

**ADSORPTION OF PHENOL POLLUTANTS FROM AQUEOUS SOLUTION
USING Ca-BENTONITE/CHITOSAN COMPOSITE**
(*Adsorpsi Polutan Fenol dari Larutan Berair Menggunakan Komposit Ca-Bentonit/Kitosan*)

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Abstract

Phenolic compounds are organic pollutants that are toxic and carcinogenic. The presence of phenol in the environment can be adverse to human and the environmental system. One method that is effective to reduce the phenol is adsorption. In this study, the adsorption of phenol in aqueous solution using Ca-bentonite/chitosan composite was investigated. Chitosan is the deacetylation product of chitin from shrimp waste. Characterization of Ca-bentonite/chitosan composite was done by using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy-Energy Dispersive X Ray Spectroscopy (SEM-EDX). Batch adsorption studies were performed to evaluate the effects of some parameters such as initial concentration of phenol, composite weight, pH and contact time. The results showed that FTIR spectra of Ca-bentonite/chitosan composite presented the characteristic of peak of Ca-bentonite and chitosan that confirmed the successful synthesis of composite. The SEM-EDX characterization results showed Ca-bentonite surface coverage by chitosan and the presence of carbon and nitrogen elements in Ca-bentonite/chitosan composite indicated that chitosan had bonded with bentonite. The optimum condition of adsorption of Ca-bentonite/chitosan to phenol was obtained at 125 mg.L⁻¹ of concentration in which the weight of composite was 1.0 g, the pH of solution was 7, the contact time was 30 minutes, and the capacity of adsorption was 12.496 mg.g⁻¹.

Keywords: adsorption, bentonite, chitosan, composite, phenol, pollutant

Abstrak

Fenol merupakan polutan organik yang bersifat toksik dan karsinogenik. Keberadaan fenol di lingkungan berbahaya bagi manusia dan sistem lingkungan. Salah satu metoda yang efektif digunakan untuk mengurangi fenol adalah adsorpsi. Pada penelitian ini dipelajari kemampuan komposit Ca-bentonit/kitosan untuk mengadsorpsi fenol. Kitosan diperoleh dari hasil deasetilasi kitin yang diekstraksi dari limbah udang. Karakterisasi komposit Ca-bentonit/kitosan dilakukan menggunakan Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy-Energy Dispersive X Ray Spectroscopy (SEM-EDX). Metoda Batch digunakan untuk mempelajari proses adsorpsi dengan parameter meliputi konsentrasi awal fenol, berat komposit, pH larutan dan waktu kontak. Hasil penelitian menunjukkan bahwa spektra FTIR komposit Ca-bentonit/kitosan merupakan gabungan dari serapan Ca-bentonit dan kitosan. Hasil karakterisasi menggunakan SEM-EDX menunjukkan permukaan Ca-bentonit tertutup oleh kitosan, keberadaan unsur karbon dan nitrogen pada komposit Ca-bentonit/kitosan mengindikasikan telah terbentuknya ikatan Ca-bentonit dengan kitosan. Kondisi optimum adsorpsi fenol menggunakan komposit Ca-bentonit/kitosan diperoleh pada konsentrasi awal fenol 125 mg.L⁻¹, berat komposit 1,0 g, pH larutan 6 dan waktu kontak 30 menit dengan kapasitas adsorpsi sebesar 12,496 mg.g⁻¹.

Kata kunci: adsorpsi, bentonit, fenol, kitosan, komposit, polutan

INTRODUCTION

Phenol and phenol derivatives are classified as organic toxic and priority pollutants in the waters (Bhatnagar and Minocha, 2009). The US EPA classifies phenol as one of the compounds of pollutants requiring removal from wastewater. The presence of phenol in the waters will lead to the decline of water quality and disruption of aquatic ecosystems. The concentration of phenol as low as 0.1 mg.L⁻¹ can cause undesirable and deleterious effects in the water (Mahajan, 1994). Phenols may

be formed as a result of natural processes like decomposition of organic matter by fungi and plants (Swart *et al*, 1998). Phenols is also used in pesticide, disinfectant and reagent in chemical analysis. Some of the industries that produce wastewater containing phenol are oil, gasoline, paper, coal, petrochemical, pharmaceutical, textile, plastics and steel (Rocha *et al*, 2007; Uddin *et al*, 2007).

Phenols in small concentration have toxic effects on human health. Phenol which contaminates human body may cause protein

degeneration, tissue erosion, and paralysis of the nervous system, and adverse effects on the kidney, the liver and the pancreas (Knop and Pilato, 1985). Therefore, it is necessary to remove the phenol from industrial wastewater before discharging it into the environment.

Various methods were attempted to release phenol from wastewater such as biological treatment, catalytic, wet oxidation and adsorption technology (Girish and Ramachandra, 2012). Adsorption method is currently used and is considered the most effective method in removing pollutants. The forces that contribute to this adsorption process are the combination of two important factors, the adsorbate affinity towards the solvent and the adsorbate affinity towards the adsorbent (Lynam *et al.*, 1995). Many adsorbents can be used to remove phenol from aqueous solutions such as organobentonite (Shen, 2002), activated carbon (Srihari and Das, 2009), porous clay heterostructure (Cardenas *et al.*, 2005), and chitosan (Rahmi, 2007).

The low adsorption capacity is the major problem regarding its possible adsorption capacity. The effectiveness of adsorption increases if the adsorbent is modified. In this study, the composite of chitosan and Ca-bentonite were used to adsorb phenol from aqueous solution. Chitosan contains –OH and –NH₂ groups that can be chemically modified with bentonite by cross linking (Zhang *et al.*, 2013). Modification of adsorbent may increase the chemical stability and adsorption capacity. In this study, chitosan or poly (β-1-4)-2-amino-2-deoxy-d-glucopyranose is prepared from chitin by deacetylation and chitin extracted from waste of shrimp. The shrimp waste used was composed of shrimp's skin, tail and head.

The bentonite consists mostly of montmorillonite. They are characterized mainly by Al octahedral sheet placed between two Si tetrahedral sheets. The bentonite has physical and chemical properties, such as large surface area, cation exchange, absorptive affinity for organic substances, anorganic ions and as supportive material for chitosan (Senturk *et al.*, 2009; Futalan *et al.*, 2011). Some studies on composite of chitosan-montmorillonite investigated the removal of dyes (Monvisade and Siriphannon, 2009), heavy metals and diazinon (Permatasari *et al.*, 2010).

The present study investigated the adsorption of phenol from aqueous solution using composite Ca-bentonite/chitosan in batch experiment. Therefore, Ca-bentonite/chitosan composite can be used as an effective adsorbent and it has high adsorption capacity for reducing phenol from the environment.

EXPERIMENTAL METHOD

Materials and Instrumentation

The raw bentonite used in the study was obtained from Jambi and the shrimp waste was obtained from shrimps export companies in Palembang. All reagents used for grading analysis were obtained from Merck (Germany) including HCl, CaCl₂, NaOH, NaOCl and phenol. The other materials used in this study were Whatman paper No.42, aquadest and deionized water.

Instruments used in the study included glassware, oven (Fisher scientific 655 F), mechanical shaker (Edmund Buhler BC 25), pH meter (Schott Gerate CG 820), analytical balance (Mettler AE 166), UV-Vis Spectrophotometry Shimadzu 1240 which was used to measure phenol concentration and analyze functional groups using FTIR (Shimadzu 5400). Whereas the morphology and elements materials were examined by using SEM-EDX (JEOL -JSM 1400).

Procedure

Preparation of Ca-bentonite

The raw bentonite was sieved to get average sized particles of about 200 meshes. About 400 g of bentonite was activated with 800 mL HCl 1 % for 4 h. It was then washed with deionized water until neutral pH was achieved and dried in the oven at 110 °C. To get the Ca-bentonite, bentonite was immersed in 800 mL CaCl₂ 1 M for 48 h. After that, Ca-bentonite was washed with deionized water and dried in the oven at 110 °C. The Ca-bentonite was then characterized using FTIR and SEM-EDX.

Chitin and chitosan isolation

This procedure consists of four stages, namely deproteinization, demineralization, depigmentation, and deacetylation (No *et al.*, 2003; Hariani and Fatma, 2007). About 500 g of shrimp waste was dissolved in NaOH solution (3.5 %, w/v) with a ratio of 1:10 (w/v) and heated at 70 °C for 2 h. The mixture was cooled and filtered. The residue was then added with HCl 1.0 N solution with a ratio of 1:15 (w/v), stirred for 30 min at room temperature, washed with deionized water and dried at 60 °C for 4 h. The residue was added with acetone and stirred for 30 min and then filtered. After that, the residue was bleached by using NaOCl 0.315 % (w/v) with a ratio of 1:10 (w/v) and washed with deionized water. The result obtained is called chitin. The chitin obtained was then added with NaOH of 50 % (w/v) with a ratio of 1:10 (w/v), and heated at a temperature of 150°C for 6 h. The mixture was then filtered and washed with deionized water until it reached a neutral pH, and then dried in oven at 70 °C for 1 h. Chitosan was obtained which included

water content, ash content, degree of deacetylation and then it was characterized by using FTIR and SEM-EDX.

Preparation of ca-bentonite/chitosan composite

About 10 g of chitosan was dissolved in 300 mL CH₃COOH at pH 4. The mixture was stirred at 200 rpm for 1 h. Bentonite (50 g) was slowly added into the solution and was stirred for 2 h. The composite was then centrifuged at 3000 rpm for 30 min. After that, it was filtered and washed with deionized water until it reached a pH solution of ± 7, and then dried in an oven at 70 °C for 1 h (Tran *et al*, 2010). The composite was then characterized using FTIR and SEM-EDX. The deacetylation degree was calculated with the following equation:

$$DD = \frac{(A_{1600} / A_{3450}) \times 100}{1.33} \quad (1)$$

In which DD is deacetylation degree, A₁₆₆₀ and A₃₄₅₀ are absolute heights of absorption bands of amide and hydroxyl groups.

Adsorption experiment

Adsorption experiments were carried out with 100.0 mL of phenol solution at a constant speed of 120 rpm at room temperature. The adsorption of phenol onto composite Ca-bentonite/chitosan was studied under different conditions including initial concentration of phenol (50, 75, 100 and 125 mg.L⁻¹), the weight of composite (1, 2, 3 and 4 g), the pH of solution (5, 6, 7, 8 and 9) and the contact time (30, 45, 60, 75 and 90 min). The concentration of phenols in the supernatant was measured using UV-Vis Spectrophotometer at a wavelength of maximum absorbance (505 nm). The amount of phenol adsorbed was calculated with the following equation formula:

$$qt = \frac{(C_o - C_t)V}{ms} \quad (2)$$

in which *qt* is the adsorption capacity of the composite (mg.g⁻¹) at the equilibrium; C_o and C_t are the initial and the equilibrium phenol concentration (mg.L⁻¹) respectively; V is the volume of solution (L) and *ms* is the mass of the composite (g).

RESULTS AND DISCUSSION

The objective of this study was to prepare Ca-bentonite/chitosan composite as an adsorbent for adsorption of phenol in aqueous solution, to characterize the composite and to investigate the effects of initial concentration of phenol, the composite weight, the pH and the contact time. FTIR and SEM-EDX analyses were used to characterize the Ca-bentonite/chitosan composite.

Characterization of Ca-Bentonite/Chitosan Composite

Table 1 shows the quality of chitosan made from waste shrimp. The qualities of chitosan include water content, ash content and degree of deacetylation according to the chitosan quality trade standard. The degree of deacetylation of the chitosan indicates the amount of acetyl groups on chitin which is converted into the NH₂.

The FTIR spectra for the chitosan, Ca-bentonite and the composite of Ca-bentonite-chitosan were examined and shown in Figure 1. FTIR spectrum of chitosan is characterized by the following absorption bands of O-H groups which appeared at 3,438.5 cm⁻¹ overlapped with N-H

Table 1. Quality of chitosan.

Parameter	Chitosan	Standard quality of chitosan
Water content (%)	2.17	< 10.0
Ash content (%)	1.59	< 2.0
Degree of deacetylation (%)	7.81	> 70.0

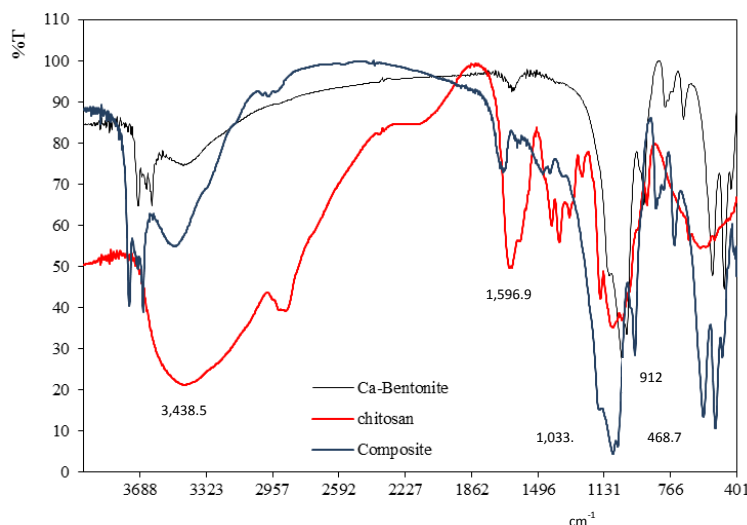
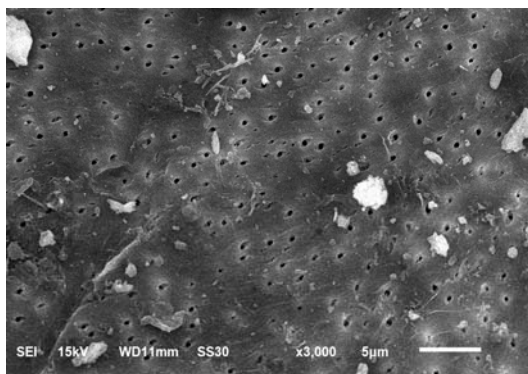


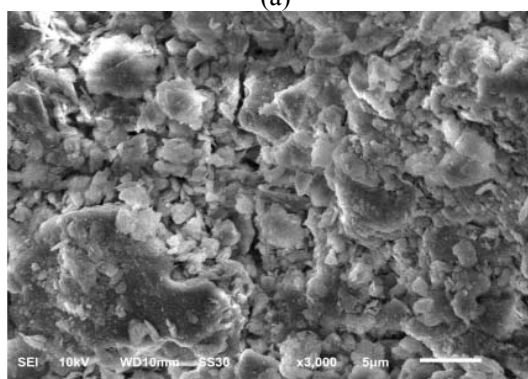
Figure 1. Spectra FTIR of chitosan, Ca-bentonite and Ca-bentonite/chitosan composite.

Table 2. Result of elemental identification of chitosan, Ca-bentonite and composite.

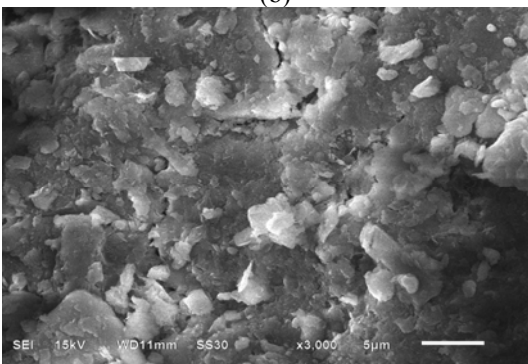
Elements	Chitosan (% w)	Ca-bentonite (% w)	Ca-bentonite/chitosan composite (% w)
C	48.41	-	16.56
N	49.35	-	15.28
O	0.64	50.03	38.44
Na	-	0.01	0.02
Ca	1.60	2.63	8.45
Mg	-	0.22	0.23
Al	-	17.85	9.31
Si	-	29.14	10.50
Fe	-	0.12	1.21



(a)



(b)



(c)

Figure 2. SEM micrograph of samples (a) chitosan, (b) Ca-bentonite and (c) Ca-bentonite/chitosan composite.

amine and the peak of amine also appeared at $1,596.9 \text{ cm}^{-1}$. The peak at $2,885.3 \text{ cm}^{-1}$ is attributed to C-H of the backbone polymer and clarified the existence of bending vibration at $1,377.1 \text{ cm}^{-1}$. The

primary amine group existence at $1,251.7 \text{ cm}^{-1}$ and group of bands from $1,100\text{-}1,020 \text{ cm}^{-1}$ indicated C-O-C and C-O stretching vibration.

The spectra FTIR of Ca-bentonite/chitosan composite at peaks $1,033.8$ and 468.7 cm^{-1} were the Si-O stretching and bending vibration which confirmed the presence of montmorillonite. Typical montmorillonite also appeared at peaks 912.3 cm^{-1} which was the stretching vibration of Al-O-Al. The FTIR spectra of Ca-bentonite/chitosan composite presented the characteristic of peaks of Ca-bentonite and chitosan which confirmed the successful synthesis of Ca-bentonite/chitosan composite. Bentonite was modified with organic cations to increase the adsorption capacity. The bonds between the bentonite and chitosan are hydrogen bonds (Hitzky *et al*, 2005).

The SEM micrographs of Chitosan, Ca-bentonite and Ca-bentonite/Chitosan composites which were taken at 3000 magnification are shown in Figure 2. This image illustrates that the surface of chitosan is tight and porous and after forming a composite with Ca-bentonite, it appears that Ca-bentonite is covered by chitosan. An elemental identification of surface features was performed by using EDX, the result is presented in Table 2.

Adsorption of the Phenol Using Ca-Bentonite / Chitosan Composite

Effect of initial concentration

The effect of initial concentration was carried out by contacting 1.0 g of composite with 100.0 mL of phenol solution of different concentrations of phenol (50 to 150 mg.L^{-1}). The adsorption process of phenol onto Ca-bentonite/chitosan depended on the initial concentration of phenol. The adsorption capacity of composite increased from concentration of phenol 50 to 125 mg.L^{-1} . Figure 3 shows that removal of phenol by adsorption using the composite was rapid initially and then slowed down until it reached an equilibrium because of the limited amount of the composite. In this study, the adsorption capacity of the composite at the initial concentration of phenol 125 and 150 mg.L^{-1} was not different.

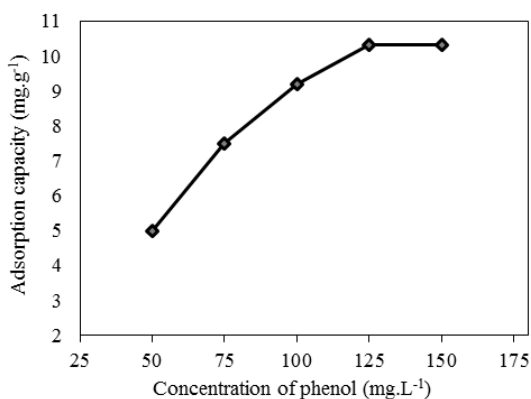


Figure 3. Effect of initial concentration for adsorption capacity of phenol onto composite

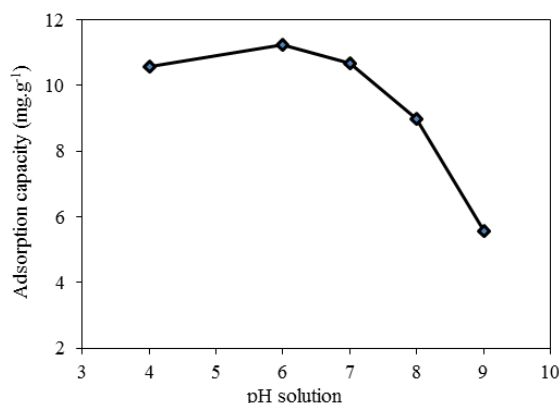


Figure 5. Effect of pH solution for adsorption capacity of phenol onto composite

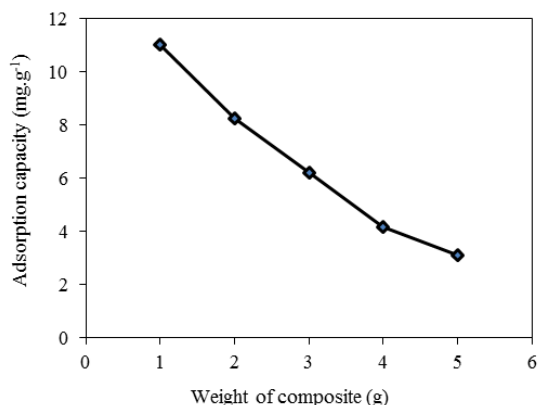


Figure 4. Effect of composite weight for adsorption capacity of phenol onto composite

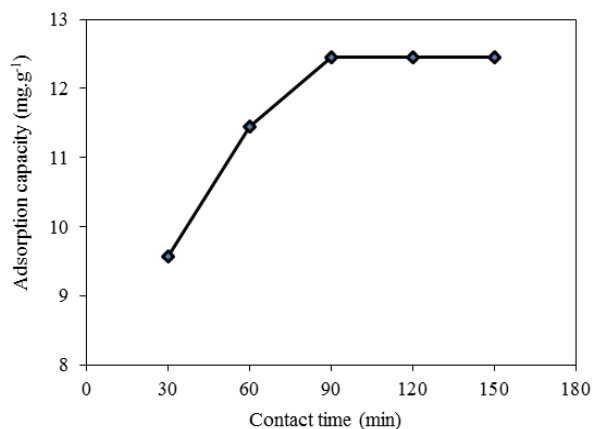


Figure 6. Effect of contact time for adsorption capacity of phenol onto composite

Effect of composite weight

Figure 4 shows the amount of phenol removed using various weight of the composite. The effect of composite weight was obtained by using 100 mL of phenol solution 125 mg.L⁻¹ with different weight of the composite (1 to 4 g). The amount of phenol per gram composite decreased with the increase of the weight of the composite. Increasing the amount of adsorbent reduces the unsaturation of the adsorption site, so the number of such sites per unit mass comes down (Hashem, 2012). In this study, 1.0 g of composite Ca-bentonite/composite was fixed as the optimal weight to adsorb phenol in the aqueous solution with adsorption capacity of 12.466 mg.g⁻¹.

Effect of pH solution

The pH of the solution was an important variable for adsorption process because it controlled the adsorption of phenols on the solid-liquid interface. In this study, the effect of the pH of the solution on the adsorption capacity of composite was analyzed with the pH range between 4 and 9. Figure 5 reflects that the acidic pH can offer more adsorption sites on composite for phenol

removal than the alkaline pH. The adsorption mechanism of phenol onto composite is electrostatic attraction. In acidic solution, amido group of chitosan reacts with H⁺ producing -NH₃⁺ (Dai *et al*, 2012). An interaction occurs between the -NH₃⁺ with phenolate (C₆H₅O⁻). In addition, Ca-bentonite has a support material for chitosan and also electrostatic interaction occurs between Ca²⁺ on bentonite and phenolate.

Shen (2012) obtained phenol adsorption using organobentonite at pH 4. Ling *et al* (2009) using chitosan to removal phenol from water obtained that adsorption capacity of phenol does not change in the range pH 5-9 but decreased after pH 10. Saravakumar and Kumar (2013) observed that the uptake of the phenol by sodium zeolite constant in the pH range of 3 to 6. Therefore, pH of the solution for the experiment is observed at pH 6 with adsorption capacity of 11.234 mg.g⁻¹.

Effect of contact time

The adsorption capacity of phenol increased with the increase of time and finally reached saturation. The longer the contact time, the more phenols interact with the composite. Figure 6

presents the effect of the contact time on the adsorption of phenol onto the composite.

The adsorption capacity of composite increased significantly from 30 to 90 min and then adsorption capacity became constant. It can be seen that the maximum contact time obtained at 90 min with adsorption capacity of 12.496 mg.g^{-1} .

The phenol concentration in the effluent should be appropriate standard quality before it is discharged into the environment. The wastewater can be discharged into the environment if the concentration of phenol is between $0.5\text{-}1.0 \text{ mg.L}^{-1}$ in accordance with KEP. No.51/MENLH/10/1995 (Anonim, 1995). The amount of concentration of phenol in natural water is between 0.01 and $2.0 \text{ }\mu\text{g.L}^{-1}$ (Michalowicz and Duda, 2004). The use of phenol in various activities especially in industrial activities causes the increase of its concentration in the environment. One of the important parameters that determine the toxicity of phenol and its derivatives is pKa. Ka is a compound dissociation constant and pKa is log of Ka. Phenol and its derivatives that have a small pKa value is hydrophobic and is more toxic. If the value of pKa is similar, the transport rate depends on the length of side aliphatic chain (Michalowicz and Duda, 2007).

Adsorption capacity is the performance or the ability of the adsorbent to adsorb pollutants in the equilibrium. The adsorption capacity indicates how phenol is distributed in the Ca-bentonite/chitosan and aqueous solution. Adsorption capacity of the composite is used to calculate the amount of phenol in the wastewater to be adsorb by the composite. In the adsorption process an adsorbent with a large adsorption capacity should be used. An optimum adsorption process of Ca-bentonite/chitosan composite to adsorb phenol in batch experiment is at initial concentration of 125 mg.L^{-1} , the weight of composite is 1.0 g , the pH of the solution is 6 and the contact time is 90 min and an adsorption capacity of 12.496 mg.g^{-1} . The result is better than the adsorption of phenol using commercial activated carbon (Srihari and Dash, 2009) and chitosan modified with salicylaldehyde (Ling *et al*, 2009), each of which has an adsorption capacity for phenol of 11.01 and 2.22 mg.g^{-1} .

CONCLUSION

The adsorption of phenol from aqueous solution using Ca-bentonite/chitosan was investigation. The results indicated that adsorption process of the composite was considerably affected by initial concentration of phenol, weight of composite, pH solution and contact time. It has

been found that composite Ca-bentonite/chitosan is very good adsorbent to removal phenol from aqueous solution. The adsorbent can used to commercialize for treatment of wastewater containing phenol pollutants in industrial scale to the future.

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