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ADSORPTION STUDY OF MERCURY SPECIES FROM AQUEOUS SOLUTION USING THIOCARBAMOYL CHITOSAN

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ABSTRACT

Thiocarbamoyl chitosan was successfully synthesized, characterized and tested for mercury removal from aqueous solutions. The chemical structure of thiocarbamoyl chitosan was identified by using the Fourier-Transformed Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) for morphology surface analysis. EDX plot was further confirmed the presence of elemental sulfur on chitosan backbone with weight percentages calculate to be 14.58%. Elemental Analysis (CHNS) was demonstrated the value of 0.55 account to be substitution degree of thiocarbamoyl chitosan. Various parameters such as influence of pH, weight of sorbent, initial concentrations, exposure time, stirring rate and presence of competitor ion was tested. In adsorption isotherm batch experiment, Langmuir model can be fitted well with correlation coefficient value, R^2 = 0.983-0.997 only for methyl and ethyl species. Maximum adsorption at monolayer for each species was obtained at 15.03 (MeHg), 11.59 (EtHg) and 27.17 mg/g (Hg (II)), respectively. For inorganic species, Freundlich model was found can be fitted well with R^2 = 0.948. The experimental data was demonstrated to follow pseudo second-order kinetics with rate constant of 1.077 (methyl mercury), 1.12 (ethyl mercury) and 1.01 g/mg/min (inorganic mercury), respectively.

Key words: Thiocarbamoyl chitosan, Mercury, Water treatment.

INTRODUCTION

Chitosan (poly-n-glucosamine) is a biopolymer product, commercially yield through alkaline de acetylation process of chitin. Chitosan showed a significantly difference not only

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in terms of chemical structure (amine group $–NH_2$) but soluble in organic acid medium compared than chitin[1]. However, the usage of chitosan directly in water treatment still being limited due to insoluble in water especially nearly pH neutral[2]. Thus, chemical modifications is alternative ways to make chitosan are being capable to react as biosorbent especially metal sorption into aqueous solution. The modifications of chitosan was involved the additional of hydroxyl group (-OH) and amine group ($-NH_2$) on the structure of chitosan[2,3].

The presence of functional groups in chitosan structure (primary hydroxyl group at C-6, secondary hydroxyl group at C-3 and amino group at position C-2) makes chitosan easily chemically modified. One of the chitosan derivatives is called as thiocarbamoyl chitosan, which is synthesized by grafting thiourea on chitosan backbone[4]. An additional of sulfur functional group not only enhances the adsorption capacity of chitosan derivative but it allows choosing a more specific of metal sorption[5]. In the literature, few reports have been published by applying this sorbent on various metals removal[5-7]. Thiocarbamoyl chitosan also was reported to be very effective for mercury sorption especially in acidic medium[8].

Since, the toxicity of mercury species is very dangerous to our lives, then it imperative to initiate removal study of these pollutants from aqueous solutions. Therefore, the aim of study is to evaluate the optimize condition for thiocarbamoyl chitosan that can be effectively used as sorbents for mercury species removal in the aquatic environment.

EXPERIMENTAL

Chitosan was purchased from Chito-chem (Malaysia) thiourea and glutaraldehyde (Sigma Aldrich, USA). Metal salts (methyl mercury, ethyl mercury and inorganic mercury, copper, arsenic and zinc) as analytical grade were purchased from Sigma Aldrich (USA). Characterization of sorbents was determined by Fourier Transform Infrared Spectroscopy (Model GX Perkin-Elmer, USA) and Scanning Electron Microscope (Philip XL Series XL30). Element analysis was performed using CHNS analyzer (Model EA1112 Thermo Finnigan, USA). Residual concentrations of mercury were determined by using gas chromatography instrument-electron capture detector (Model CP3800 Varian, USA).

Synthesis of thiocarbamoyl chitosan

Synthesis process was started by preparing a mixture of 10 g thiourea with 5 mL glutaraldehyde in 200 mL of deionized water before keep left for overnight. Then, 10 g of chitosan were added to mixture solution with constant stirring for 50 hrs at 24°C. The chitosan derivatives then was filtered and rinsed several times with deionized water prior to air dried overnight. The synthesis yield obtained approximately 8.2 g, which equivalent to

82%. This method was firstly introduced by Chauhan et al.[7] and they did some modifications during this study.

Characterization of thiocarbamoyl chitosan

Physical characterization of chitosan derivative was determined by using infrared spectroscopy (FTIR) in order to determine the structure and presence of functional groups. Sample was prepared by mixing thiocarbamoyl chitosan and potassium bromide (KBr) powder in a ratio of 1:10. The mixture then was introduced to pressure being pellet form.

Scanning electron microscope (SEM) was used to observe the surface morphology of pure chitosan and thiocarbamoyl chitosan. Sample was completely dried to obtain good scanning image. The substitution degrees of chitosan derivative was estimated using elemental analyzer CHNS. The percentage change in elemental content then can be compared through theoretical calculations. It can be expressed as equation 1.

$$\text{Substitution Degree} = [(C/N_{thiocarbamoyl} - C/N_{pure\ chitosan})/11] \quad \ldots(1)$$

Optimization of mercury sorption

Thiocarbamoyl chitosan was tested on sorption of mercury in term of pH influence, initial concentration, weight of sorbent, stirring rate and time. The batch experiment was conducted to determine the optimum sorption of mercury in each parameter. In general, 20 mg of sorbent was introduced into 100 mL deionized water with spiked of 100 µL mercury solutions. The condition then was adjusted regarding of subject study. For pH effect, initial solutions were adjusted by an additional of hydrochloric acid or sodium hydroxide (0.1 M) in the range of pH 2-7. Meanwhile, the initial concentration of mercury solutions were set up in the range of (1, 2, 5, 7 and 10 ppm), weight of sorbent (10, 20, 40, 60 and 80 mg), stirring rate (200-1200 rpm) and agitation time (10, 20, 30, 40 and 50 mins).

Interfere of competitor ions were performed by preparing a series of mixture solutions containing Cu (II), As (II), Ag (II) and Zn (II) with spiked volume was 100 µL. The concentration of mercury residue that remaining into solution was determined by using gas chromatography instrument-electron capture detector (GC-ECD) and fitted matched with linear calibration curve (0.1-1 ppm). Other metals were determined by using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Sorption isotherms

Sorption isotherms were obtained by direct contact of 60 mg thiocarbamoyl chitosan sorbent into 100 mL deionized water with mercury spiked at different level of concentrations. Batch experiments were conduct based on the optimum conditions for parameters tested. Final outcome were calculated by using the Langmuir and Freundlich isotherms model. Linearized form of Langmuir isotherm model can be expressed[8] as equation 2.

$$c/Q = c/Q_0 + K_s/Q_0 \qquad \ldots(2)$$

Where Q is the amount of metal adsorbed per unit weight at equilibrium concentration (mg/g), c is the final concentration in the aqueous solution (mg/l), Q_0 is define as the maximum adsorption at monolayer coverage (mg/g) and Ks is a constant of the Langmuir model (mg/L). Second model, Freundlich isortherm then can be expressed in linearized form[8] as equation 3.

$$\text{Log } Q = \text{Log } k + (1/n) \text{ Log } c \qquad \ldots(3)$$

Similarly to Eq. 2, Q and c are define as amount of metal adsorbed and final concentration into solution. *k* is a Freundlich constant representing the adsorption capacity, and n value is denote to the adsorption intensity.

Kinetic study

In the batch experiments, 60 mg sorbent was introduced to 100 mL solution by knowing the initial concentration of mercury solution. Samples are regularly collected, filtered and analyzed for plotting the relative metal concentration (residual concentration/initial concentration) versus time. To identify the mechanism of kinetic sorption such as mass transfer and chemical reaction, two kinetic models are used to test the experimental data. Sorption rate can be obtained by using two kinetic models, namely first pseudo-order and second pseudo-order. Adsorption of metal can be calculated using formula[8] expressed in equation 4 and 5.

$$\text{In } (Q_e - Q_t) = \text{In } Q_e - k_1 t \qquad \ldots(4)$$

$$1/(Q_e - Q_t) = 1/Q_e + k_2 t \qquad \ldots(5)$$

Where Q_e and Q_t are representing the amounts of metal adsorbed (mg/g) at equilibrium and at time t, and k_1 and k_2 is define as the rate constant of pseudo first-order (min^{-1}) and pseudo second-order (g/mg/min), respectively.

RESULTS AND DISCUSSION

Characterization by FTIR and SEM

Characterization of pure chitosan and chitosan derivatives was performed at FTIR wavenumber range 4000-400 cm^{-1}. An assigned of functional group in thiocarbamoyl chitosan is shown in Fig. 1. It was necessary step to identify either the grafting thiourea cross-links occur or not on the derivative of chitosan. Successful amidation of thiocarbamoyl chitosan was obtained by the appearance of thiocarbonyl stretching band at 1622.01 cm^{-1} and S = CN band at 1401.71 cm^{-1}. Finding results in this study was similarly consistent with previous study reported by Gavilan et al.[9] The infrared spectrum assigned of functional groups in pure and derivative chitosan derivatives are summarized in Table 1.

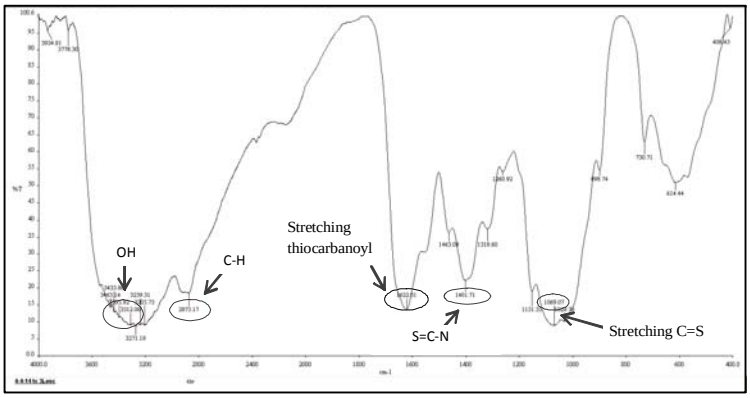
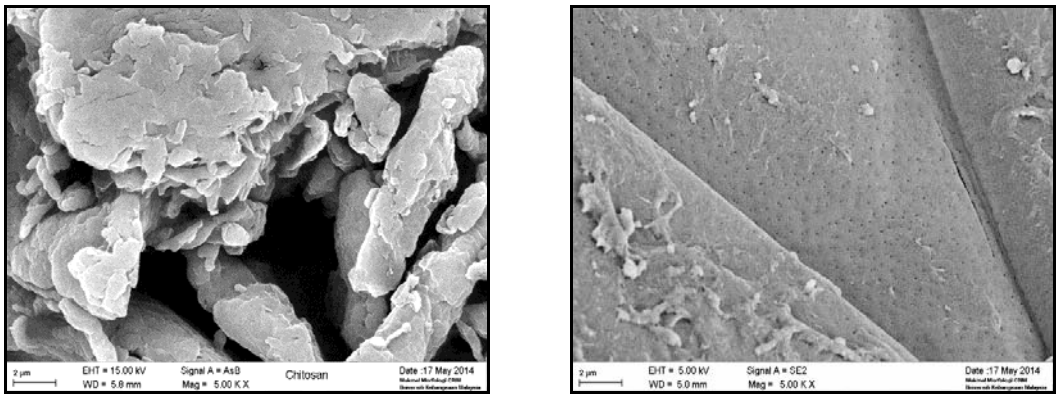


Fig. 1: FTIR spectrum assigned of thiocarbamoyl chitosan

Table 1: An assigned of functional groups in FTIR spectroscopy

Pure chitosan	Vibration band	Thiocarbamoyl chitosan	
Range (cm^{-1})		Range (cm^{-1})	Vibration band
3343	Stretching O-H	3395	Stretching O-H
2878	Stretching C-H	2875	Stretching C-H
1654	Bending N-H	1622	Stretching thiocarbonyl
1379	Stretching C-N	1401	Bending S=CN
1322	Stretching C-N	1069	Stretching C=S
1074	Stretching C-O		
600	Bending C-H		

It could be observed in Fig. 2 that the surface morphology of thiocarbamoyl chitosan possesses smooth structure and appearance of small pores rather than pure chitosan. Small pores perhaps will help in to increase the sorption process of mercury. EDX plot also proves the existence of sulfur element in chitosan backbone as illustrated in Fig. 3. Weight percentage of elemental sulfur was obtained to be 14.58% in this sample study.



(a) Pure chitosan **(b) Thiocarbamoyl chitosan**

Fig. 2: Surface morphology of (a) pure chitosan (b) derivative chitosan

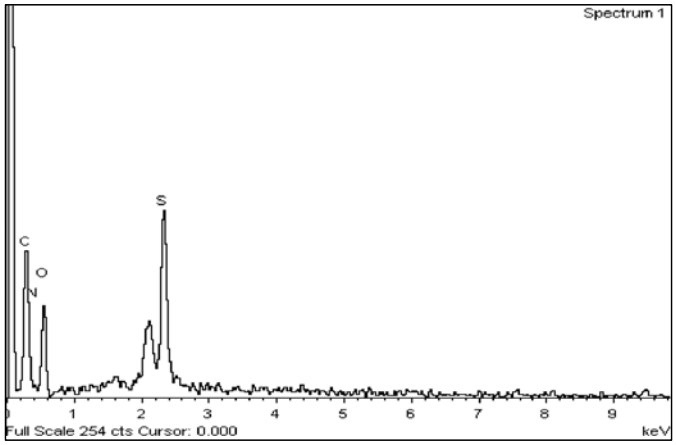


Fig. 3: EDX plot of thiocarbamoyl chitosan sample

Elemental analysis

The substitution degree of thiocarbamoyl chitosan and pure chitosan was calculated by comparing the percent ratio of C and N derived from elemental analyzer CHNS. In this study, derivative chitosan yield was account to be 0.55 degree of substitution. The

substitution degree reached for this study was lower than Gavilan et al.[9], which account in the range of 0.68-0.74. Elemental analysis of CHNS and degree of substitution for thiocarbamoyl chitosan are summarized in Table 2 and 3, respectively.

Table 2: The percentage of elemental analysis in thiocarbamoyl chitosan

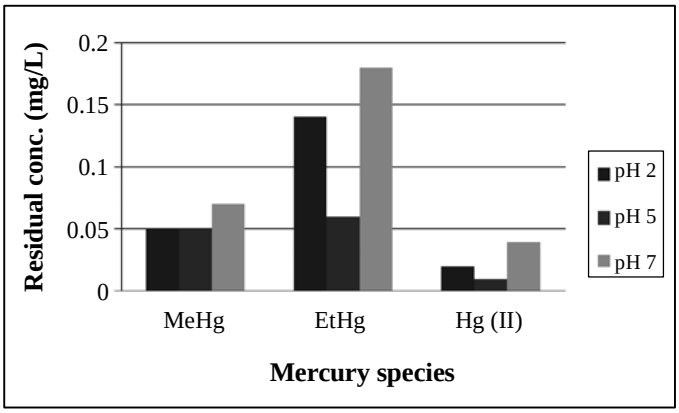
Sample	Element	Percentage of element (%)		Different
		Theoretical	Analytical	
Chitosan	Carbon (C)	44.72	38.65	6.06
	Hydrogen (H)	6.83	7.71	0.88
	Nitrogen (N)	8.70	7.74	0.96
	Sulfur (S)	-	-	-
Thiocarbamoyl chitosan	Carbon (C)	49.45	37.38	12.08
	Hydrogen (H)	6.09	7.47	1.38
	Nitrogen (N)	10.03	9.97	0.05
	Sulfur (S)	5.73	4.25	1.48

Table 3: Substitution degree of derivative chitosan

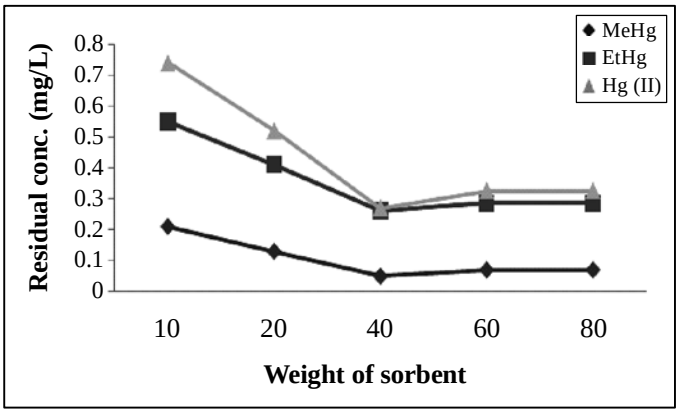
Sample	Percentage of element (%)			
	C	N	C/N	Degree substitution
Chitosan	38.65	7.74	6.00	0.55
Thiocarbamoyl chitosan	37.38	9.97	12.00	

Optimization study

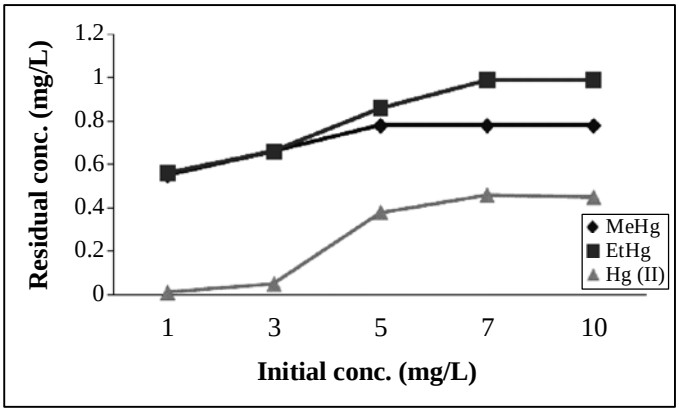
A series of mercury solution (0.001-1 ppm) was prepared to set up linear calibration prior to mercury residue were analyzed by GC-ECD. In this study, correlation coefficients of linear calibration (R^2) were obtained at 0.979 (CH_3Hg), 0.990 (C_2H_5Hg) and 0.992 ($HgCl_2$), respectively. All of mercury species has shown good reduction of level concentrations (> 90 %) at pH 5. According to Arrascue et al.[10], the functional groups of chitosan (amine) will more easily protonated in acidic medium and do the sorption of metal ions. Amine group is known as strong bases possess higher retention with strong acids rather than weak acids[11]. Furthermore, the binding process may through interaction with sulfur groups with contribution of free amine groups[8]. Finding results for batch experiment of optimization study (5 variables) were presented in Fig. 4.



(a) Initial pH



(b) Weight of Sorbent



(c) Initial concentration

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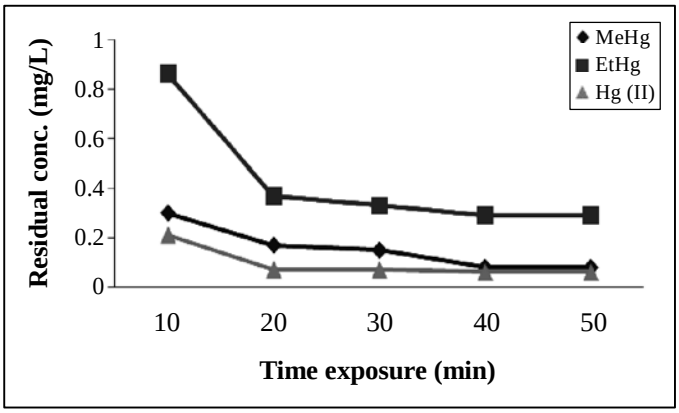
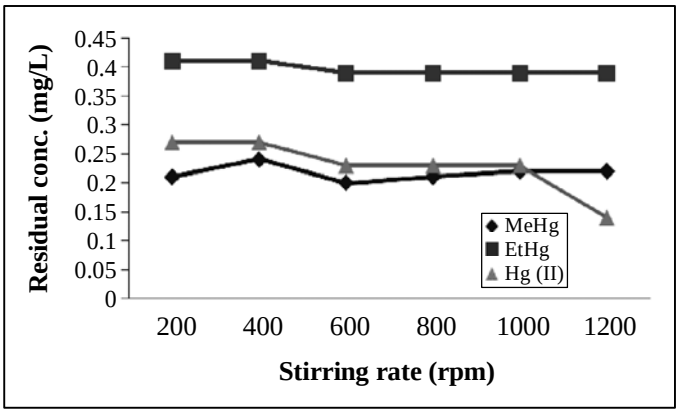


(d) Exposure time



(e) Agitation effect

Fig. 4: Batch experiment of optimization study (5 variables)

An experiment was then performed by the additional of sorbent with different weight into mercury spiked solution. The optimal sorption of mercury was achieved at 60 mg of thiocarbamoyl chitosan with more than 90% for methyl and inorganic species. An additional weight after 60 mg into 1 ppm solution has shown that mercury reduction was negligible. Hence, further experimental was performed on thiocarbamoyl chitosan to evaluate optimal concentrations of mercury can be absorbed by constant weight of sorbent. After 5 ppm concentrations of only methyl mercury residue seem to be saturated that it has reached an optimal level. It was reflecting the knowledge that selectivity sorbent to methyl mercury much lower than others.

Agitation effect was evaluated by set up a series of time sorbent exposure into solution starting from 10 to 50 mins. After stirring for 40 mins, mercury residue concentration is only

0.029, 0.081 and 0.299 ppm for inorganic mercury, methyl and ethyl mercury, respectively. The percentage sorption of methyl mercury is optimal at 79.5%, 60.4 and 77% for ethyl and inorganic mercury when thiocarbamoyl chitosan was exposed at stirring rate 600 rpm. Mixing is having strong influent to control rate of mercury sorption results. In this study, mercury species has shown different level of sorption due to kinetic stable properties.

Selectiveness of thiocarbamoyl chitosan was performed by preparing a series of mixture solution containing 4 different types of metals. The analysis of results shown that thiocarbamoyl chitosan have highest sorption capacity as ranked on copper > mercury > arsenic > zinc. Residuals metal concentrations (%) after exposure with chitosan derivative is 25.60% (copper), mercury (41.37%), arsenic and zinc (72.89%, 72.92%), respectively. Retention capacity of copper metal is higher than others due to presence of excess chloride ions. It was known that copper can be greatly generate many complexes form using chloride as a bridge but chloride did not influence the sorption capacity for mercury[11,12].

Sorption isotherms and kinetics

The analysis of Langmuir isotherm model was affirmed that mercury species adsorption on thiocarbamoyl chitosan can be fitted very well with R^2 value (0.880-0.997), as shown in Fig. 5.

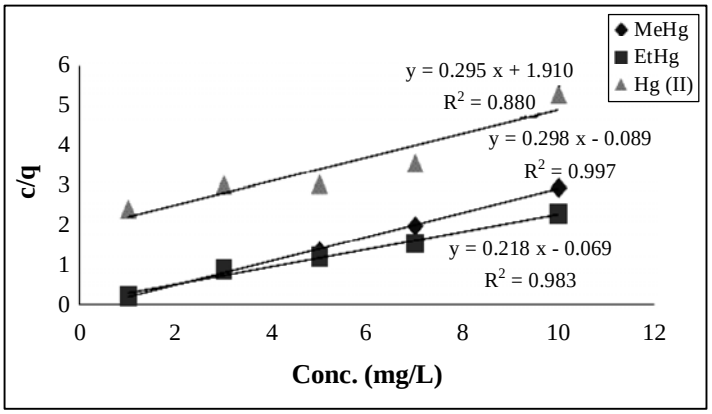


Fig. 5: Langmuir isotherm model of mercury adsorption

A high value of adsorption capacity Q_0 would sustains the hypothesis that strong interactions occur between the functional groups of sorbent and mercury species into aqueous solutions. In this study, it was observed that the maximum adsorption at monolayer coverage for each species is 15.03 (MeHg), 11.59 (EtHg) and 27.17 mg g^{-1} (Hg (II)), respectively.

The positive values of maximum adsorption capacity strengthen the idea that chitosan produced on a laboratory scale has a good capacity to adsorb pollutant.

Low correlation coefficients of methyl and ethyl mercury adsorption (R^2 = 0.715, 0.896) presumed that Freundlich isotherm model was unfitted with experimental data. Contrarily, the result of inorganic mercury was indicated that it was fit well with R^2 = 0.948 as presented in Fig. 6. The adsorption capacity, *k* and adsorption intensity (n) of this model were defined for each species as methyl; 28.5 (2.27) mg/g, ethyl; 202 (0.01) and inorganic mercury; 83.4 (0.29) mg/g, respectively. There is only methyl mercury has high intensity of adsorption under the concentration range studied. If n is less than 1 the intensity of adsorption is only good at high concentrations[13].

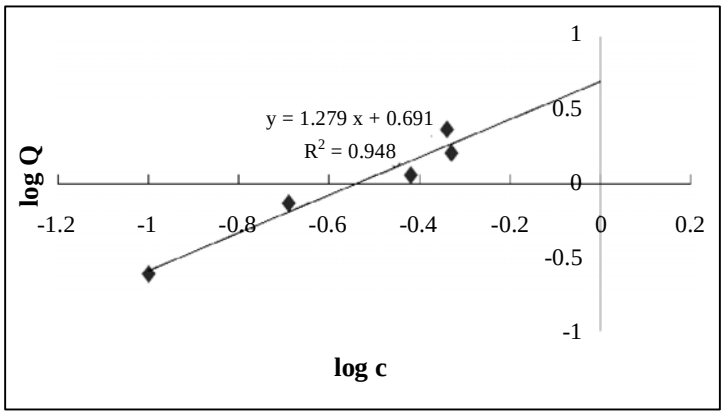


Fig. 6: Freundlich isotherm model of inorganic mercury adsorption

Adsorption kinetics should be taken to explain how the process of adsorption occurs and the factors that influence the adsorption process[14]. The rate of adsorption of mercury on thiocarbamoyl chitosan was tested by using two basic kinetic model of pseudo first-order and pseudo second-order. Final results were presented in Figs. 7 and 8, respectively.

In first order equation, the correlation coefficient (R^2) for methyl, ethyl and inorganic mercury adsorption is low. It was explicate that the kinetic model pseudo first-order is not suitable for describing the kinetics of mercury species adsorption of mercury by thiocarbamoyl chitosan under the concentration range studied. There is no contradict outcome since previous study by Gavilan et al.[9] as well prescribed that kinetic adsorption of Hg (II) were controlled by combination of pseudo second-order and intraparticle diffusion rate.

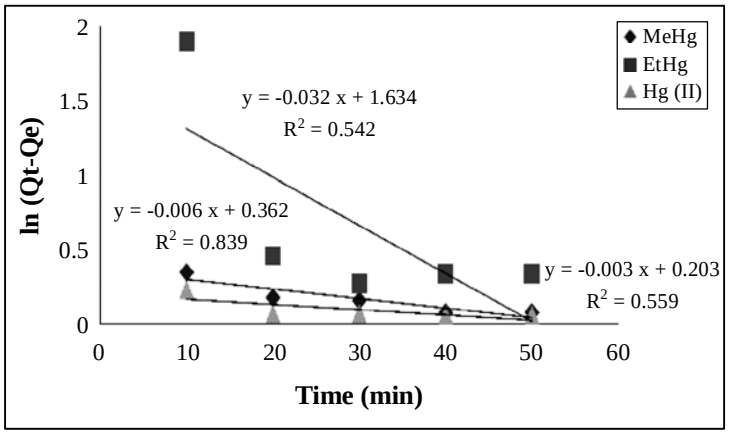


Fig. 7: The plot of pseudo first order equation at various times

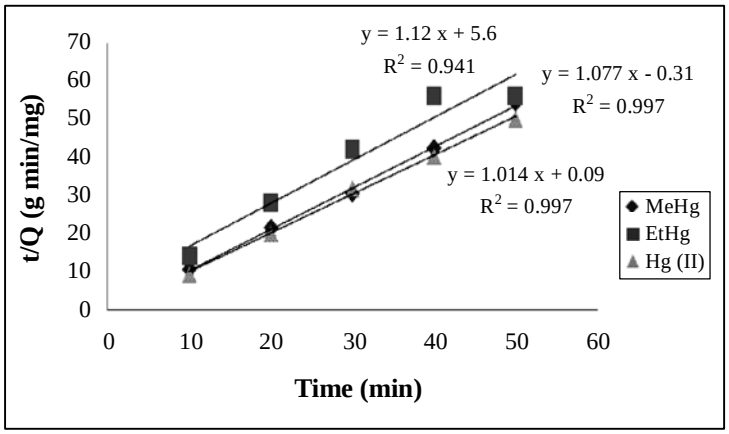


Fig. 8: The plot of pseudo second-order equation at various times

Pseudo second-order kinetic model then was performed, result in high correlation coefficient for each species (R^2 = 0.941-0.997), which affirmed that adsorption processes followed the pseudo second-order kinetics. This result explicate that the chemical absorption rate is considered as rate controller or limiting step. According to Mubarak and Abdullah[15], pseudo second-order kinetic model was used to describe the phenomenon of rate controller in chemical adsorption rather than mass transfer.

The rate constant, k_2 was calculate experimentally by plotting the slopes and intercepts of graph t/Q against t. In this study, rate constant for the pseudo second-order is obtained to be 1.077 (methyl mercury), 1.12 (ethyl mercury) and 1.01 g/mg/min (inorganic mercury), respectively.

CONCLUSION

Thiocarbamoyl chitosan was successfully synthesized. FTIR, SEM and EDX clearly demonstrated the existence of functional group (amine and hydroxyl) and elemental sulfur on chitosan backbone with weight percentage calculate to be 14.58%. Elemental analysis was indicated the value of 0.55 to be substitution degree of thiocarbamoyl chitosan.

Similarly, optimum conditions for mercury species sorption was denote in aqueous solution at pH 5, weight of sorbent (60 mg) and mixing time (40 min). In contrast, methyl mercury was optimized after additional of 5 ppm but not to others. Agitation effect test was performed successfully differentiate the level of adsorption based on species which reflect to kinetic stable properties. Adsorption isotherms and kinetic test was demonstrated that Langmuir model (except inorganic mercury) and pseudo second-order can be fitted better than other models under the concentration range studied.

This study was successfully revealed that toxic pollutant such as methyl and ethyl mercury could be treated with low cost sorbent like thiocarbamoyl chitosan. Perhaps, this idea can be extend onto others metal species and applicability removal into real samples with further improvement in next study.

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