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Elimination of Cr(VI) in Laboratory Wastewater Using Chitosan Coated Magnetite Nanoparticles (chitosan@Fe_3O_4)

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Abstract

Chromium (Cr) is one of the heavy metals that has adverse effects on the environment especially Cr(VI). Thus, the chitosan coated magnetite nanoparticles (chitosan@Fe_3O_4) as the adsorbent was developed for removal of Cr(VI) in this work. Several factors influencing for chitosan coating on the nanoparticles such as amount of chitosan and crosslinking reagent including volume and cross-linkage time were studied. Additionally, adsorption isotherms for adsorption of Cr(VI) on chitosan@Fe_3O_4 were investigated also. The results showed that adsorption capacity of the proposed adsorbent with optimal coating conditions was 16.94 ± 0.41 mg/g. In addition, it was found that adsorption isotherm of chitosan@Fe_3O_4 was correspondence with Langmuir isotherm. For adsorption and desorption study, the optimal pH was 2 with 120 min adsorption time while optimal eluent for desorption was 0.1 M NaOH with 180 min desorption time. Moreover, chitosan@Fe_3O_4 could be reused for Cr(VI) removal at least 5 times. Furthermore, the proposed chitosan@Fe_3O_4 was applied for Cr(VI) elimination in laboratory wastewaters. The results obtained that all laboratory wastewaters after treatment by chitosan@Fe_3O_4 passed the wastewater quality standards of Pollution Control Department (PCD) in Thailand.

Keywords: Chitosan; Nanoparticles; Chromium; Wastewater; Metal removal

1. Introduction

Nowadays, water contaminations is one of the major problems of pollutions of the environment. Especially, accumulation of the heavy metals such as Cu(II), Pb(II), Co(II), Zn(II), Cd(II), Cr(III) and Cr(VI) has become continuously enlarging in natural resources (Sivakami *et al.*, 2013; Naeemullah *et al.*, 2016; Azizi *et al.*, 2016). These heavy metals are widely used not only in industries, agriculture or domestics but also in laboratories (Aydın & Aksoy, 2009; Hena, 2010; Putra *et al.*, 2017). Waste generated from laboratories specially wastewaters is not similar to waste generated from other resources because laboratory wastewaters have a complex matrix to treat, various types and forms including high concentration and toxicity (Vijayaraghavan & Balasubramaian, 2013; Lou & Chang, 2007; Alves *et al.*, 2005). Thus, to prohibiting these metals for the environmental explosion, the waste water treatment systems are needed.

Contamination of heavy metals especially chromium (Cr) is an important problem of environmental pollutions. In nature, two oxidation states of Cr exist Cr(VI) and Cr(III). Generally, Cr(VI) is higher toxicity than Cr(III) (Chwastowski, 2017; Liang *et al.*, 2017). Thus, many countries attempt to control amount of Cr(VI) contaminating in water resources through assessment of the agencies such as United States Environmental Protection Agency (US-EPA), Bureau of Indian Standards (BIS) and Pollution Control Department (PCD) for United States, India and Thailand, respectively. Particularly, in Thailand the limitation of Cr(VI) quantity in natural and waste waters do not have to exceed 0.05 and 0.25 mg/L, respectively (Bhatt *et al.*, 2015; Notification of the National Environment Board No.8, 1994). Hence, development of waste water treatment methods is necessary for wastewater quality control. Normally, the methods have been used effectively for Cr(VI) removal in wastewater samples for example solvent extraction, chemical precipitation, ion exchange, membrane separation and electro-chemical deposition (Sivakami *et al.*, 2013; Kumari *et al.*, 2015; Khishamuddin *et al.*, 2018). However, these techniques have some disadvantages as toxicity of chemicals, expensive equipment and long periods for pretreatment process (Zhang *et al.*, 2013). As our reviewing, the adsorption recently remains a very popular method for removal of the metals including Cr(VI) because of its easiness, simplicity and effectiveness. However, improvement of adsorption efficiency by adsorbent surface adjustment has been increasingly developed especially the use of various types of biopolymer (Ge *et al.*, 2012) for example agarose (Mokaddem *et al.*, 2014; Pandy *et al.*, 2009; Zhang *et al.*, 2017), alginate (Yu *et al.*, 2017; Wang *et al.*, 2016), cellulose (Zhou *et al.*, 2004; Madivoli *et al.*, 2016) and chitosan (Salih & Ghosh, 2018; Okoya *et al.*, 2014; Khairkar & Raut, 2014).

Chitosan is a polyacrylate copolymer that can be found in natures. The major beneficial properties of chitosan are biological compatibility, environmentally friendly, inexpensive and effectively metal capture. Therefore, chitosan is widely applied in wastewater treatment processes especially using chitosan as adsorbent for metal adsorption system (Igberase & Osifo, 2015; Bhatt *et al.*, 2017; Shi *et al.*, 2017). However, the adsorbent separation is mainly limitation for using of chitosan only as the adsorbent. Therefore, to solve this problem, the use of some materials having paramagnetic property has been gradually applied in the wastewater treatment process (Wang *et al.*, 2012; Keyhanian *et al.*, 2016). The material that has magnetic property and popularly be applied as the adsorbent in wastewater treatment is magnetite (Fe_3O_4) nanoparticles. These nanoparticles have unique physical and chemical properties such as small size effect, quantum-tunnel effect and low toxicity (Wang *et al.*, 2018; Hariani *et al.*, 2018). However, these Fe_3O_4 nanoparticles are highly sensitive to air oxidation and acidic conditions unbearable. Thus, modification of the nanoparticle surface to enhance capability and stability is required for application in many fields (Saini *et al.*, 2018). Additionally one of biodegradable polymers fashionable used for modifying of Fe_3O_4 nanoparticle surface is chitosan. Particularly, the chitosan with specific functional groups has been more interesting (Wang *et al.*, 2015).

Moreover, to improve the chemical and physical properties of chitosan adsorption, the chitosan crosslinking using the particular reagents such as epichlorohydrin (Sahin *et al.*, 2011), sodium tripolyphosphate (Nasution *et al.*, 2017) and glutaraldehyde (Okolo *et al.*, 2013; Kildeeva *et al.*, 2009; Akakuru & Isiuku, 2017) were used. However, it was observed that glutaraldehyde was extensively used as the reagent for crosslinking of chitosan (Elwakeel, 2010; Song *et al.*, 2018). The mechanism of crosslinking occurs via bi-functional amino groups that involved in the chitosan configuration to increasing the structure stability and acidic inertness (Beppu *et al.*, 2007).

As above reasons, thus the major objective of this work is to modify the magnetite nanoparticles (Fe_3O_4) by coating with the chitosan in order to enhance efficiency of Cr(VI) adsorption. Moreover, the purposed chitosan@Fe_3O_4 can be potentially applied as the adsorbent to eliminate Cr(VI) in laboratory wastewaters.

2. Materials and Experiments

2.1 Materials

All chemicals used in this work were analytical grade reagent (AR-grade). Chitosan with molecular weight of 50,000-190,000 Da amu from Sigma-Aldrich (Island), 25% glutaraldehyde from Loba Chemie (India), acetic acid from Qrec (New Zealand) and paraffin oil from Fisher Scientific (USA) were used for coating Fe_3O_4 Cr(VI) standard solutions were prepared from $K_2Cr_2O_7$ (Ajax Finechem, New Zealand). 1,5-Diphenylcarbazide (DPC) as a complex reagent and sulfuric acid were purchased from Loba Chemie, India. Distilled water passing Milli-Q Plus System (Millipore) was used throughout all the experiment.

2.2 Preparation of chitosan@Fe_3O_4 and characterization

This experiment was adapted from Li *et al.*, (2008). In briefly, the magnetite nanoparticles (Fe_3O_4) were synthesized by using co-precipitation method of Fe(III) and Fe(II) with molar ratio 2:1 in NH_4OH was used for preparation of Fe_3O_4 nanoparticles. The synthesized Fe_3O_4 nanoparticles were washed with absolute ethanol (99.5%) and then added with 10 mL paraffin oil and 0.16 mL span-80. To prepare the chitosan, appropriate chitosan amount was dissolved in 1.0% aqueous acetic acid and mixed well with Fe_3O_4 that already mentioned. For chitosan cross-linkage reaction, 0.50 mL of 25% glutaraldehyde was added into the mixture containing chitosan and Fe_3O_4 and after that the mixture was totally stirred. Next, these particles were gathered through magnetic field for separation. The chitosan@Fe_3O_4 particles were filtered and washed with deionized water and absolute ethanol, respectively for several times. Then filter to remove all noncross-linkage chitosan was needed. Finally, the products were dried in an oven at 50°C for 12 hr. In addition, the optimum conditions such as amount of chitosan, volume of 25% glutaraldehyde and crosslinking time were investigated in this experiment.

For the Fourier transform infrared (FT-IR) characterization, all the particles (chitosan@Fe_3O_4, Fe_3O_4 nanoparticles and chitosan) were dried at 60°C for 12 hr. 2 mg of each particles was mixed with 200 mg KBr. Next, the mixed particles were compressed into a pellet and then analyzed at wavenumber of 400-4000 cm^{-1} by using FT-IR spectrophotometer from SPECORD 210 plus (Perkin-Elmer). Additionally, the surface morphologies, particle diameters and elemental analysis of chitosan@Fe_3O_4 and naked Fe_3O_4 were performed by using a transmission electron microscope (TEM) from Tecnai20 (Philips) and an energy dispersive X-ray spectrophotometer (EDX) from LEO 1450 VP (Carl Zeiss). The procedures for TEM and EDX were done as following. The solutions containing the mixture of absolute ethanol and 0.01 g of each particle were sonicated for 10 min and then 0.5 μL the mixture was dropped on Grid Formvar Film on 400, FF 400-H-CH). After that, it was dried under room temperature. Furthermore, these prepared particle diameters were investigated using SemAfore 5.21 program.

2.3 Adsorption experiments

The adsorption experiment section carried out by using chitosan@Fe_3O_4 as the adsorbent was done as following. The amount of 0.020 g chitosan@Fe_3O_4 was added into 10 mL Cr(VI) solutions at various concentrations (10-250 mg/L) and mixed well using shaker for appropriate time. Next, the chitosan@Fe_3O_4 adsorbent was separated out from the solutions of Cr(VI) under the magnetic field. After that 0.5 M sulfuric acid and 0.7% 1,5-diphenyl carbazide (DPC) were added into the Cr(VI) solutions and mixed immediately. Leave them for 5 min, then the absorbance at 542 nm was measured using a UV-Visible spectrophotometer. Finally, the adsorption efficiency (q_e) was calculated following the equation (1). (Zhang *et al.*, 2013; Liang *et al.*, 2017)

$$q_e = \frac{(C_o\text{-}C_e)\times V}{m} \qquad (1)$$

Where q_e (mg/g) is the adsorption efficiency. C_0

and C_e (mg/L) are the initial and equilibrium concentrations of Cr(VI), respectively. V (L) is the solution volume and m (g) is mass of chitosan@Fe_3O_4.

Additionally, the optimum conditions for Cr(VI) adsorption using chitosan@Fe_3O_4 for instant adsorption time and solution pH were studied in this section. Moreover, all experiments were replicated in triplicate samples at each condition and average values were reported.

2.4 Adsorption isotherm model

Two adsorption isotherm models: Langmuir and Freundlich were studied in this work. For methodology, the different initial concentrations of Cr(VI) in the range of 25-250 mg/L was studied. After adsorption by using chitosan@Fe_3O_4, the Cr(VI) concentrations as equilibrium (C_e) were determined. Eventually, these results were evaluated for adsorption isotherm models of Langmuir and Freundlich (Liu *et al.*, 2018; Adamczuk, 2015).

The Langmuir isotherm equation is given as follows:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{2.1}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L C_e} + \frac{C_e}{q_m} \tag{2.2}$$

Where q_e and q_m (mg/g) are the adsorption efficiency at equilibrium and maximum adsorption efficiency for a single layer adsorption model, respectively. C_e (mg/L) is concen-tration of Cr(VI) at equilibrium. K_L (L/mg) is the Langmuir constant for monolayer adsorption.

The Freundlich isotherm equation is given as follows:

$$q_e = \frac{x}{m} = K_f C_e^{\frac{1}{n}} \tag{2.3}$$

$$log\, q_e = log \frac{x}{m} \tag{2.4}$$

$$log \frac{x}{m} = log\, K_F + \frac{1}{n} log\, C_e \tag{2.5}$$

Where q_e (mg/g) and C_e (mg/L) are the adsorption efficiency and concentration of Cr(VI) at equilibrium, respectively. 1/n is heterogeneity factor. K_F (L/mg) is the Freundlich constant indicating adsorption capacity for multilayer adsorption.

2.5 Reusability of chitosan@Fe_3O_4

Reusability or well known as re-generation of adsorbent is important for the wastewater treatment system especially adsorption process. Thus, the reusability of chitosan@Fe_3O_4 as the adsorbent in here was studied. The chitosan@ Fe_3O_4 particles through after adsorption of Cr(VI) were washed with distilled water for several times. Then, they were eluted by suitable reagent with appropriate time. After that, the concentration of eluted Cr(VI) was determined based on Cr(VI)-DPC complex using UV-Visible spectrophotometry. In addition, %adsorption and %desorption were calculated following the equations (3.1) and (3.2), respectively (Igberase & Osifo, 2015). Therefore the procedure above mentioned in this section was called as the 1st adsorption-desorption cycle. If all process is repeated, it is called as the 2^{nd} adsorption-desorption cycle, and so on.

$$\%Adsorption = \frac{(C_o\text{-}C_e)}{C_o} \times 100 \tag{3.1}$$

Where C_0 and C_e (mg/L) are concentrations of Cr(VI)at originality and equilibrium, respectively.

$$\%Desorption = \frac{C_e}{C_o} \times 100 \tag{3.2}$$

Where C_e and C_0 (mg/L) are concentrations of released Cr(VI) and adsorbed Cr(VI), respectively.

Additionally, the optimum conditions of chitosan@Fe_3O_4 reusability for Cr(VI) adsorption such as types of eluent, eluent concentrations, elution time and adsorbent reusability performance were investigated.

2.6 Sample preparation

Laboratory wastewater samples in this work were collected from different groups of students attended in the Instrumental Analytical

Chemistry Laboratory course (Department of Chemistry, Faculty of Science, Burapha University). All samples were preserved by using nitric acid (Qrec, New Zealand) until pH 2 and kept in the refrigerator at 4°C before used (Notification of the National Environment Board No.8, 1994). For adsorption experiment, all samples were done following the procedure in the 2.2 section.

3. Results and Discussion

3.1 Synthesis of chitosan coated magnetite nanoparticles

3.1.1 Weight of chitosan

In this work, chitosan was used for coating the magnetite nanoparticles in order to increase the adsorption efficiency of Cr(VI). Then, the weight of chitosan that effect on the adsorption was studied. As the results, it was observed that the heavier the chitosan amount, the higher the adsorption efficiency was obtained (Figure 1). Moreover, adding of chitosan from 0.02 g to 0.20 g provided slightly improvement of the adsorption efficiency. Increasing of the adsorption efficiency causes enhancing of amino group (-NH_2) in chitosan in which Cr(VI) was adsorbed. Figure 4 illustrated a proposed scheme of Cr(VI) adsorption on chitosan coated magnetite nanoparticles. As the results, however, it was observed that at 0.30 g chitosan, the adsorption efficiency was steady. Therefore, 0.20 g chitosan was selected as the optimal amount of chitosan used for coating the magnetite nanoparticles.

3.1.2 Volume of 25% glutaraldehyde

Glutaraldehyde as a crosslinking agent apparently affected on the adsorption efficiency of Cr(VI) for chitosan coated magnetite nano-particles. Increasing the volume of 25% glutaraldehyde, thereby reducing the Cr(VI) adsorption efficiency (Figure 2). The cause was from lacking of amine group (-NH_2) in the chitosan coated on magnetite nanoparticles by cross-linking through the glutaraldehyde. The adsorption efficiency of Cr(VI) depends on quantity of amine. The proposed adsorption scheme was

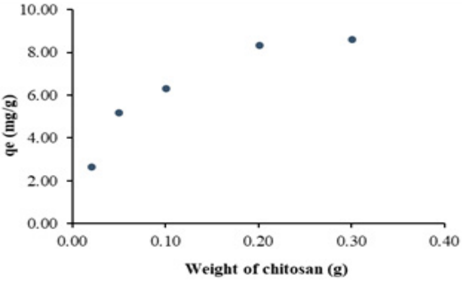


Figure 1. The plots of the relationship between adsorption efficiency (q_e) and chitosan weight.

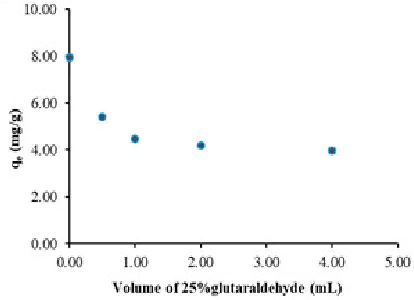


Figure 2. The plots of the relationship between adsorption efficiency (q_e) and volume of 25% glutaraldehyde

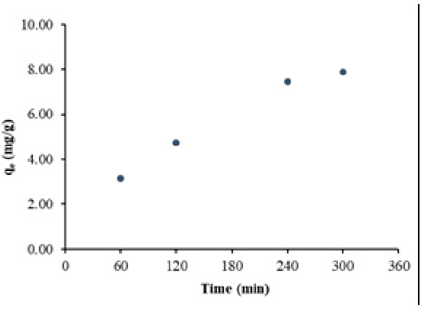


Figure 3. The plots of the relationship between adsorption efficiency (q_e) and crosslinking time.

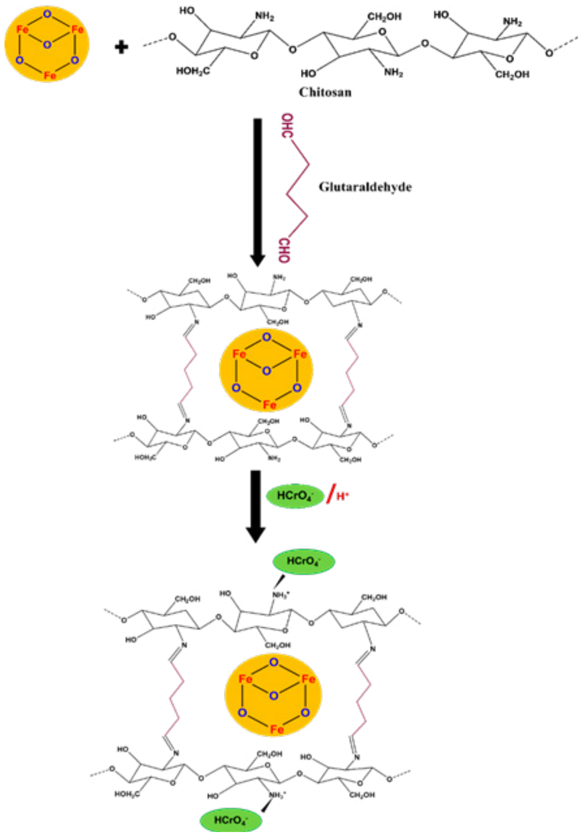


Figure 4. A schematic illustration for adsorption of Cr(VI) with chitosan coated magnetite nanoparticles (chitosan@Fe_3O_4).

illustrated in Figure 4. But, at no adding of 25% glutaraldehyde condition, some chitosan flakes and chitosan flake encapsulated magnetite nano-particles were observed, which may effect on reduction of the particles magnetism. Thus, a 0.50 mL of 25% glutaraldehyde was selected for the next study.

3.1.3Effect of crosslinking time

Time for crosslinking of chitosan coated on the magnetite nanoparticles was investigated. As shown in Figure 3 the results showed that the longer time gave, the greater adsorption get. To balance between the adsorption efficiency and time consuming, 240 minutes was chosen as the optimum condition in this work because this

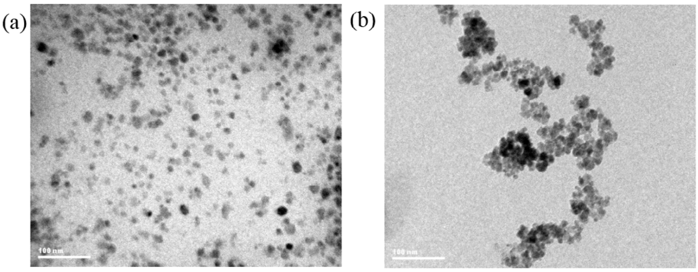
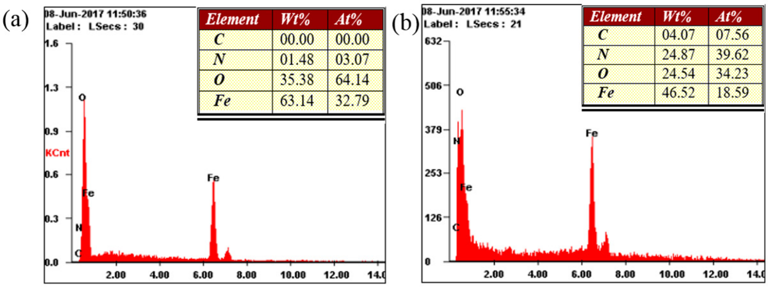


Figure 5. TEM images of (a) Fe_3O_4 and (b) Chitosan@Fe_3O_4



(a)

Element	*Wt%*	*At%*
C	00.00	00.00
N	01.48	03.07
O	35.38	64.14
Fe	63.14	32.79

(b)

Element	*Wt%*	*At%*
C	04.07	07.56
N	24.87	39.62
O	24.54	34.23
Fe	46.52	18.59

Figure 6. The EDX spectra of (a) Fe_3O_4 and (b) chitosan@Fe_3O_4

time period gave a suitable adsorption efficiency and acceptable time consuming.

3.2 Characterization

3.2.1 Transmission electron microscope (TEM)

The TEM images of naked and chitosan coated magnetite nanoparticles were illustrated in Figure 5. The synthesized magnetite nanoparticles were spherical in shape with average diameter of 8.88 ± 2.30 nm (Figure 5(a)) while the chitosan coated magnetite nanoparticles have a same shape with the naked particles but its average diameter (14.91 ± 3.46 nm) are larger than that of the magnetite nanoparticles as shown in Figure 5(b). Thus, it was obtained that chitosan can be coated on the magnetite nanoparticles due to increasing of the particle size.

3.2.2 Energy dispersive X-ray spectroscopy

The Energy dispersive X-ray: EDX spectra of the naked and chitosan coated magnetite nano-particles were shown in Figure 6. It was observed that both of them presented of iron and oxygen. However, the small amount of nitrogen appeared in the naked magnetite nanoparticles (Figure 6(a)), it may cause from contamination during preparation. As shown in Figure 6(b), the spectrum of chitosan coated magnetite nanoparticles indicated that weight ratio of nitrogen and carbon enlarged owing to coating of chitosan on the particles.

3.3.3 Fourier-transform infrared spectro-scopy

Characterization of the synthesized materials by FT-IR was investigated to confirm the accomplishment of chitosan that was coated on the naked magnetite nanoparticles. Figure 7 represents the FT-IR spectrum of all materials such as chitosan, naked magnetite nano-particles: Fe_3O_4 and chitosan coated magnetite nanoparticles: chitosan@ Fe_3O_4. The peaks at 1662, 1386 and 1079 cm^{-1} of chitosan spectra (gray line in Figure 7) were attributed to NH_2 bending vibration, O-H stretching of alcoholic group and C-N stretching in chitosan (Rajput *et al.*, 2016). The peaks at 639 and 589 cm^{-1} appeared in all Fe_3O_4 and chitosan@Fe_3O_4 (blue and orange lines in Figure 7) which were designated the Fe-O group (Sulistyaningsih *et al.*, 2017; Pham *et al.*, 2016). Additionally, chitosan@Fe_3O_4 spectra, the peaks at 1466 and 1062 cm^{-1} observed in orange line of Figure 7

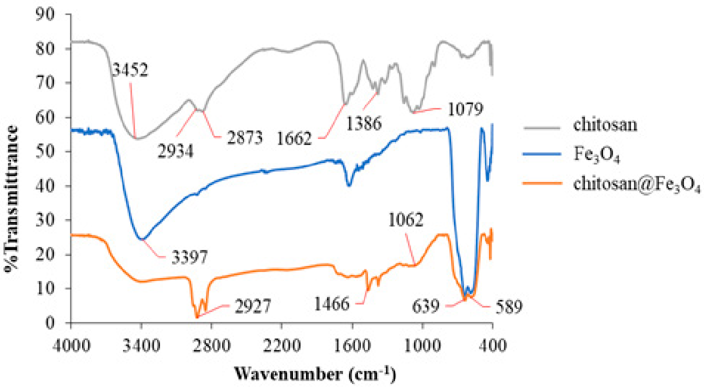


Figure 7. FT-IR spectra of chitosan (gray), the naked magnetite nanoparticles: Fe_3O_4 (blue) and chitosan coated magnetite nanoparticles: chitosan@Fe_3O_4 (orange)

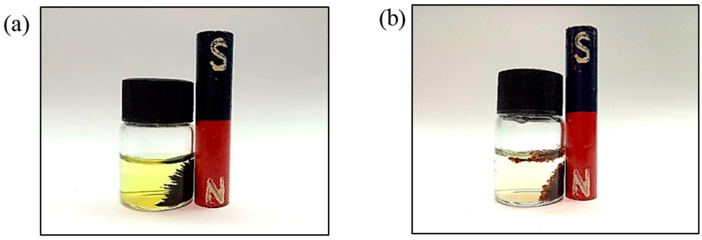


Figure 8. (a) Fe_3O_4 and (b) chitosan@Fe_3O_4 in 10 ppm Cr(VI) solution under a moderate magnetic field.

were ascribed the shift of NH_2 group and C-N in chitosan because of chitosan cross-linkage. Thus, the FT-IR results of chitosan@Fe_3O_4 indicated that chitosan should be participated to the magnetite nanoparticles. Based on the presented above (TEM, EDX and FT-IR), it was confirmed that chitosan successfully covered on the magnetite nanoparticles. Furthermore, the magnetic properties of Fe_3O_4 and chitosan@Fe_3O_4 were shown in Figure 8. Both Fe_3O_4 and chitosan@Fe_3O_4 were placed in the Cr(VI) solutions. These synthesized nanoparticles were separated under a moderate magnetic field. In addition, it was observed that period of time for separation of both adsorbents was different. The separation time of chitosan@Fe_3O_4 was slightly slower than that of naked-Fe_3O_4. Besides, the yellow color of Cr(VI) solution in which chitosan@Fe_3O_4 were immerged gave pale (Figure 8(b)). Thus, it suggests that Cr(VI) can be adsorbed on the chitosan@Fe_3O_4.

3.3 Adsorption study

3.3.1 Adsorption time

The adsorption time affected on the adsorption efficiency was studied in this work. Various adsorption times from 10 to 120 min were investigated. The results showed that the adsorption efficiency was rapidly increased at the initial adsorption time (10-60 min). But after that time (90-120 min), the adsorption efficiency was quite steady as shown in Figure 9(a). Thus, the selected time of Cr(VI) adsorption was 120 min for further experiments owing to giving the constant adsorption efficiency.

3.3.2 pH of Cr(VI) solution

pH of solution strongly involved varying of Cr(VI) species. Several Cr(VI) species at different pH were illustrated in Table 1. Therefore, this experiment was conducted to study the effect of pH on Cr(VI) adsorption using chitosan@Fe_3O_4. As recognized, chitosan as biopolymer can adsorb Cr(VI) at pH between 2 and 5 (pH 2-5) due to the protonated charge of $-NH_2$ in chitosan which enhances the adsorption efficiency of chitosan (Liang *et al.*, 2017; Szabó *et al.*, 2018). While, at pH more than or equal to 6 (pH≥6), the competition between CrO_4^{2-} and OH- in order to be adsorbed on the surface of chitosan occurs. Hence, the efficiency of Cr(VI) adsorption should be reduced (Hena, 2010). In this experiment, pH between 2 and 5 that affected on the adsorption efficiency were investigated. The results showed that at pH 2-4, the Cr(VI) adsorption efficiency was dropped while at pH 5, the efficiency was enlarged (Figure 9 (b)). As above mentioned, at pH 2-4, Cr(VI) forms were $HCrO_4^-$ and $Cr_2O_7^{2-}$ (Table 1) and chitosan were protonated. Thus, at the lowest pH (pH 2), adsorption efficiency of Cr(VI) was highest compared to others owing to a strongly condition corresponding to Piyamangala *et al.* (2008).

Additionally, it was found that stability of chitosan was loss at pH<2 (Dima *et al*, 2015). As the results, the adsorption efficiency of Cr(VI) at pH 5 was increased due to changing of Cr(VI) to Cr(III) as a phenomenon of "adsorption coupled reduction" (Miretzky & Cirelli, 2010). Changing of Cr(VI) to Cr(III) that affected on the detection system based on the reaction between Cr(VI) and DPC reduced the complex absorbance. Thus, the reduced absorbance of the complex did not truly cause from adsorption of Cr(VI) on the surface of chitosan@Fe_3O_4. Accordingly, the increased adsorption efficiency at pH 5 did not cause from adsorption of Cr(VI) but cause from none complex formation. Therefore, the solution at pH 2 was selected as optimum pH for adsorption of Cr(VI) because of enlarged adsorption efficiency and steady chitosan.

Moreover, the adsorption efficiency of Cr(VI) between chitosan@Fe_3O_4 and Fe_3O_4 were also studied in this work. The results illustrated that the Cr(VI) adsorption efficiency using chitosan@Fe_3O_4 as the adsorbent gave higher than the Cr(VI) adsorption efficiency using naked-Fe_3O_4 as shown in Table 2. Furthermore, it was surveyed that chitosan@ Fe_3O_4 showed the greater adsorption efficiency

Table 1. The species of Cr(VI) under different pH conditions

pH of Cr(VI) solution	Form of Cr(VI)	References
<1	H_2CrO_4	Hena, 2010
2-4	$Cr_2O_7^{2-}$	Miretzky & Cirelli, 2010; Liang *et al.,* 2017
4-6	$HCrO_4^-$	Svancara *et al.*, 2004
>6	CrO_4^{2-}	Nematatollahzadeh *et al.*, 2015; Liang *et al.*, 2017
>8	CrO_4^{2-}	Dima *et al.,* 2015; Hena, 2010

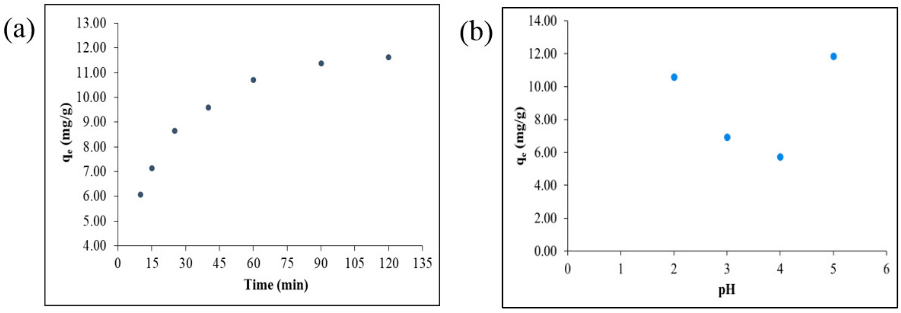


Figure 9. The plots between adsorption efficiency (q_e) and (a) time for Cr(VI) adsorption and (b) pH of Cr(VI) solutions.

Table 2. The comparison of absorption efficiency between Fe_3O_4 and Chitosan @Fe_3O_4.

Adsorbent	Average size (nm)	q_e* (mg/g)	References
Fe_3O_4	20-40	2.4	Chowdhury & Yanful, 2010
Fe_3O_4	200-300	9.95	Zhang et al., 2014
Fe_3O_4	150-250	8.9	Kumari et al., 2015
Fe_3O_4	15-36	13.35	Martinez et al., 2015
Fe_3O_4	7-11	1.18	In this work
Chitosan@Fe_3O_4	12-18	16.94	In this work

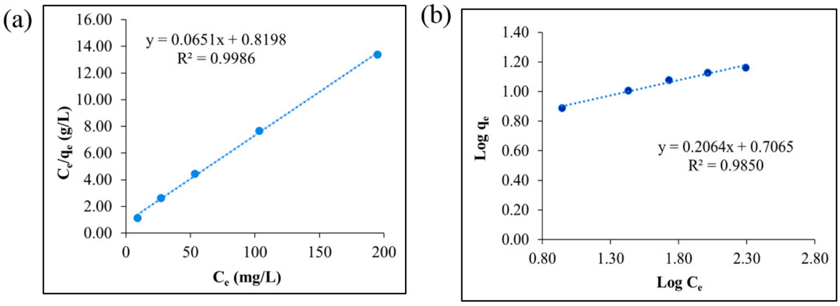


Figure 10. Fitting of (a) Langmuir and (b) Freundlich isotherm models for Cr(VI) adsorption using chitosan@Fe_3O_4

compared to the naked-Fe_3O_4 in others (Table 2). Consequently, it indicated that chitosan@ Fe_3O_4 has the capability for adsorption of Cr(VI).

3.4 Adsorption isotherm models

Langmuir and Freundlich isotherm models are usually studied to analyze the adsorption properties of adsorbent surface. Generally, Langmuir model is acceptable for monolayer adsorption while Freundlich model is satisfactory to heterogeneous adsorption on the adsorbent surface (Liu *et al.*, 2018; Jiang *et al.*, 2018). Thus, these were studied to evaluate the distribution of Cr(VI) on the surface of chitosan@ Fe_3O_4 in here. To estimate the adsorption models, the fittings of these two models were shown in Figure 10. The results illustrated that all data of Langmuir and Freundlich isotherm models were fitted in linearity. However, it was observed that the correlation coefficient value (R^2) of Langmuir isotherm model ($R^2 = 0.9986$) was better than that the Freundlich isotherm model ($R^2 = 0.9850$). Therefore, it indicated that Langmuir isotherm model may be more appropriate for predicting of adsorption of Cr(VI) on the surface of chitosan@Fe_3O_4. In addition, the q_m value indicating the binding energy and the K_l value for the adsorption strength were also shown in Table 3.

3.5 Reusability of chitosan@Fe_3O_4

One of the prominent problems of wastewater treatment process is adsorbent reusability or regeneration. Thus, in this work, the parameters for reusability such as types of eluent, effect of eluent concentration and elution times were investigated.

3.5.1 Eluent types

The ability of nitric acid (HNO_3), ethylenediaminetetraacetic acid (EDTA), hydrochloric acid (HCl) and sodium hydroxide (NaOH) as the eluents for elution of Cr(VI) from chitosan@Fe_3O_4 was studied. The results found that NaOH gave the highest %desorption as shown in Figure 11. At the condition greatly contained NaOH, the negative species of Cr(VI) such as $H_2CrO_4^-$ and $Cr_2O_7^{2-}$ adsorbed on the chitosan@Fe_3O_4 were deprotonated by Na+ from NaOH corresponding with Elwakeel, (2010). Thus, the negative species of Cr(VI) were eliminated from the adsorbent (chitosan@ Fe3O4). As this reasons, NaOH was selected as the optimum eluent for removal Cr(VI) adsorbed on the chitosan@Fe_3O_4 surface for reusability study.

3.5.2 Effect of eluent concentration

Concentrations of NaOH as the eluent affected on the adsorbent reusability were studied. The results showed that the concentrations of NaOH were increased (0.01-0.10 M), %desorption increase were obtained. However, higher concentrations of NaOH were provided (0.20-0.50 M), the constant %desorption was achieved as shown in Figure 12(a). In addition, after elution at high concentrations of NaOH (≥0.20 M), several small pieces of chitosan observed were separated from chitosan@ Fe_3O_4 owing to weakening of chitosan in basic condition (Kumirska *et al.*, 2011). Therefore, 0.10 M NaOH was selected for further.

3.5.3 Elution time

The chitosan@Fe_3O_4 nano-particles added into 50 ppm Cr(VI) solution at various time for elution were investigated. Based on the studied results, elution time parameter influenced on the %desorption of Cr(VI). Figure 12(b) shows that the enlargement of elution time, %desorption performance increased at the first (from 30 to 60 min) and then gave stable (from 120 to 240 min). Thus, the elution time at 180 min was appropriate time because it gave

Table 3. The parameters of Langmuir and Freundlich isotherm models for Cr(VI) adsorption using chitosan@Fe_3O_4

Langmuir isotherm			Freundlich isotherm		
qm (mg/g)	KL (L/mg)	R^2	1/n	K_f (L/mg)	R^2
15.3616	0.0794	0.9986	0.2064	5.0876	0.9850

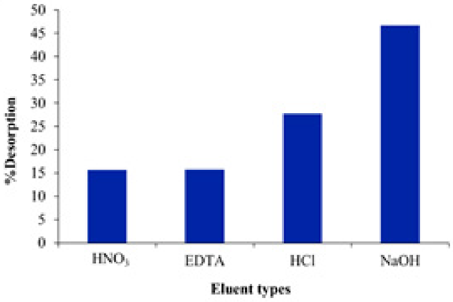


Figure 11. The plot of the relationship between %desorption and eluent types at 0.1 M per each

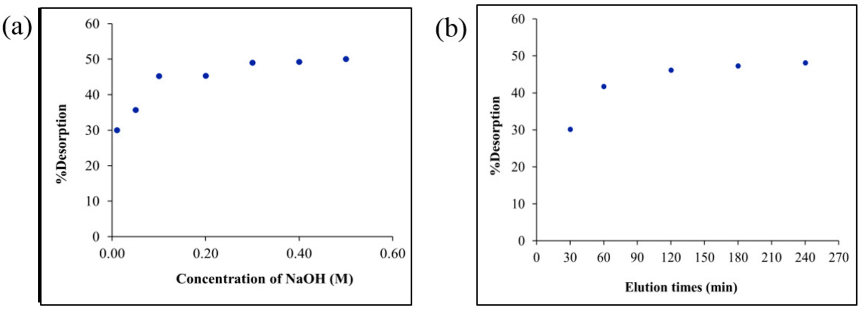


Figure 12. The plots of relationship between %desorption and (a) various concentrations of NaOH, (b) various elution times.

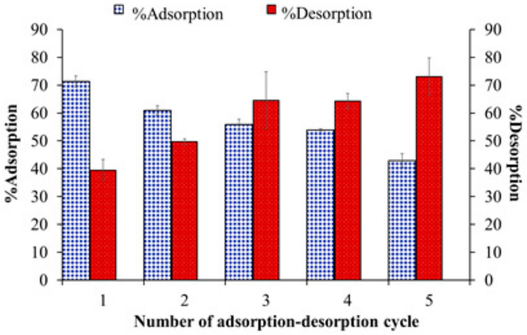


Figure 13. The plot of the relationship of %adsorption and %desorption at various adsorption-desorption cycles

Table 4. The concentrations of Cr(VI) in laboratory wastewaters before and after pretreatment by adsorption by using chitosan@Fe_3O_4

No. sample	Cr(VI) concentrations (ppm) ± SD (n=3)				
	Initial	Number of adsorption and desorption cycles			
		I	II	III	IV
1	147.24 ± 0.37	62.8 ± 3.46	17.67 ± 1.14	1.32 ± 0.09	n.d.
2	9.26 ± 0.66	0.40 ± 0.20	n.d.	-	-
3	64.65 ± 0.34	17.43 ± 3.53	2.82 ± 0.31	n.d.	-

* n.d. = not detected

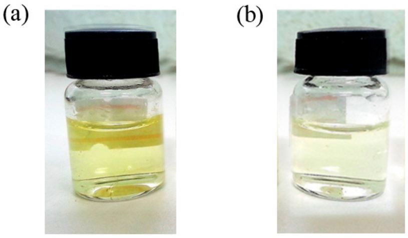


Figure 14. Photos of before (a) and after (b) adsorption of Cr(VI) solution (64.65 ppm) in sample 3

suitable %desorption. In addition, this time was not too long for doing the experiment.

3.5.4 Performance of adsorbent reusability

Reusability of chitosan@Fe_3O_4 for Cr(VI) adsorption was performed in this section. The chitosan@Fe_3O_4 reusability was done according to 2.5 section as the first cycle and then repeat this procedure again for the next cycles. The obtained results showed that %adsorption was continuously decreased while %desorption became unceasingly enhance in 5-cycle adsorption-desorption reusability (Figure 13). Then, reducing of %adsorption may cause chitosan@Fe_3O_4 degradation. But, for %desorption increasing, the reason might be the remaining of Cr(VI) adsorbed on the adsorbent in the previous cycle, so Cr(VI) concentration of the leaching obtained in the former cycle was higher than that in the later cycle (the calculation of %desorption was shown in 2.5 section).

3.6 Application in real samples

Laboratory wastewaters used as the real wastewater samples in this work were treated by chitosan@Fe_3O_4. These samples were done consistently with the adsorption experiment in 2.3 section. The results illustrated that Cr(VI) in the wastewater samples was adsorbed on chitosan@Fe_3O_4 (Table 4). Additional,concentrations of Cr(VI) in all samples after pretreatment were lower than that the wastewater quality standards of Pollution Control Department (PCD) and of United States Environmental Protection (US EPA) (Notification of the National Environment Board No.8, 1994; Sugashini & Gopalakrishnan, 2012; Song *et al.*, 2016). Figure 14 shows the example of laboratory wastewater sample before and after treatment by using chitosan@Fe_3O_4.

4. Conclusions

In this work, the chitosan@Fe_3O_4 or adsorbent synthesized by a co-precipitation method were characterized by FT-IR, TEM and EDX. The synthesized chitosan@Fe_3O_4 could be confirmed by the results from these techniques. Diameter of the chitosan@Fe_3O_4 prepared was 14.91±3.46 nm and gave the magnetic property. Additionally, the adsorption of Cr(VI) on surface of chitosan@Fe_3O_4 was well fitted to Langmuir isotherm model as a single layer adsorption. Langmuir adsorption capacity (qm) in the studied concentration range of Cr(VI) was 15.3616 mg/g. Under the optimum conditions, the chitosan@Fe_3O_4 synthesized was applied for elimination of Cr(VI) in laboratory wastewater samples. The results showed that the quantities of Cr(VI) in all samples which were pretreated by adsorption of the chitosan@Fe_3O_4 reached agreement of the effluent quality standards of PCD in Thailand. Finally, the chitosan@Fe_3O_4 as the adsorbent which was prepared in this work has potentially used for Cr(VI) removal in wastewater treatment system especially in laboratory wastewaters.

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