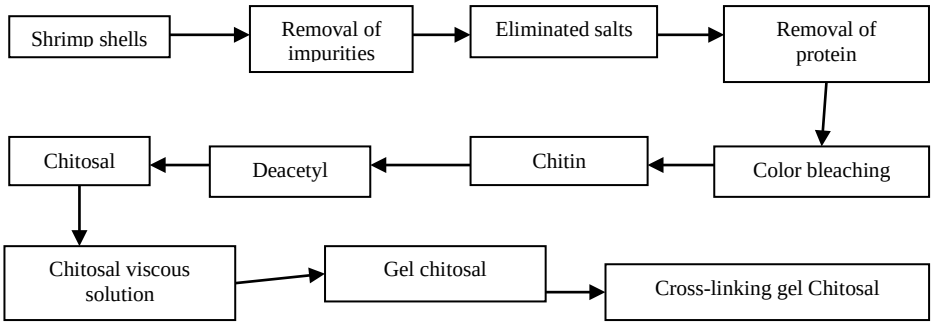

Fig. 3. ***Diagrams of chitosal modulation from shrimp shells***

Chitosal products that we modulated dissolved completely in 1% CH_3COOH1% solution, which showed purified chitosal. Moreover, we also used measurement methods of the infrared spectroscopy FTIR of chitosal products. The results indicated that there were 10 the infrared spectrums were found (Fig. 7). That were the peaks with the wave (cm^{-1}): 3,424.19; 2,937.49; 2,096.31; 1,641.45; 1,399.91; 1,318.54; 1,069.95; 898.51; 460.67; 431.72. There were 5 infrared spectrums with the same wave as the 5 standard group (-NH_2: 1,641.45 cm^{-1}; -OH: 3,424.19 cm^{-1}; -CH_2: 1,399.91 cm^{-1}; and C-O-C: 1,069.95 cm^{-1}; the C-O-C-glucoside: 898.51 cm^{-1}). Each peak position was characterized for every chemical group in the molecular structure of chitosal.

Fig. 4. ***Chitin***

Fig. 5. ***Chitosal gel***

Fig. 6. ***Cross-linking chitosal gel***

Electron microscopy was used to determine rugged surface and the structure of chitosal gel particles. The results are shown in figure 8. The analysis also showed that the product is full of the characteristic functional groups of chitosal molecules. Once again, confirming that the chitosal products that we modulated it is chitosal.

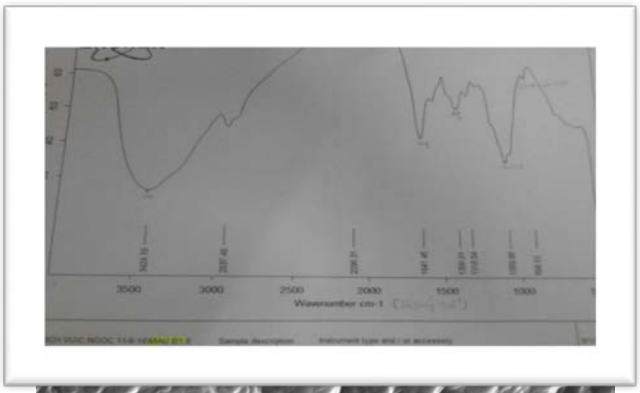

Fig. 7. ***The infrared spectroscopy of chitosal gel***

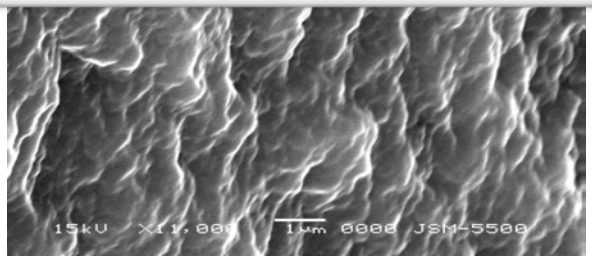

Fig. 8. ***The rugged surface of chitosal gel***

3.1. Calculate discharge and water recharge load

Below are the the results of the parameter's calculation which are: the surface area of the column, volumetric of chitosal in adsorption column, volumetric the porosity chitosal layer in the column as well as discharge and water recharge load at the difference water retention time.

Table 1. ***Calculating the parameters of the model***

Parameters	**Formula**	**Results**		
		h_1	**h_2**	**h_3**
The surface area of the column (m^2)	Acolumn =(Π xD^2)/4	$1.26*10^{-3}$	$1.26*10^{-3}$	$1.26*10^{-3}$
Volumetric of chitosal in adsorption column (m^3)	Vcolumn = Acolumn* h chitosal	$0.13*10^{-3}$	$0.26*10^{-3}$	$0.38*10^{-3}$
volumetric the porosity chitosal layer in the column (m^3)	Vr = Vcolumn * the porosity (45%)	$0.06*10^{-3}$	$0.11*10^{-3}$	$0.17*10^{-3}$

Table 2. ***Discharge, water recharge load*** **at** ***the water retention time.***

Water retention time (minute)	**Discharge Q (liter/h) Q = Vr / t**			**Water recharge load N= Q/Acolumn (liter/m^2.h)**		
	h_1	**h_2**	**h_3**	**h_1**	**h_2**	**h_3**
15	0.23	0.46	0.68	180	360	539.8
30	0.11	0.23	0.34	90	180	270
45	0.08	0.16	0.23	59.7	120.3	180
60	0.06	0.11	0.17	45.4	90	134.6
90	0.04	0.08	0.11	30.3	59.7	90
120	0.03	0.06	0.09	22.3	45.4	67.7

3.2 Adsorption efficiency

In the first experiment, with initial Pb^{2+} concentration of 6.98 mg/l, when the wastewater went through the filter column at the water retention time of 15 minutes, the Pb^{2+} adsorption efficiency at the column h_1, h_2, h_3 were 32.8 %, 41.98% and 56.3% respectively. Meanwhile, at the water retention time of 30 minutes, 45 minutes, 60 minutes, the adsorption efficiency only increased from 8.31% to 10.47% at the h_1 column, from 10.6% to 16.9 % at the h_2 column and from 7.02% to 22.78% at the h_3 column. In this experiment, we still have not found the optimal water retention time. So, we conducted a further experiment at higher lead concentration (15.7mg/l).

The lead adsorption efficiency of chitosal in the second experiment at 3 columns tended to be similar to the first experiment. However, the efficiency of lead adsorption of each chitosal column in this second experiment only reached ½ of the efficiency of lead absorption of the first experiment at all 3 adsorption columns in the same water retention time. This indicated that the lead adsorption capacity of chitosal columns was inferior at the higher lead concentrations. We used Duncan's method in ANOVA analysis to test the adsorbed Pb^{2+}concentration at the different water retention time in the same filter column. The results showed that there was no significant difference between the Pb^{2+} adsorbed levels at the water retention times of T60, T90 and T120 in column h_1 (Table 3).

Table 3: ***Using the Duncan method to test the adsorbed Pb^{2+}* content *(Pb^{2+}15.7mg/l).***

Water retention time	h_1	h_2	h_3
T0	0	0	0
T30	3.29a	4.55a	5.80a
T60	4.78b	6.55b	8.23b
T90	4.84b	7.02c	8.30bc
T120	4.91b	7.12c	8.47c
CV%	3.12	1.58	1.16

Note: *The same word, not significantly different*

Therefore, we could use the h_1 column at the optimal water retention (60 minute) because the saturated chitosal material already reached 30.44% adsorption efficiency and did not increase significantly thereafter. In column h_2, the test results showed that there were significant differences among the adsorbed lead levels at all the water retention times at the confidence level of 95% except, the water retention time of 90 minutes and 120 minutes. Therefore, we chose the optimal time of 90 minutes for the h_2 column, and the adsorption efficiency achieved was 44.71%. Similarly, the optimum water retention time was 90 minutes for the h_3 column and the adsorption efficiency reached 52.87%.

Table 4 showed that there were significant differences at the confidence level of 95% about the adsorbed lead content at the chitosal columns in the same the water retention time. It means the arrangement of the chitosal thickness was suitable. We can conclude that the thicker chitosal column had higher adsorption.

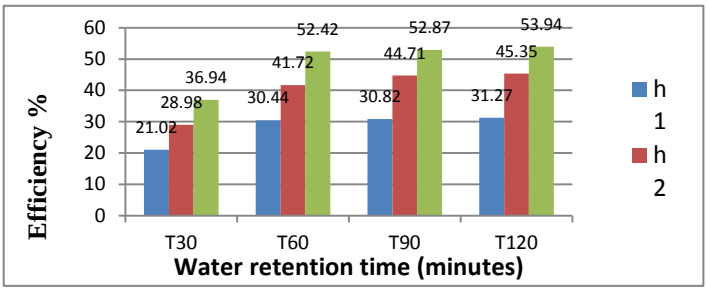

Fig. 9. Pb^{2+} adsorption efficiency of the chitosal column at the different water retention time (Pb^{2+}15.7mg/l).

Table 4. ***Using Duncan method to test the adsorbed pb^{2+} content of the chitosal columns in the same the water retention time (Pb^{2+} 15.7mg/l).***

The chitosal column	The adsorbed pb^{2+} content (mg/l) at the water retention time T60	The adsorbed pb^{2+} content (mg/l) at the water retention time T90
h1	4,78a	4,84a
h2	6,55b	7,02b
h3	8,23c	8,33c
CV%	1,37	1,05

Note: *The same word, not significantly different*

The initial pH value was 7.79, but after 15-30 minutes it dropped sharply to around 3.5 to 4.25 for both experiments and fluctuated around this value at the retention time later. This confirmed that our materials have a very good Pb^{2+} treatment ability in wastewater at pH = 3-4. This is consistent with the research of Luciana de Oleveira Franco (2004) who concluded that"At pH = 4, all the metals are adsorbed very good by chitosal" and with Suchada Ampin (2002) who reported that "The best metals adsorption capacity of cross-linked chitosal gel particles at pH<5, except Hg^{2+}". The main adsorption process here was the process of complexes forming between Pb^{2+} ions with groups of -NH_2. This group had H^+ exchange ability to form complexes with Pb^{2+} metal ions. This link was formed from the covalent links between the Pb^{2+} metal ions and nitrogen atoms in chitosal to form the electronic giving and receiving links.

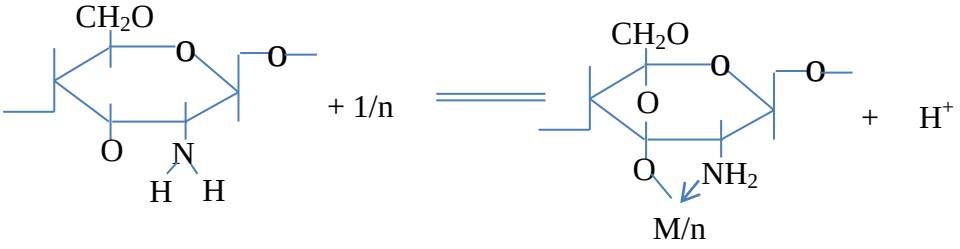

Fig. 10. ***The structure of chitosal associated with ion Mn^+***

4. CONCLUSIONS

We have synthesized chitosal gel particles with diameter 3.5mm and good solubility in 1% CH_3COOH solution. We have not found the optimal retention time

for lead adsorption results in the 1st experiments (lead concentration 6.98 mg/l). However, through the 1st experiment we do conclude that the lead concentration had an impact on adsorption efficiency. In the second experiment with an initial lead concentration 15,7mg/l we have identified 60-minute as the optimal retention time for column h_1 and adsorption efficiency reached 30.44%; Column h_2 and Column h_3 had optimal retentioon time of 90 minutes and adsorption efficiency reached 44.71%; 52.87% respectively. We have some recommendations based on our results: Research is needed to identify methods to optimise chitosal gel compression to avoid the broken gel in the adsorption process with greater flow; research is needed to identify the characteristics of the chitosal membrane as well as features of chitosal material to raise the metal adsorption efficiency in wastewater treatment; we recommend work to compare the chitin adsorption efficiency and chitosal to choose the best adsorption material with the lowest cost for the processing of metals treatment in wastewater.

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