Adsorption Capacity of Chitosan Beads in Toxic Solutions

P. Setthamongkol, J. Salaenoi

Abstract—The efficiency of chitosan beads processed from 4 marine animal shells; white leg shrimp (*Litopenaeus vannamei*), mud crab (*Scylla* sp.), horseshoe crab (*Carcinoscorpius rotundicauda*), and cuttlefish bone (*Sepia* sp.), for the adsorption experiments of ammonia and formaldehyde were investigated. The porosities of chitosan from the shells looked like beads were distinctly examined under SEM. The original pores of those shells on the surface areas compose of evenly fine pores. The shell beads of cuttlefish bone and horseshoe crab show the larger probably even porosity, while on those white leg shrimp and mud crab contain various large and fine pores. The best adsorption at pH 9 in 18 mg/l ammonia at 2 hours yield on cuttlefish bone, horseshoe crab, mud crab and white leg shrimp with the average percent of 59.12, 51.45, 45.66 and 43.52, respectively. Within 30 minutes the formaldehyde absorbers (at pH 5 in 8 µg/ml) revealed 46.27, 26.56, and 18.04 percent capacities in cuttlefish bone, mud crab and white leg shrimp beads; while 22.44 percent in the horseshoe crab at pH 7. The adsorption capacities and the amounts of beads showed a positive correlation. The adsorption capacity relationship between pH and the gas concentrations were affected by these qualities of chitosan beads.

Keywords— chitosan, adsorption, ammonia, formaldehyde

I. INTRODUCTION

CHITOSAN is a polysaccharide compound (2-amino-2deoxy-D-glucose), which is mostly obtained from deacetylation of chitin, a poly (*N*-acetyl-D-glucosamine) [1]. Chitosan is able to be dissolved in an acid solution medium below pH 6 by the interaction between hydroxyl (-OH) and amine (-NH$_2$) groups [2]. Therefore, chitosan shows a very high adsorption ion through several mechanisms including; chemical interaction, such as chelation, electrostatic interaction, as well as ion exchange, or the formation of ion pairs [3]. Furthermore, the adsorption of chitosan depends upon the size of pore structures, which can control the processes of forming chitosan beads, such as filling the porous additives or controlling the porosity by freeze drying [4], in order to increase the surface area of chitosan beads. Therefore, the size of porous and surface electron can affect chitosan adsorption.

The chitosan is also applied to biomedical multipurpose uses by adding the components in pills for controlling drug diffusion [5], as a sedimentary substance to separate protein and fat from water in water treatment [6], as a color eliminator in waste water [7] and as ionic trapper (Copper and Mercury) in waste water from industrial factories.

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Chitosan beads produced by dissolving chitosan in citric acid or formic acid before adding NaOH or NaOH-Methanol do strengthen them, but the pore size depends on the intensities of chitosan solvents, deacetylation, types and forms of original substances [8]. Chitosan can be extracted from invertebrate shells such as, shrimps, prawns, crabs and insects [9]. It also safeguards humans, animals and the environment. In addition, chitosan can be recycled and recover its adsorption ability via two different processes, physisorption and chemisorptions, and can eliminate the toxic gases from the atmosphere. The chitosan beads from 4 marine animal shells: white leg shrimp shell, mud crab shell, horseshoe crab shell and cuttlefish bone, were processed. The beads would be treated through various experiments for the adsorption of ammonia and formaldehyde gas capabilities. The influence of adsorbent concentration, adsorption time, initial solution concentration and pH has been analyzed in detail to fulfill the purposes of understanding the adsorptions of chitosan.

II. MATERIALS AND METHODS

A. Materials

Chitosan beads were prepared from 4 marine animal shells; white leg shrimp shell (*Litopenaeus vannamei)*, mud crab shell (*Scylla sp.)*, horseshoe crab shell (*Carcinoscorpius rotundicauda*) and cuttlefish bone (*Sepia sp.).* Degrees of deacetylation of chitosan were evaluated by Colloid Titration Method [10]. The original chitosan was individually analyzed on the dissolution, viscosity and physical characteristics, such as external surface area and porous volume by Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) Surface Area Analyzer Method prior to the chitosan preparation.

B. Preparation of chitosan beads

The chitosan solution, with a concentration of 4 %v/v, was obtained by dissolving the original chitosan in 2 %vols acetic acid solution and intensive stirring in room temperature for at least 48 h. The mixture was added by syringe into an aqueous solution of KOH : ETOH with a concentration ratio of 1:1, under mild magnetic stirring. The microspheres were stirred for 24 h at room temperature and then intensively washed with distilled water. Then, the chitosan beads were examined for their characters under SEM.

C. Methods

In the batch studies, the effects of concentration of ammonia and formaldehyde removal efficiencies by chitosan were examined by using ammonium hydroxide solutions and formaldehyde solutions. Thus, 5 g of wet chitosan beads were placed in a flask, contracted with 30 ml of ammonium hydroxide or formaldehyde solutions (5 g chitosan/ 30 ml solution), shaken at 150 rpm, 25°C and collected at time periods; ½, 1, 2, 3, 4 h. Chitosan was then filtered out and measured for its remaining concentrated solution.

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The solution of concentrated ammonia was calculated by equation (1) and formaldehyde was calculated by second degree parabola equation from 1 - 10 µg / ml formaldehyde standard curve (2). The removal efficiency for the remaining solvent was calculated by equation (3). All the data was reported by using average values derived from triplicate replications.

$$\text{Ammonia concentration (mg/l)} = \frac{(A-B) \times N \times 1400}{\text{Sample volume (ml)}} \quad (1)$$

Where: A and B are used in volume (ml) of H_2SO_4 in the titration sample and blank, respectively, N is the concentration of H_2SO_4 (normality: N)

$$y = 8.7757x^2 + 11.078x - 0.0116 \dots (R^2 = 0.9959) \quad (2)$$

Where: y and x are absorbance (Abs) and concentration of formaldehyde, respectively.

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C)}{C_0} \times 100 \quad (3)$$

Where: C_0 and C are the concentrations of ammonia solution before and after the interaction with chitosan, respectively.

D. Effect of pH and concentration on ammonia solution

The optimum concentration of ammonia solution, period of time, pH value and volume of chitosan beads could be formally assigned after the completion of batch experiments. The solutions were calibrated with hydrochloric acid and sodium hydroxide to pH values ranging from 8 to 10. The samples were analyzed by the titration method [11]. The parameter treatments are shown as following;

TABLE I
THE PARAMETER TREATMENTS OF AMMONIA ADSORPTION

Characters	Parameter treatments
1. Species of chitosan beads	white leg shrimp, mud crab, horseshoe crab and cuttlefish bone
2. Concentration of NH_4OH	18, 20, 22, 24 mg/l
3. Period of activated time	½, 1, 2, 3, 4 h
4. pH	8, 9, 10
5. Wet chitosan beads	5, 10, 15 g

E. Effect of pH and concentration on formaldehyde solution

At this phase of the experiment, the optimum concentration of formaldehyde solution, period of time, pH value and volume of chitosan could also be formally assigned. The solutions were calibrated with hydrochloric acid and sodium hydroxide to pH values ranging from 5 to 9. The samples were analyzed by the British Pharmacopocia Method [12]. The parameter treatments are shown as following;
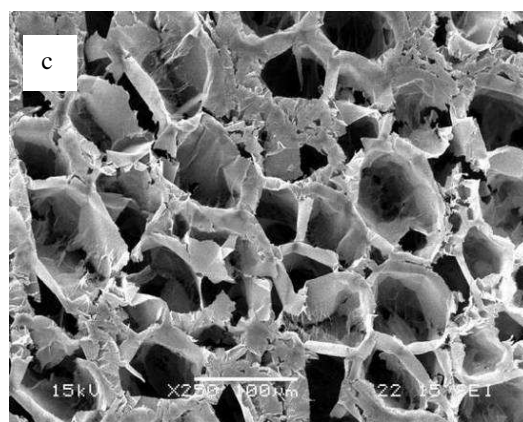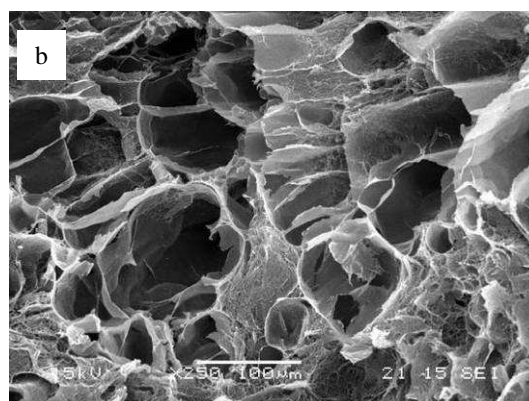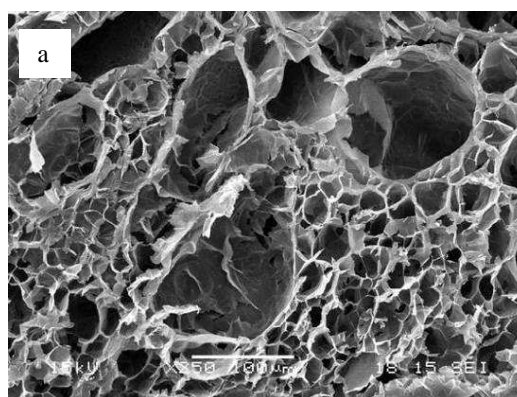
TABLE II
THE PARAMETER TREATMENTS OF FORMALDEHYDE ADSORPTION

Characters	Parameter treatments
1. Species of chitosan beads	white leg shrimp, mud crab, horseshoe crab and cuttlefish bone
2. Concentration of CH_2O	4, 6, 8, 10 µg/ml
3. Period of activated time	½, 1, 2, 3, 4 h
4. pH	5, 7, 9
5. Wet chitosan beads	5, 10, 15 g

III. RESULTS AND DISCUSSION

A. Physical characteristics of chitosan beads

Chitosan from mud crab, white leg shrimp, cuttlefish bone and horseshoe crab shell indicated a moderate degree of deacetylation, that is, 69.30, 66.74, 64.29 and 60.94 %, respectively. Viscosity and dissolution properties of white leg shrimp chitosan revealed the highest values, followed by mud crab chitosan. The surface area and pore diameter of original chitosan were in the range of 60.27 $\times 10^{-2}$ to 93.08 $\times 10^{-2}$ m^2/g and 26.77 to 116.02 A^o, respectively. Therefore, original chitosan was developed as chitosan bead to increase porous and surface area.

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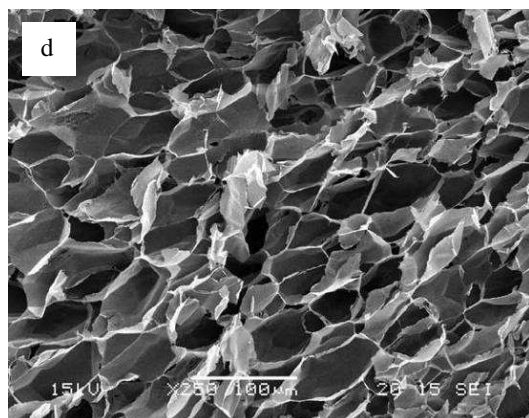International Journal of Chemical and Molecular Engineering
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Fig. 1 SEM images on the internal surface are a of chitosan beads (x250): a, white leg shrimp; b, mud crab; c, cuttlefish bone and d, horseshoe crab

The bead cross sections were examined under SEM (x250) for their characteristics. They were generally incomplete spherical shapes; varying in size and strength, depending on their viscosities of the related species. The average diameters of the chitosan beads from white leg shrimp, horseshoe crab, mud crab and cuttlefish bone were 4.23, 4.08, 3.88 and 2.52 millimeter, respectively. The cuttlefish bone and the horseshoe crab were composed of almost regularly shaped pore sizes; 71.4 to 57.1 micrometer, respectively. The pore diameter was compared by scale with SEM. The pore sizes of both white leg shrimp and mud crab chitosan beads presented high variations of 21.4 to 164.3 micrometer and 57.1 to 135.7 micrometer, respectively (Fig. 1).

B. Ammonia Adsorption

1. Effect of pH and concentration on ammonia solution

Ammonia evaporation was tested within 48 h and the results show that the evaporation rate of ammonia was low from 1 min to 8 h, while the initial adsorption ratios was increase and gradually decreased to a constant level at 4 hours. Thus, the reduction of ammonia within 4 h was caused by adsorption rather than evaporation.
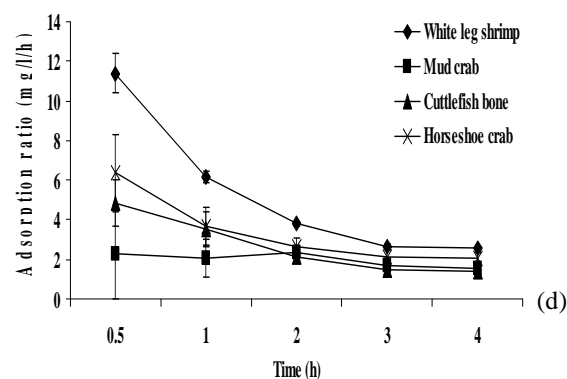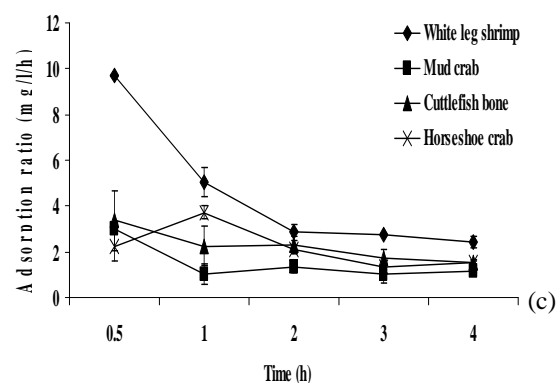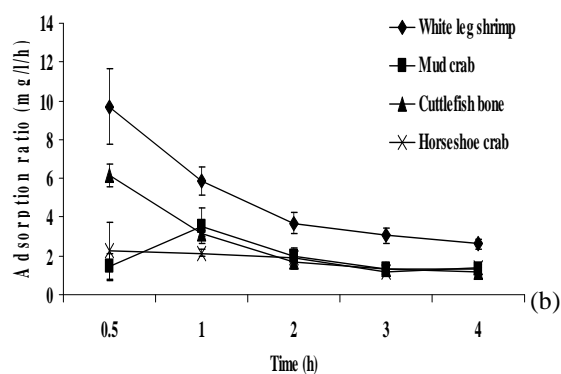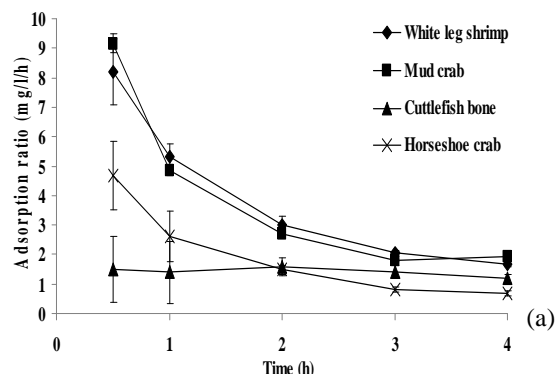

Fig. 2 The averages of adsorption ratios on 4 chitosan beads from initial ammonia concentrations: a, 18 mg/l/h; b, 20 mg/l/h; c, 22 mg/l/h; and d, 24 mg/l/h

The adsorption activities in 18 mg/l initial ammonia solutions do gradually decrease with time, and 2 h durations were sufficient to reach sorption equilibriums. After absorbing, ammonia volume was reduced to 27 ml. The average adsorption ratio of chitosan from mud crab, white leg shrimp, horseshoe crab and cuttlefish bone were 9.15, 8.21, 4.67, and 1.49 mg/l/h, respectively.

Which consistent with the degree of deacetylation of chitosan. Thus an increase in degree of deacetylation generally gives an increase of protonated amine groups and adsorption capacity [13]. However, chitosan beads from white leg shrimp probably showed the highest adsorption ratio, while those from mud crab and horseshoe crab posted low adsorption

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efficiencies in higher concentrations of ammonia solutions (Fig. 2). The white leg shrimp chitosan with has both small and large pores in one bead has ability to absorb molecules of different sizes, better than other types of chitosan with smaller pore size, when increasing the concentration of the solution.

The variations of ammonia adsorption in percent by chitosan beads at pH 9 are approximately 35.86, 29.43, 28.93 and 17.61 % on horseshoe crab, cuttlefish bone, mud crab and white leg shrimp, respectively. The pH values in ammonium solutions obviously play an important role on the ion exchanging. At low pH, the ammonium ions have to compete with hydrogen ions among the exchange sites along with evaporation to the atmosphere, and when in the higher pH, the ammonium ions are transformed to aqueous ammonia [14]. Therefore, the reductions of ammonia are caused rather by adsorption than evaporation. The 2 types of hydroxyl group of chitosan, primary alcohol (-CH$_2$OH) and secondary alcohol (-CHOH) are weak bases, the electron pairs (-NH$_2$) can persuade a bond of cation (Fig. 3a).

The ammonia uptake capacities of 5, 10 and 15 g of wet chitosan beads are increased positively. The beads of cuttlefish bone, horseshoe crab, mud crab, and white leg shrimp adsorb ammonia up to 59.12, 51.45, 45.66 and 42.52 % in 15 g treatments, respectively (Fig. 3b). The chitosan beads further increase surface area when in contact with the absorbed substances.
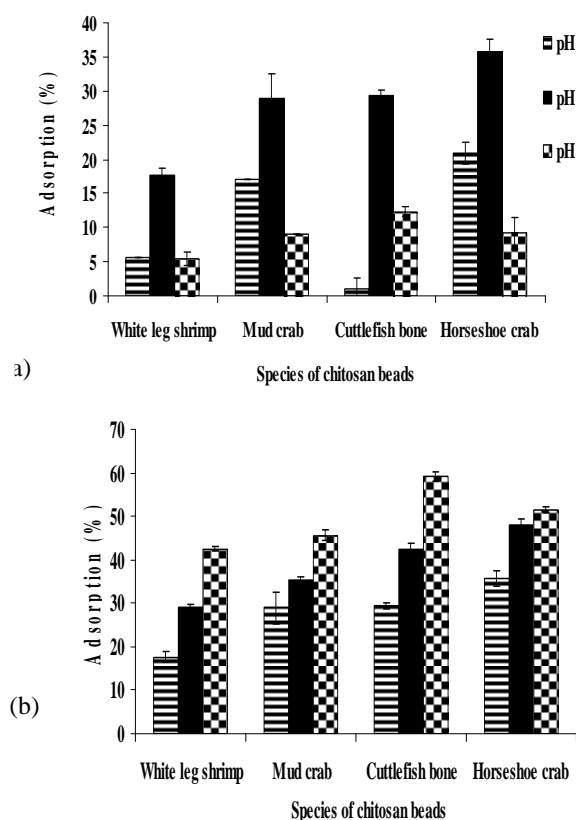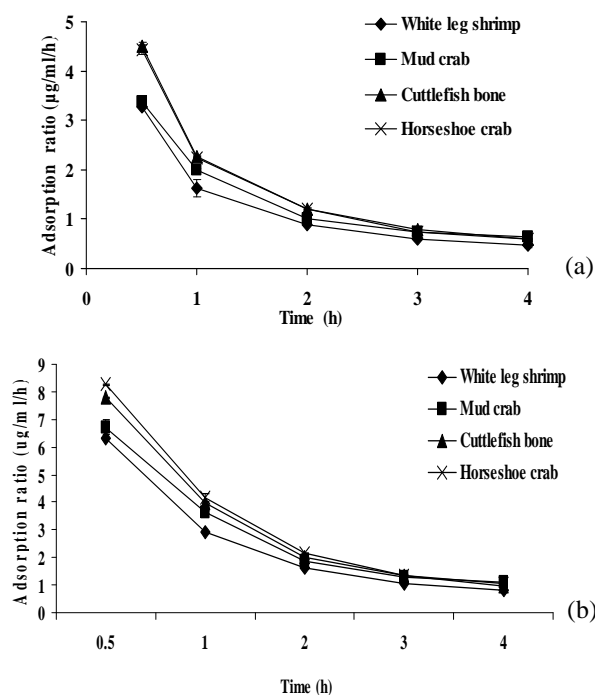
C. Formaldehyde adsorption

1. Effect of pH and concentration on Formaldehyde solution

The initial research on formaldehyde uptake capacity by beads at 1 min to 48 h had indicated low evaporation at 1 min to 16 h and had the highest adsorption ratio at 30 min, and also constantly decreased toward their equilibrium in 8 µg/ml media. Therefore, the 1 min to 4 h activated times had been formally tested and proven. The formaldehyde adsorption ratios (µg/ml/h) for the beads of horseshoe crab, mud crab, cuttlefish bone and white leg shrimp were averaged at approximately 8.26, 7.44, 7.02 and 6.35 µg/ml/h, respectively. The final formaldehyde uptake activities were about 70 to 80 percent complete within 30 min and the removal rates became slower compared to their activated times (Fig. 4).

The chitosan beads show the percent of maximum adsorped ability at 46.27, 26.56, 22.44 and 18.04 % on cuttlefish bone, white leg shrimp, horseshoe crab and mud crab at pH 7, 5, 7 and 5 in formadehyde media (Fig. 5a). The pKa values of chitosan in the amino groups fall at pH 6.3 to 7, [15] because when pH is below pKa of chitosan, the amino groups are almost completely ionized, and the charge density of chitosan increases; thus, chitosan shows very high adsorption capability ion [16]. The pH does influence due to, both the characteristics of the exchanging ions and the characteristics of the chitosan themselves. The formaldehyde uptake capacity decreases with an increase of pH. A pH lower than 5 does not have a positive adsorption due to the swelling ratio of crosslinked chitosan, which increased in low pH (pH >5) solution and rose sharply against pH less than 3.3 [17]. This could be confirmed that, in an acidic medium the amino group on chitosan protonized, so that the hydrogen bond between chitosan and silk fibroin were broken and the network was dissociated.

Fig. 3 The average removal efficiency from different pH of ammonia solutions (a) and wet chitosan beads (b)

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(c)

(b)

Fig. 5 The average adsorption (%) on various pH of formaldehyde
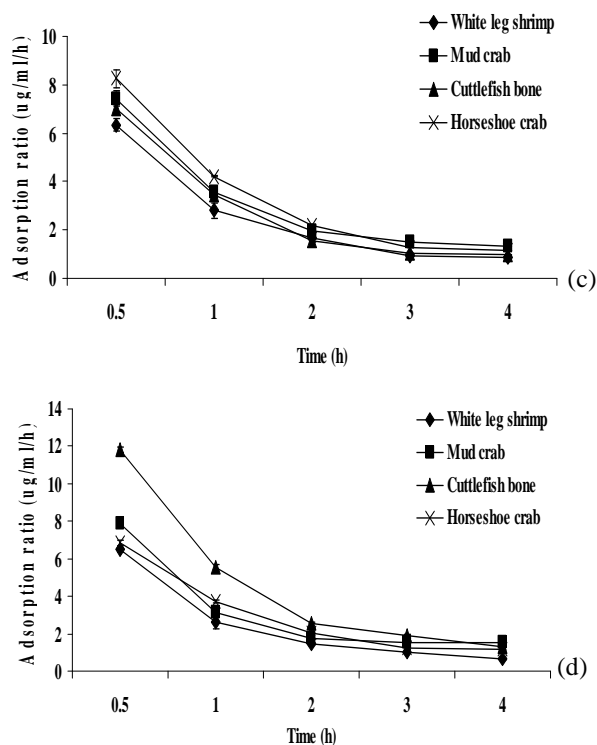solutions (a) and wet chitosan beads (b)

(d)

Fig. 4 The average adsorption ratios of 4 chitosan beads from initial
formaldehyde concentrations: a. 4 µg/ml/h; b. 6 µg/ml/h;
c. 8 µg/ml/h; d. 10 µg/ml/h.

The best, adsorbent removal of ammonia and formaldehyde solution is cuttlefish bone chitosan bead, with large regularly porous absorbed effectively smaller molecules on. The other chitosan beads contain both small and large pores, which are unable to absorb large molecules. This results in low efficiency. Chitin from squid pens has β–structure which is different from α–structure of crustacean chitin. The polymer chains of β–structure have strong intermolecular hydrogen bonding. While β–chitin has weak inter molecular interaction, but the β–chitin has greater reactivity to the deacetylation and chemical modification than α–chitin, [20]. That is, chitosan from cuttlefish bone will have high reaction more so than chitosan from white leg shrimp and mud crab.

The formaldehyde uptake capacities of 5, 10, and 15 g chitosan beads increased positively over medial solutions. The percentage of adsorption in cuttlefish bone, mud crab, horseshoe crab and white leg shrimp averaged around 63.73, 54.98, 47.35 and 47.31 %, respectively (Fig. 5b). The chitosan beads also increased their surface area in contact with the substances to be absorbed, but Choong and Kwang [18] have had opposite results on the dosage used in mercury ion tests. The surface chemistry does affect the formaldehyde adsorption more than texture characteristics of the surface area and pore volume [19].
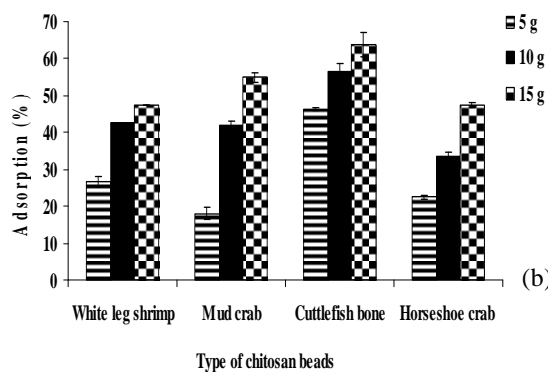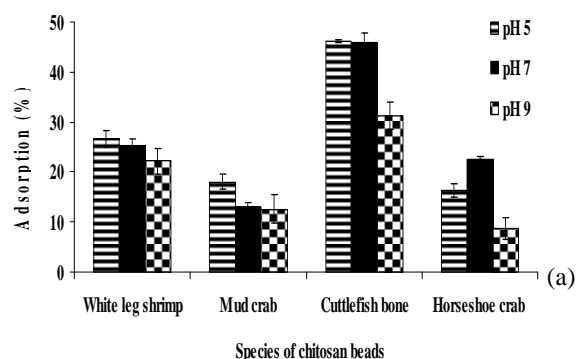
IV. CONCLUSIONS

The chitosan beads dosage, pH, concentration of ammonia and formaldehyde have an influence on chitosan adsorption. The optimum conditions were found to be a pH of 9, 15 g dosage of chitosan beads, 18 mg/l concentration of ammonia and a 2 h time period for the ammonia adsorption (59.12-42.52%). Chitosan bead from cuttlefish bone had the highest adsorbent, followed by horseshoe crab, mud crab and white leg shrimp. The formaldehyde adsorption experiments had optimum conditions at 15 g dosage of chitosan beads, 8 µg/ml concentration of formaldehyde to adsorb 30 min at pH 5, exception on horseshoe crab (pH 7) to reduce formaldehyde (18.04-46.27%). The chitosan beads order of maxima adsorbents were those from cuttlefish bone, white leg shrimp, horseshoe crab and mud crab, respectively.

(a)

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