



CHITOSAN-BENTONITE: THE SAFE ADSORBENT FOR PESTICIDES RESIDUES IN DRINKING WATER

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ABSTRACT

Bentonite materials modified by organic/amino agents were proven to be available as adsorbent for many applications. Especially for drinking water (that some time contaminant by organic and pesticides residues), it should be noticed that the adsorbent is safe for human. By the previous study, some amino-bentonites were successfully synthesized and were proven as the excellent adsorbent for diazinon, carbaryl, glyphosate, and endosulphane pesticides. The weaknesses of amino-bentonites are unstable to UV irradiation, high temperature of medium and time immersion in water. By the research, chitosan-bentonite was proven to be an adsorbent for pesticides residues in drinking water, instead of amino-bentonite. The easier to prepare, the cheaper, and the stability to high temperature of medium (water) make chitosan-bentonite preferable to use. Chitosan-bentonite showed good performance to adsorb diazinon pesticide as well as to glyphosate, with the percentage of adsorption was 80% in averages. It was also shown that diazinon adsorbed onto the surface of adsorbent through chemisorption interaction, especially through hydrogen bonding.

Key words: chitosan, bentonite, adsorption, pesticide

BACKGROUND

Since many years ago, bentonite is used as adsorbent especially for inorganic materials/pollutants ion on using exchange mechanism with Ca^{2+} ion that intercalated in the inner structure of bentonite.

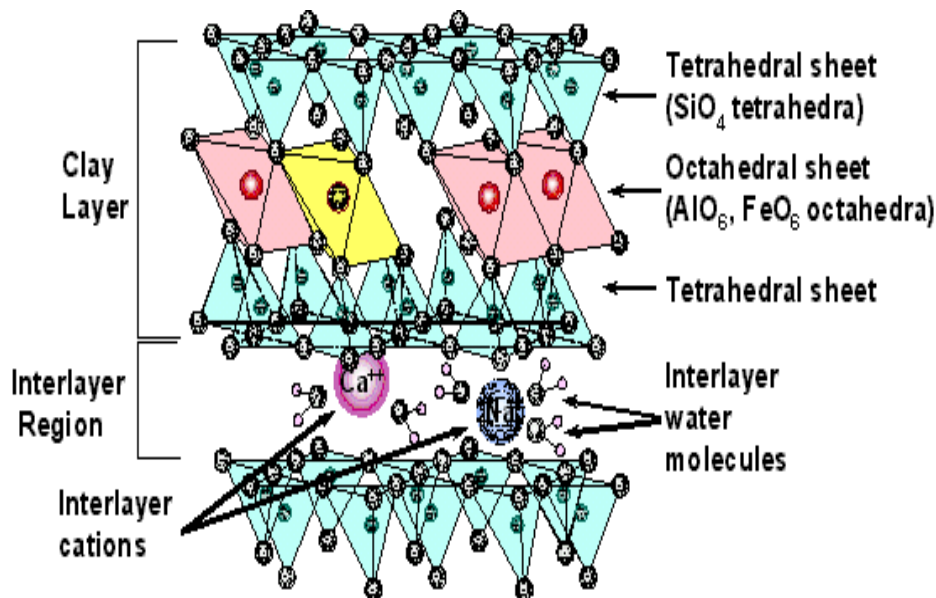


Fig.1. Inorganic pollutant such as mercury ion exchange the Ca^{2+} ion in the interlayer region of bentonite structure

Unfortunately, bentonite show less performance for organic pollutants adsorption because of it is not enough site to nonpolar interaction. To increase the adsorption capacity, bentonite has successfully modified to be organo-bentonite.

By the research, it was proven that bentonite modified by organic materials such as histidine showed good performance to adsorb organic pollutant as well as inorganic pollutant. It was studied that histidine-bentonite showed good capacity. Nearly 95 % pesticides adsorbed from 200 ppm pesticides solution in water (50 mL) on using 5 grams of adsorbent. The good performance of histidine-bentonite would be caused by the strong interaction between adsorbent and pesticides itself. It has proved through sorption-desorption design experiment, that hydrogen bonding provided the greatest portion (~61%) to the mechanism of interaction. It was also proven that the bonding energy found to be ~ 21 kJoule; this is agreed with the prerequisite to chemisorption mechanism. Even though the histidine-bentonite is the great performance, the save, and the low price adsorbent, but it showed some weaknesses, such as

unstable to high temperature, UV irradiation, and long immersing time in water. The histidine was destroyed and released from bentonite, so the performance to adsorb pesticides turned to decrease. By the research, it has found that chitosan can be used instead of histidine, showed the better performance (~100% adsorbed with the same condition above), and more stable.

Chitosan is a biopolymer of poli- β (1-4)-2-amino-2-deoksi- D-glukosa *poly-N-acetyl-D-glucoseamine*, that can be derived from polysaccharide of chitin 1-4)-2-asetamido-2-deoksi-B-D-glukosamin.

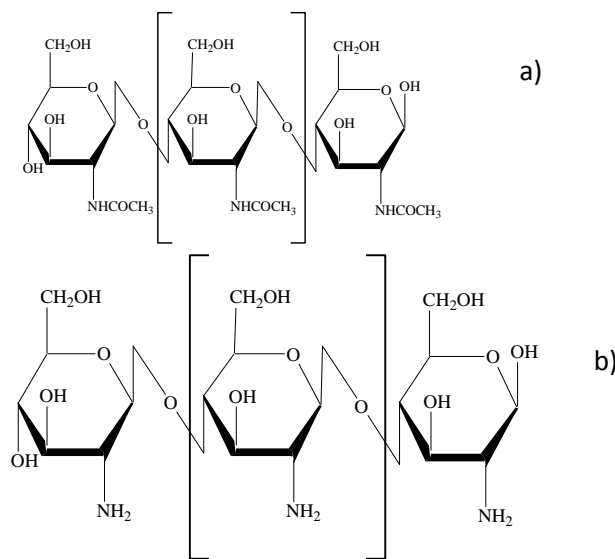


Fig. 2. Chitin (a) and chitosan(b) structures (Li dan Kegley, 2005)

The differences between chitin and chitosan are in nitrogen content and degree of deacetylation. Chitin has nitrogen less than 7%, whereas chitosan is more than 7% (Widodo *et al.*, 2005). Revol dan Marchessault (Khan *et al.*, 2002) mention that chitin has a deacetylation degree less than 75%, and chitosan would be more than it.

METHODS

The research was carried out in research laboratory of Chem. Dept. of UPI, and the measurement of XRD and SEM was at research and developmental centre of ocean-geology body of Bandung-

Indonesia. The steps of activities were prepare bentonite (activation by Ca^{2+}); synthesize chitosan from crust shell by deacetylation methods; determine optimum condition of modifying bentonite by chitosan such as optimum bentonite mass and contact time; synthesize bentonite-chitosan; characterize of bentonite before and after modified on using IR and XRD spectrometric, and SEM; performance test of bentonite-chitosan to pesticide (diazinon). Diazinon standard and chitosan standard were prepared from p.a. grade, meanwhile others (CaCl_2 , acetic acid, and other reactants) were prepared from technical grade.

RESULT AND DISCUSSION

Chitosan was made by deacetylation of chitin to change the amide groups of chitin into amine groups to be chitosan chains. The mechanism of deacetylation in basic condition is described in Fig. 3. The process was successfully done to transform most of chitin to chitosan with deacetylation degree as much as 87.04 %

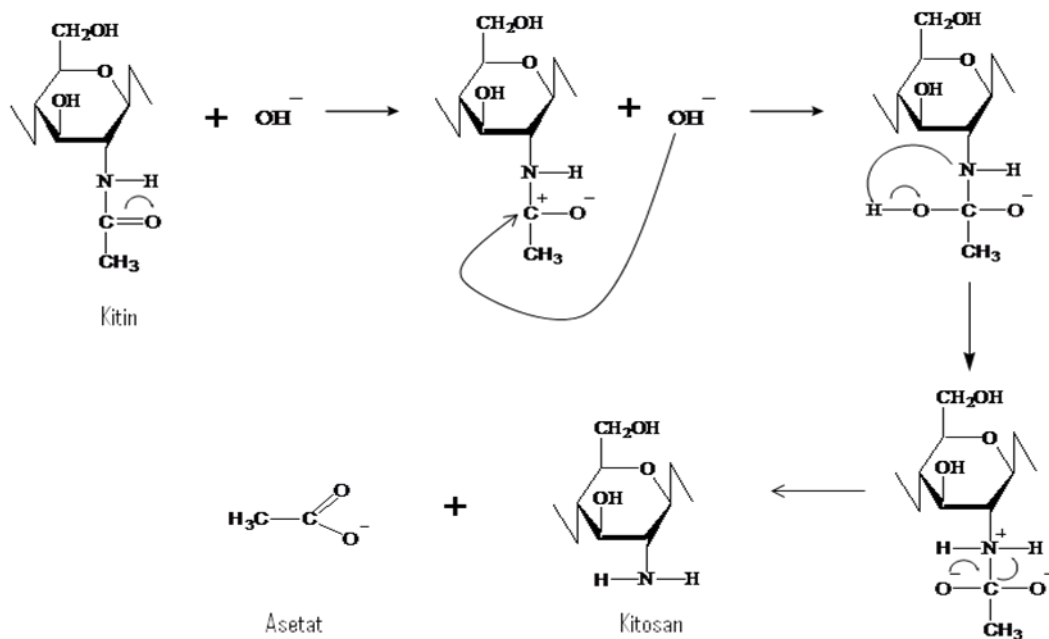


Fig.3. The mechanism of deacetylation reaction of chitin in basic media

The transformation chitin into chitosan will easily observed from the FTIR spectra measurement before and after acetylation. Figure 4 is FTIR spectra of chitin (a) and chitosan (b). The peak of 1654.8 cm^{-1} is belong to $\text{C}=\text{O}$ group of amide rings of chitin (5A), and was disappear at chitosan spectra (B).

Instead of it, the 3433.1 cm^{-1} peak of O-H and N-H stretch is arisen as well as 1589.2 cm^{-1} of N-H (NH_2 group) bending vibration. Moreover, the 2920 cm^{-1} of C-H and $-\text{CH}_2-$ stretch vibration, the 1423.4 cm^{-1} and 1589.2 cm^{-1} of bending vibration of C-H from $-\text{CH}_2-$ groups, the 1153.4 cm^{-1} $-\text{C}-\text{O}$ stretch vibration, the 1033.8 cm^{-1} C-O-C stretch vibration (glucosamine ring) were responsible to chitosan structure.

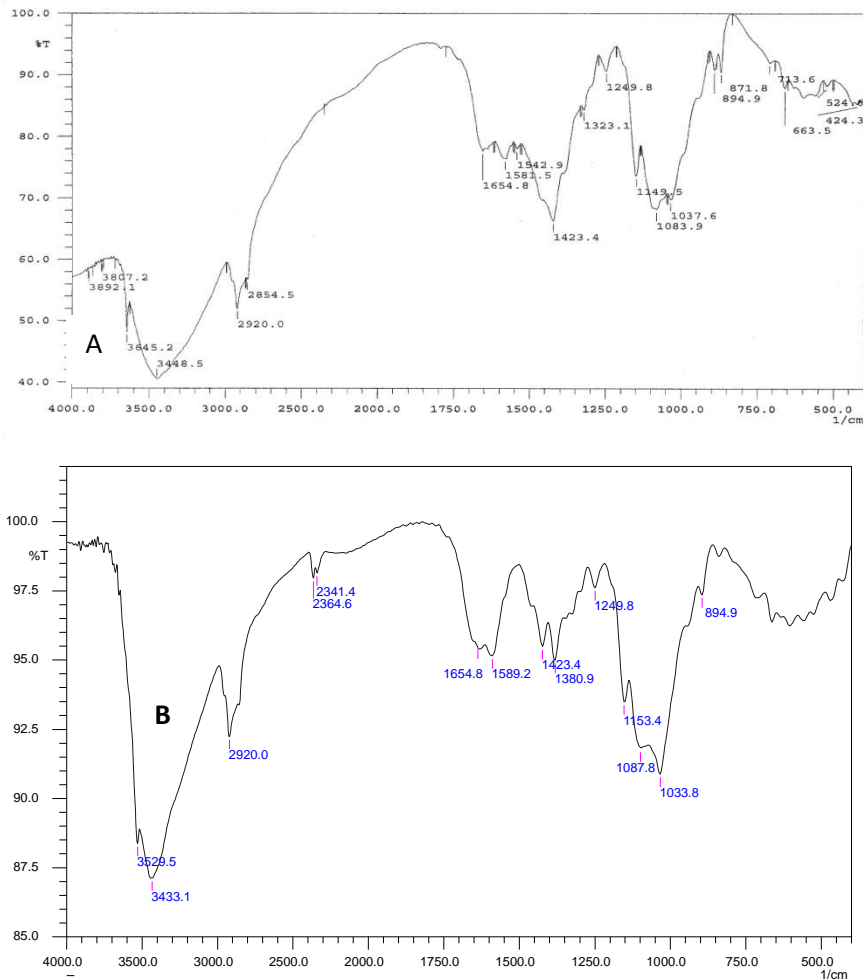


Fig. 4. FTIR Spectra of Chitin (A) and Chitosan (b) after Deacetylation

Chitosan-bentonite was made by equilibration of Ca-bentonite into chitosan solution under pH controlled (pH 3 with acetic acid, under definite condition. chitosan-bentonite performance are more soft white materials, less pores, and smoother than bentonite itself. This is because of commonly organic bulky species come into contact with bentonite through outer layer interaction (Fitri, 2005). The difference of FTIR spectra between Ca-bentonite and chitosan-bentonite give simple explanation to the modification of Ca-bentonite by chitosan.

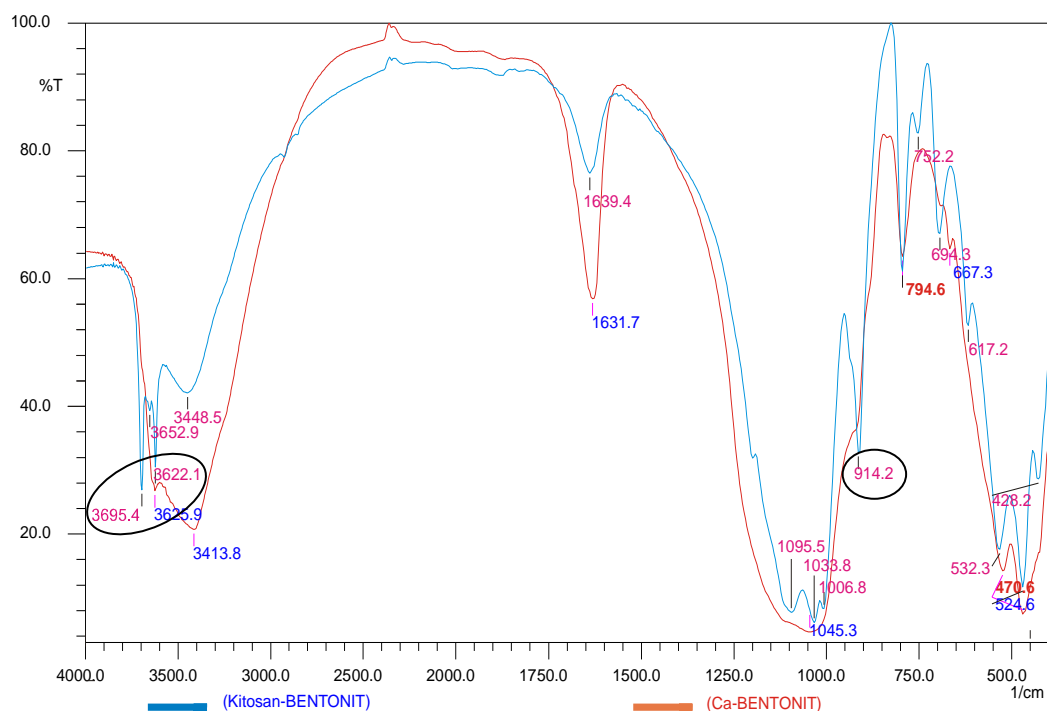


FIG.4. FTIR Spectra of bentonite before (brown line) and after (blue line) modified by chitosan

The change of bentonite spectra after equilibrium with chitosan showed that the modification process that is caused by interaction chitosan-bentonite, was run well. There are some shifts of wave number of bentonite spectra found, such as 667.3 cm^{-1} to 694.3 cm^{-1} , 1631.7 cm^{-1} to 1639.4 cm^{-1} , 3413.8 cm^{-1} to 3448.5 cm^{-1} and 3625.9 cm^{-1} to 3622.1 cm^{-1} . The new peaks of 3695.4 cm^{-1} , 1033.8 cm^{-1} , 914.2 cm^{-1} indicate N-H stretch, C-O-C stretch of glucosamine ring, and C-C stretch of sacharide. The 1045.3 cm^{-1} of Si-O stretch of bentonite structure was disappeared after modification. This is probably due to covering Si-O layer by chitosan structure. Moreover, the 1045.3 cm^{-1} peak in chitosan-bentonite is sharper than in Ca-bentonite, that is caused by chitosan and Si-O group interaction, so chitosan covered the surface of bentonite. The increase of wave numberis responsible to the more strong interaction between chitosan and bentonite. Hydrogen bonding between water molecules is predicted weaker than hydrogen bonding between chitosan-bentonite.

Compare to Ca-bentonite, the appearance of chitosan-bentonite is nearly unchanged, as it is showed by XRD spectra in Fig. 5.

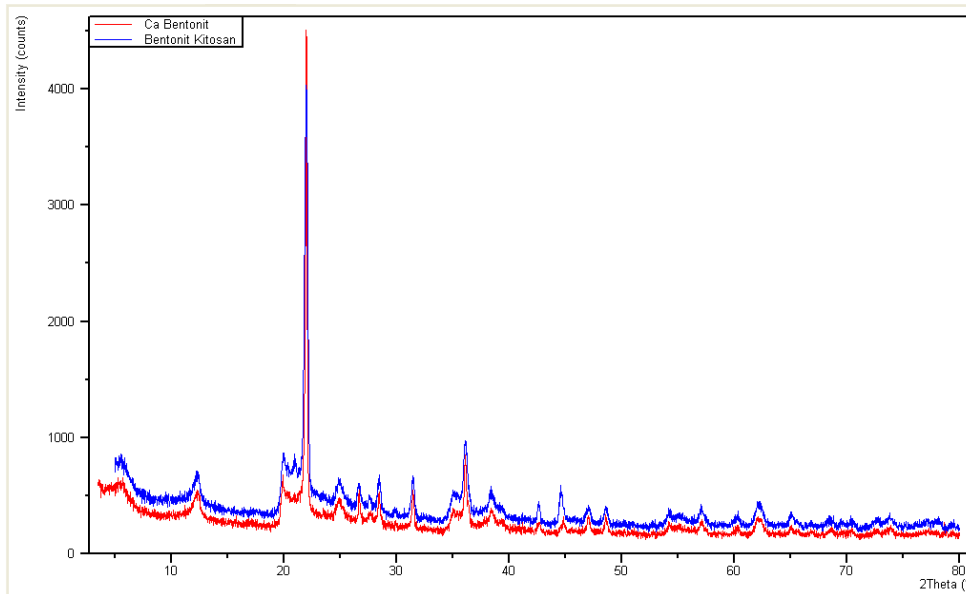


Fig. 5. XRD Spectra of (a) Ca-Bentonite dan (b) chitosan-Bentonite

The character absorption of monmorilonite (Ca-Bentonite) is showed by the values of 2θ these are 5.31; 19.88; dan 28.45 with the d values are 15.74 Å, 4.46 Å, dan 3.13 Å. The values of 2θ and d of both of bentonite and chitosan-bentonite are as follows.

Table 2. XRD data of Ca-bentonite and chitosan-bentonit

2θ		d(Å)	
Ca-Bentonite	Chitosan-bentonite	Ca-Bentonite	Chitosan-bentonite
15.74	15.30	5.31	5.77
4.46	4.43	19.88	19.98
3.13	3.08	28.45	28.96

The similarity of XRD patterns can be predicted as the result of outerlayer interaction of chitosan and bentonite surface. The argument was strengthened by SEM photos of bentonite, before and after interacted with chitosan as it is showed in Fig. 6. It is showed that Ca-bentonit more porous than chitosan-bentonite. This will be due to the fact that chitosan molecules/species interacted with bentonite onto the surface. This is agreed with the appearance of SEM photos of both of materials.

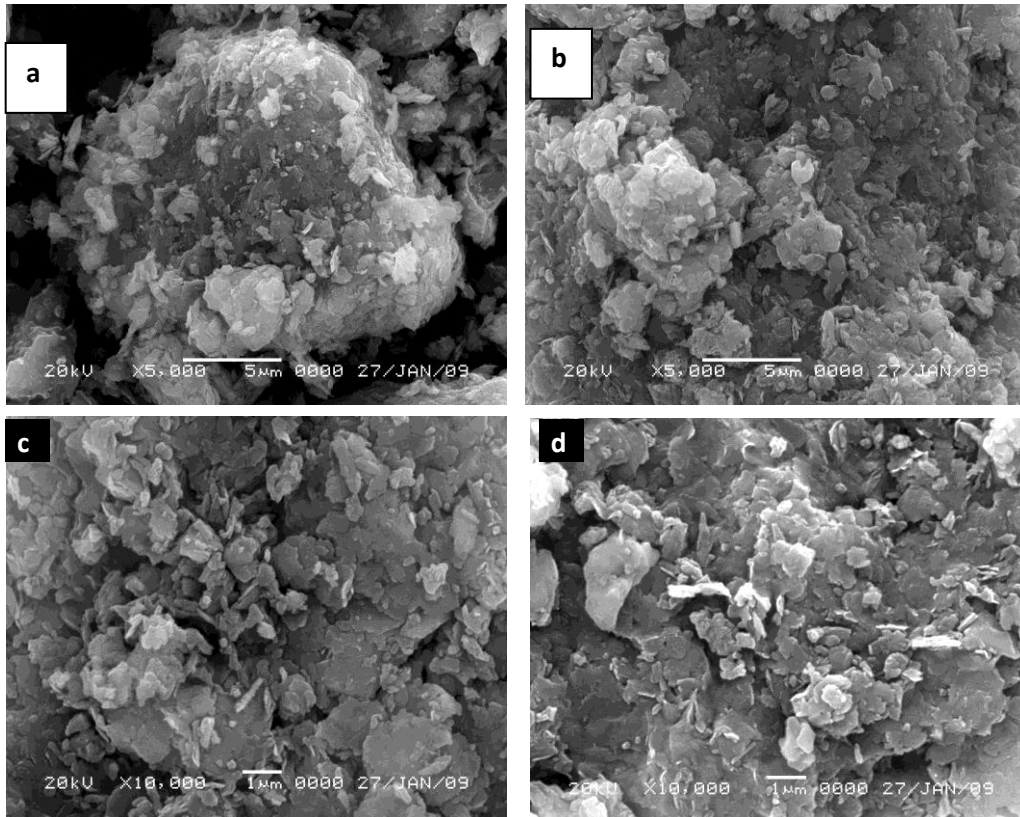


Figure 6. SEM photos of Ca-bentonite (a, b) and chitosan-bentonite (c,d)

Figure 6 shows that Ca-bentonite has a larger porosity than chitosan-bentonite that is showed by the larger size of pores of Ca-bentonite. The change of porosity is probably because of chitosan molecules interacted and cover the bentonite surface. By the research it was proven that chitosan strongly adsorbed onto bentonite surface, as indicated in Fig.7.

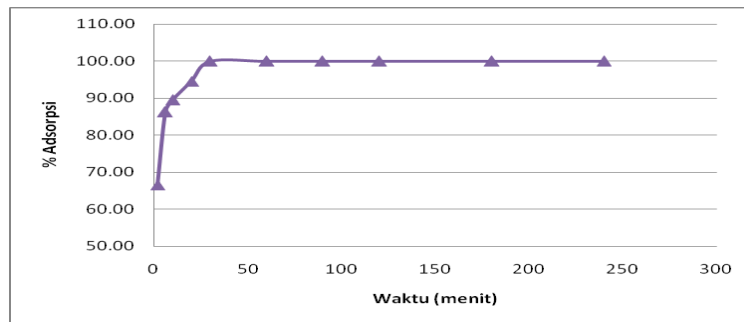
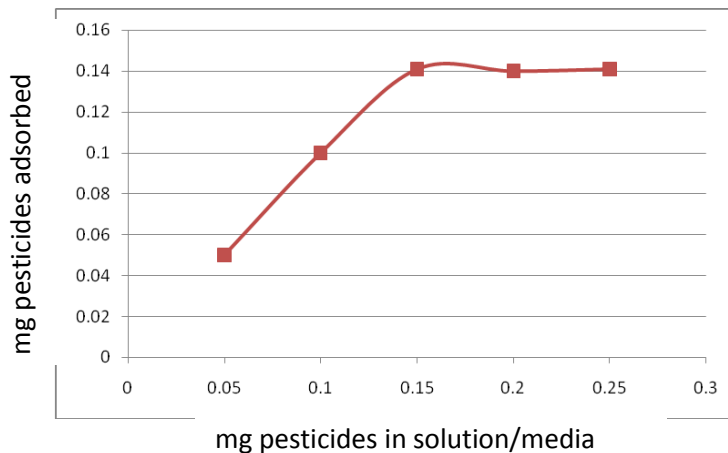


Fig.7. All of chitosan completely interrelated with bentonite after 50 minutes equilibration (mass ratio bentonite: chitosan = 1 :180)

The performance of Chitosan-bentonite adsorbent was examined to pesticides residues (diazinon) in synthetic drinking water. Adsorption process was maintained by equilibration of 0.5 gram chitosan-bentonite in 10 mL of 5,10,15,20, and 25 ppm pesticides solution (under pH water ~6.5 while stirring continually at 180 rpm under room temperature condition ,25°C). After equilibration, the un-adsorbed pesticide residue in supernatant is examined on using spectrometric UV technique. Adsorption data of diazinon by chitosan-bentonite is shown in Fig.8.



It is showed that diazinon adsorbed onto 0.5 g chitosan bentonite reached maximum capacity as much as 0.141 mg diazinon/ 0.5 g adsorbent, so it means that the capacity adsorption of chitosan bentonite to diazinon is 141 mg/kg . This is a high prospect of chitosan-bentonite adsorbent, so it should be followed up with study of theoretical aspects of adsorption on using chitosan-bentonite, such as mechanism of adsorption, kinetic, and also energy involved.

CONCLUSION

Chitosan-bentonite was proven to be an adsorbent for pesticides residues in drinking water, instead of amino-bentonite. The easier to prepare, the cheaper, and the stability to high temperature of medium (water) make chitosan-bentonite preferable to use. Chitosan-bentonite showed good performance to adsorb diazinon pesticide, with the capacity of adsorption was 282 mg diazinon/kg adsorbent. It was predicted that diazinon adsorbed onto the surface of adsorbent through chemisorption interaction. The next research should be focused in theoretical aspects, such as mechanism of adsorption, kinetic, as well as bonding energy involved.

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