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Research Article

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Grafting, cross-linking and blending of chitosan as adsorbent Cr (VI) ions from artificial waste water with adsorption-fluidization method

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ABSTRACT

In this research chitosan was grafting with chloroacetic acid and it was cross-linking with urea-oxalic acid to form carboxymethyl-urea-oxalic acid (CMChi-UOX). The CMChi-UOX was blending with silica gel, to form blend Silica gel-carboxy methyl-urea-oxalic acid (Si-CMChi-UOX). Adsorption-fluidization Cr(VI) ions from artificial waste water were carried out in fluidized bed. The fluidized bed was filled with 200 ml artificial waste water and added amount 0.5 gram of adsorbent. The variable in this research are variety of times, temperatures and pH. The adsorption-fluidization capacity of CMChi-UOX and Si-CMChi-UOX onto Cr(VI) ions respectively were written in percent, 93.32% and 94.95% respectively, or the standard can be written as mg adsorbate/g adsorbent, 37.33 *and 37.98 respectively. The order rate of adsorption-fluidization for CMChi-UOX to Cr(VI)ions is order 1 and order 2, whereas the process of adsorption-fluidization is spontaneous. The parameter thermodynamics are* $\Delta H = 468.8347\ J\ mol^{-1}$ *adsorbate,* $\Delta G = 1.2913\ J\ mol^{-1}$, $\Delta S = 1.3631\ J\ mol^{-1} K^{-1}$ *and the process adsorption-fluidization was following Freundlich isotherm.*

Key words: CMChi-UOX, Si-CMChi-UOX, adsorption-fluidization, Cr(VI) ions.

INTRODUCTION

Adsorption is process to absorb on an absorbent surface, the compounds was attached to adsorbent known as adsorbate and compounds which is adsorb known as adsorbent [1]. Generally, adsorption use solid compounds as adsorbent; solid adsorption, including physics adsorption (by force of Van der Waals); and chemist adsorption (adsorbate molecules react with adsorbent surface through covalent or ionic bonding [2]. Adsorption isotherm are including Freundlich, Langmuir, Temkin, Redlich-Paterson, Sips and Dubini-Radushkevich isotherm [3,4]. Adsorbent have to big surface area and adsorption capacity. It does not dissolved in adsorbate whereas some influenced adsorption factors are types of adsorbent and adsorbate, surface area of adsorbent, adsorbate concentration, and adsorption temperature [5].

Fluidization is process or operation which fine particles are converted to behave like fluid when they are contacting the fine particles with liquid or gas [6,7]. Fluidization is used in industries, but fluidization is a new method in adsorption. Fluidization is influenced by some factors, such as system fluidization (gas-solid, solid -liquid, gas-solid-liquid) and rate of gas flow [6].

Clean water is vital thing for human health, such as for drinking and cooking. WHO international standard of Cr(VI) sequence maximum concentration for using of water domestic is 0.05 mg/l, whereas the limit standard concentration for ground water drinking is rejected in 0.05 mg/l [8,9]. As a vital thing, clean water is also necessary for washing, sanitation, industrial processes, agriculture and fishery. Waste water which contain Cr(VI) ions exceed threshold must be treated before it released to environment because chromium is harmful for environment and health. It can cause various cancers and adverse health effects, shown at the occupational and environmental exposure to metalloid species, for example, chromium (Cr) [10]. The reduction of Cr(VI) by reductor, such as ascorbic acid or GSH (glutathione), causes Cr(III) binding DNA. If Cr(III) binds with DNA to form Cr (III)-DNA complex , it leads to DNA lesions, single-strand breaks, formation of alkaline labile sites, genotoxicity and mutagenesis [11-14]. In addition, Cr(III)-DNA complex causes mutation and cancer [15], teratogenic in human or animal health, allergic and ulcers of the skin, ulceration in mucosa of the nasal septum, genotoxicity, mutagenicity, carcinogenic, respiratory organs carcinomas, chromosomal damage, spontaneous abortion, headache, nausea, vomiting, and diarrhea [16-21]. Physiological changes occur in plants and animals, cumulative or immediately effect in humans, are toxic by the chemical effect [8].

Enhancing capacity adsorption chitosan to metal ions can be caried out by grafting new functional groups to back bone of chitosan. Adding new functional groups can increase the adsorption sites [22], whereas cross-linking between chitosan molecules is used to improve the stability in acidic solution[3,23,24]. Chitosan grafting with chloroacetic acid resulted CMChi, which can be used in biomedical, pharmaceutical, environmental, veterinary, and metal ions adsorbent [25-33].

The photo catalyst, reverse osmoses, chemical reactions, electro dialysis, and activated carbon adsorption are conventional methods to remove Cr(VI) ions. However, some of those methods have many disadvantages, such as expensive, inefficient, time consuming, and ineffectively for concentration less than 100 mg/l [34-41]. In this research the adsorption-fluidization and grafting, cross-linking, blending of chitosan were used to enhance the method and to increase the adsorption capacity.

EXPERIMENTAL SECTION

The instruments, which used in this research, were FTIR (Shimadzu), AAS(Zeenit 700) and SEM(Zeis Evo MA10). The materials were commercial chitosan 79,56% deacethylation degree and 5,52599 x 10^5 g/mole relative mass average were used in this research. The reagents were used pro analyzed grade.

The Grafting Step,

The **g**rafting of chitosan with chloroacetic was conducted using Chen-Park 's method [42,43] :

10 g of chitosan and 100 ml acetic acid 2% were filled in 500 ml beaker glass. Then, it was stirred until chitosan is soluble and it was added with 13.50 g NaOH. The Beaker glass was put in the water bath at 50 ^oC during 1 hour, and 15 g chloroacetic acid in 20 ml isopropanol was added in drop wise solution. The next step, the reactants mixture was refluxed for 4 hours at 50^{o}C. The finishing reaction has occurred when the solution was added with 200 ml of 70% ethanol. The obtaining precipitate was dried at room temperature, and the product was characterized by FTIR spectrophotometer.

The Cross-linking step

Cross-linking of carboxymethyl chitosan, (CMChi) with cross-linker urea-oxalic-acid was carried out using modified method reported by Wang et al. [44] and Zhu et al. [45] : 2.5 g of urea and 5 g of oxalic acid were added in 200 ml distilled water and it was stirred until formed solution. Then, the solution was heated at 100 °C for 3 hours to obtain urea-oxalic acid (UOX) solution. CMChi (20 g) was added to 400 ml distilled water and stirred until all CMChi was dissolved. The solution was put into a 1000 ml three-necked round bottom glass and it was added with 100 ml UOX. The mixture solution was refluxed at 50°C for 2 hours. The precipitate which were obtained called as CMChi- UOX. Distilled water was added to the CMChi-UOX precipitate and it separated into two groups. The first group was dried in an oven at 50 °C and it was characterized by FTIR spectrophotometer. The second group of CMChi-UOX was mixed with silica gel.

The blending step

The second group of CMChi-UOX was mixed with silica gel (2 : 1) and it was stirred until homogeneous to result silica gel-carboxymethyl chitosan-oxalic acid (Si-CMChi-UOX). Finally, it was dried at room temperature. The particles profile of Si-CMChi-UOX shown at Figure 7.

The adsorption-fluidization step

The adsorption-fluidization: 200 ml artificial waste water(concentration Cr^{6+} 100 mg/l) and 0.5 gram CMChi-UOX were filled into the fluidized bed. The air flowed from the bottom of fluidized bed to lead the adsorption-fluidization process. The remaining concentration of Cr^{6+} was determined by AAS (Zeenit 700), whereas CMChi-UOX morphology was determined by SEM (Zeis Evo MA 10). In the similar method, the CMChi-UOX was replaced with Si-CMChi-UOX.

RESULTS AND DISCUSSION

Characterization of CMChi and CMChi-UOX

Characterization of CMChi was analyzed by compared the FTIR spectra of research product with reference. The FTIR spectra of CMChi shown at Figure 1, and the comparison of wave number of research product and reference shown at Table 1, data at Table 1 shown that grafting chloroacetic acid to the chitosan was successful. It describe in the similarity wave number between spectra of research product and reference. Grafting and cross-linking of chitosan formed CMChi-UOX (Figure 2. and Table 2.). Cross-linking with cross-linker urea-oxalic acid between back bone molecules of chitosan was successful. The SEM of particles and structure of CMChi-UOX shown at Figure 3, Figure 4 Figure 5, and Figure 6.

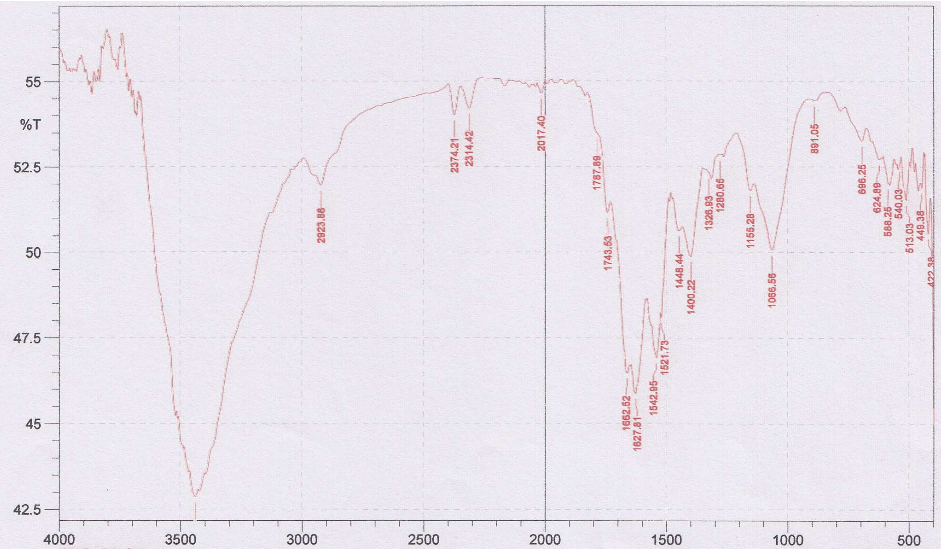


Fig 1. The FTIR spectra of CMChi

Table 1. Comparison wave number FTIR spectra of CMChi and reference[46]

No.	Functional group	Wave number CMChi(cm^{-1})	Wave number Reference(cm^{-1})
1	- COOH	2923	3000-2500
2	-C-O-C-	1066	1150-1040

Table 2. Comparison wave number FTIR spectra of CMChi-UOX and reference[46]

No.	Functional group	Wave number CMChi-UOX(cm^{-1})	Wave number Reference(cm^{-1})
1	-N(CO)N-	1629	1660
2	-(CO)NH	3431	3460-3400
3	-(CO)NH	1629	1680-1630
4	-C-O-C-	1151-1074	1150-107 0
5	-COOH	2854	3000-250 0
6	-OH bending	1400 and 1325	1410-126 0
7	-C-OH stretching	1074	115 0-104 0

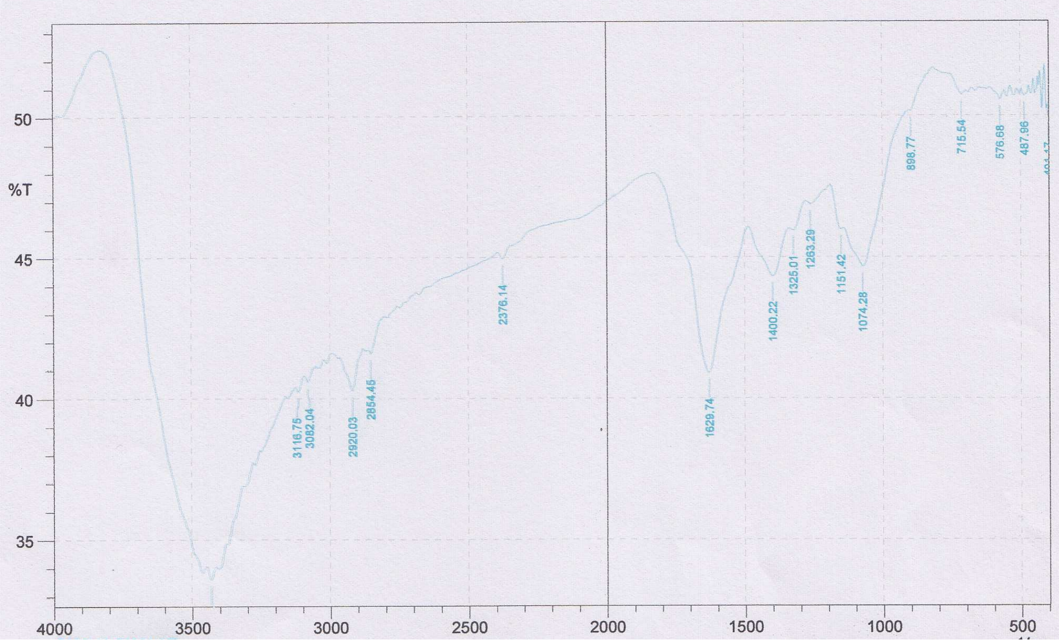


Fig 2. The FTIR spectra of CMChi-UOX

Fig 3. The particles of CMChi-UOX

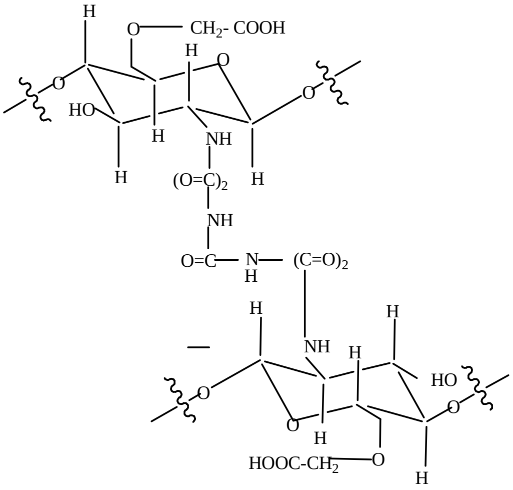


Fig 4. The structure of CMChi-UOX

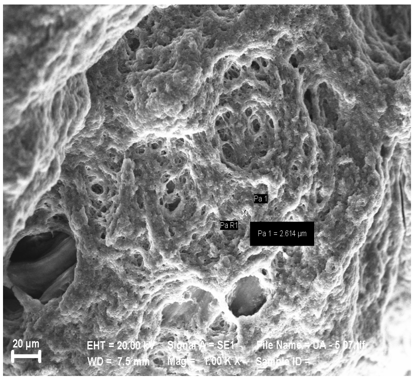


Fig 5. The SEM of CMChi-UOX

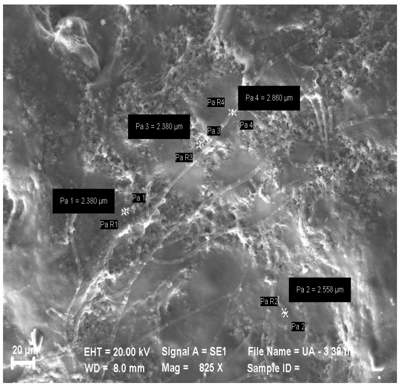


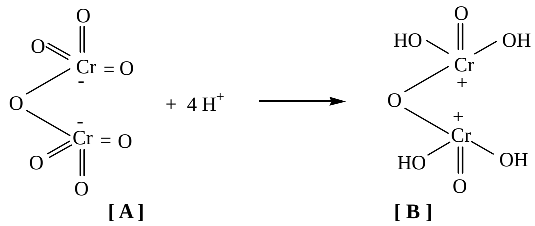
Fig 6. The SEM of CMChi-UOX after adsorb Cr^{6+}

Fig 7. The Blending of Si-CMChi-UOX

Determination of adsorption capasity

The adsorption capacity of CMChi-UOX to Cr(VI) ions calculated with formula p = [(Ci - Ca)/Ci] × 100 % and equation which formulation by Laus et al [3], p= V (Ci - Ca) /m, whereas p is adsorption capacity (in % or mg/g), Ci and Ca are concentration of Cr(VI) ions before and after adsorption-fluidization (in mg/l) respectively, m is mass of adsorbent CMChi-OX and Si-CMChi-UOX (in gram) and V are volume of artificial waste water which used in research (in ml), respectively. The operation condition in this research were (50 ^{o}C, 90 minutes and pH5), with Ci=100 mg/l, V= 200 ml, thus Ca= 6.67 mg/l (for adsorbent CMChi-UOX) and Ca =5.05 mg/l (for adsorbent Si-CMChi-UOX). In order to that, the adsorption capacity of CMChi-OX and Si-CMChi-UOX onto Cr(VI) ions are 93,33% (37.33 mg/g) and 94,95% (37.98 mg/g) respectively. The adsorption capacity of Si-CMChi-UOX and CMChi-UOX are very good, because CMChi-UOX has wide surface area, that is shown from morphology of CMChi-UOX. The morphology of this compound is not plate but bumpy, peaks, and valley (Figure 5). Because of this morphology, surface area of adsorption was increased. Fluidization method plays the main role in increasing of adsorption capacity. Fluidization is operation or process which fine particles are converted to behave like a fluid in away contacting fine particle with gas or liquid [6,7], thus individual particles is separated each other. Circulating flowed from the bottom bed to the top and return to the bottom which is causing contact completely between individual adsorbent (solid) and adsorbate (solution), therefore it was increasing the adsorption capacity. The CMChi-UOX can form chelate with Cr(VI) ions and it mechanism hypothesis shown in Figure 8.

$$K_2Cr_2O_7 \longrightarrow 2\,K^+ + Cr_2O_7^{2-}$$



[B] + CMChi-UOX⟶ The chelate complex of Cr(VI)-CMChi-UOX

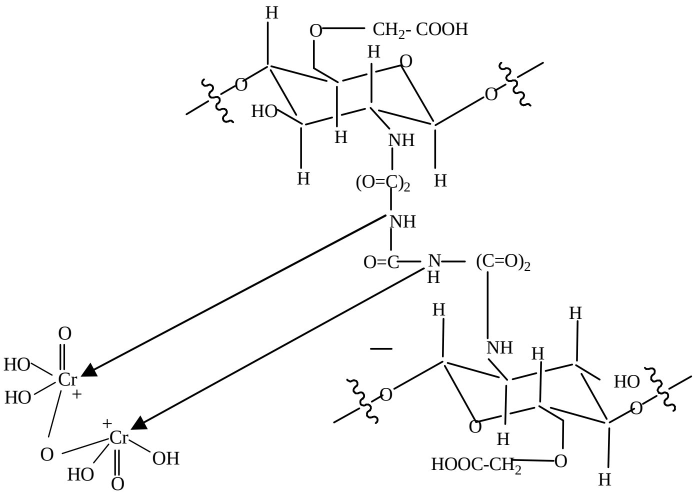


Fig 8. The hypothesis of chelate complex Cr^{6+} - CMChi-UOX

The nitrogen atom as lone pair electron donor for Cr^{+} and it forms coordination covalent bonding between N and Cr atoms, as shown at Fig 8. The chelate complex Cr^{6+}- CMChi-UOX is six atoms ring, and this chelate have conformation same as hexane (chair formed). In order to that, Cr^{6+}-CMChi-UOX chelate has small steric-hindrance chelate which is causing a stable conformation.

Determination of adsorption rate order

The equation to determinate rate of adsorption [47] is Ca$^{-(n-1)}$ = (n-1) k t + Ci$^{-(n-1)}$, where Ci and Ca are concentration of Cr(VI) before and after adsorption; k is rate of adsorption constant; n is order of rate adsorption, while t is time. From data at Table 3., the order of adsorption rate can be obtained from plot of Ca, Ca$^{0.5}$, ln Ca, Ca$^{-0.5}$, Ca^{-1} versus t resultants regression with value of square correlation coefficient R^{2} shown at Table 4. The highest value of R^{2} is 0.8895, it mean that the adsorption-fluidization rate order are order 1 and order 2.

Table 3. Correlation time and Ca for various order of adsorption rate

Time (minutes)	Ca(mg/l)	order 0	order 0.5	order 1	order 1.5	order 2
		Ca	Ca$^{0.5}$	ln Ca	Ca$^{-0.5}$	Ca^{-1}
30	9.22	9.22	3.0364	2.2213	0.3293	0.1084
45	9.00	9.00	3.0000	2.1972	0.3333	0.1111
60	8,56	8.56	2.9257	2.1471	0.3417	0.1168
75	8.36	8.36	2.8913	2.1234	0.3458	0.1196
90	8.40	8.40	2.8982	2.1282	0.3450	0.1190

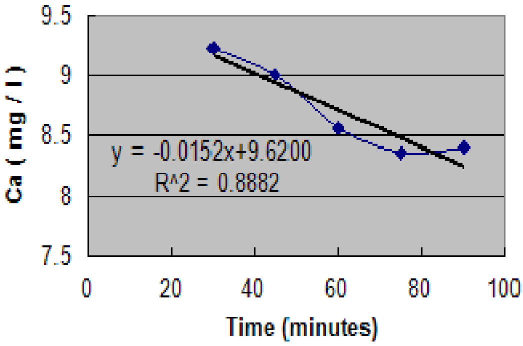


Fig 9. Plot of time VS Ca for rate of adsorption

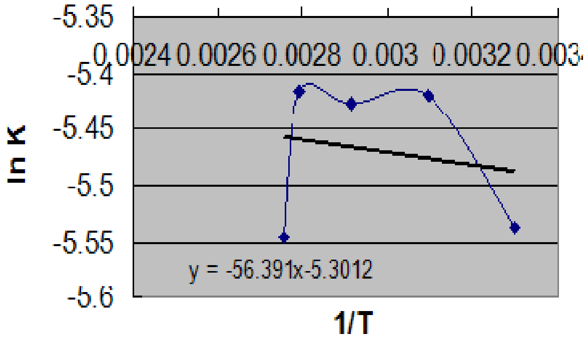


Fig 10. Plot of lnK VS 1/T order zero

Table 4. Correlation coefficient for various order of adsorption rate

Rate adsorption order :	0	0.5	1	1.5	2
Square of correlation coefficient (R^2) :	0.8882	0.8889	0.8895	0.8918	0.8895

Determination of parameter thermodynamics

Entalphy, the entalphy can be obtained from slope of curve ln K vs 1/T, therefore: ln K=ln[(x/m):Ca], where x is amount of adsorbate which attached at adsorbent, m is mass of adsorbent. The curve ln K vs 1/T resultant equation y = -56.391x - 5.3012 (Figure 10).

Table 5. Value of 1/T and lnK for m = 500 mg

T	1/T x 10^{-3}	Ca(mg/l)	x(mg/l)	x/m	[(x/m) : Ca]	ln K
303	3.3003	9.22	90.78	0.03631	0.003938	-5.5370
323	3.0959	8.28	91.72	0.03668	0.004429	-5.4195
343	2.9154	8.21	91.79	0.03671	0.004397	-5.4268
358	2.7932	8.25	91.75	0.03670	0.004448	-5.4153
363	2.7548	9.29	90.71	0.03628	0.003905	-5.5454

The slope line in Fig10. is ($-\Delta H/R$) = -56.391 K, while R is general constant for gas = 8.314 J mol $^{-1}$K^{-1}, and $-\Delta H$= -56.391 K x 8.314 J mol $^{-1}$K^{-1}, thus entalphy ΔH= 468.8347 J mol^{-1} adsorbate . Degree of freedom ΔG = -nRT ln K ads, whereas n is mol of adsorbate. At the temperature 70 ^{o}C(the maximum of adsorption capacity), amount of adsorbate is x = (Co - Ca) V = (100-8.21) 0.2 = 18.358 mg = 0.018358 g, lead to n = (0.018358) / Mr $H_4Cr_2O_7$ = 8.3445 x 10^{-5} mol.

Degree of freedom, the degree of freedom was obtained **i**f the amount of adsorbate data was inserted in equation the degree of freedom ΔG = -nRTlnK , thus ΔG = - 8.3445 x 10^{-5} (8.314) x 343 x -5.4268 =1.2913 J mol^{-1}. ΔG is positive, it means that the process of adsorption-fluidization was spontaneous and not depend on high temperature, as shown in Figure 11. The adsorption capacity at temperature 30 and 90 ^{o}C was slightly similar, and when the temperature 50, 70 and 85^{o}C, the adsorption capacity of CMChi-UOX is slightly similar.

Entrophy, the entrophy can be calculated with equation and ΔS= (ΔH-ΔG)/T= 1.3631 J mol $^{-1}$K$^{-1.}$

Determination of adsorption-fluidization isotherm

The isotherm in adsorption-fluidization can be obtained [48] by plot of log x/m VS log Ca using data in Table 5.

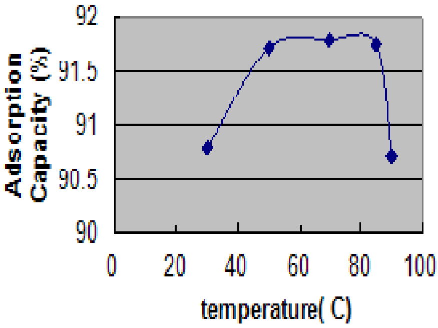


Fig.11. Plot of adsorption capacity VS temperature

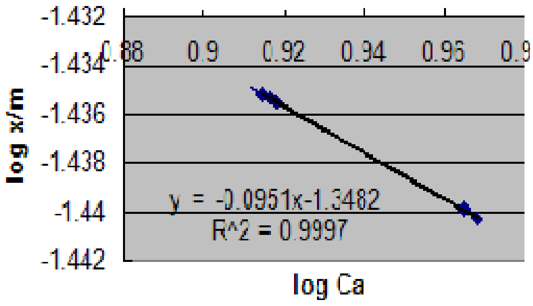


Fig 12. Plot log x/m VS log Ca

The result of Freundlich isotherm for CMChi-UOX is expressed in equation y= -0.0951x – 1.3482 and the value of square correlation coefficient is R^2 = 0.9997, as presented at Figure 12. Freundlich constant K = -1.3482 mg/l. The Langmuir isotherm [48] can be obtained from curve [Ca:(x/m)] vs Ca , with using data in Table 5., resultant curve equation was y = 19.826 x + 71.686 and R^2 = 0.3322, as presented at Figure 13.

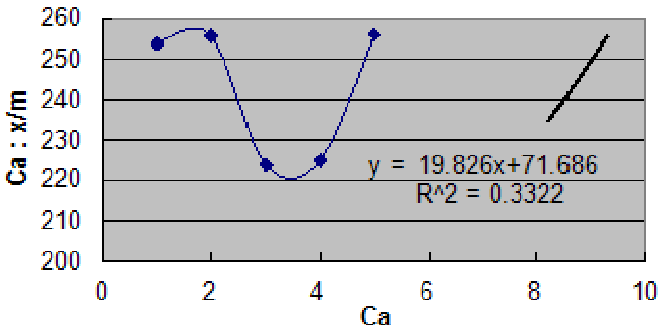


Fig 13. Plot Ca : x/m VS Ca

The linear form of the Langmuir isotherm is [Ca:(x/m)] = [1/ Kp m]+[Ca/p m], where x/m is ratio amount of absorbate per mass of adsorbent (mg/g); Ca is adsorbate concentration in solution (mg/L), K is Langmuir constant (l/mg) and pm is the maximum adsorption capacity of the monolayer which was formed in the adsorbent (mg/g) [3,49]. Figure 13., shows that [1: Kpm] = 71.686 and [1: p m] = 19.826 therefore K is 0.2765 mg/l. Because of R^2 Freundlich is higher than R^2 Langmuir, the isotherm type for this adsorption-fluidization is Freundlich isotherm.

CONCLUSION

Grafting and cross-linking of chitosan form carboxymethyl chitosan-urea-oxalic acid (CMChi-OX). Blending of CMChi-UOX with silica gel forms Si-CMChi-UOX and adsorb of Cr(VI) ions by adsorption-fluidization method with its adsorption capacity respectively are 93.33 % (37.33 mg adsorbate/g adsorbent) and 94.95 % (37.98 mg adsorbate/g adsorbent) respectively. The kinetic properties of adsorption-fluidization in this research was showed by the rate of adsorption, are order 1 and 2. The thermodynamic parameter properties of CMChi-UOX as adsorbent in adsorption-fluidization in this research are entalphy, entrophy, and degree of freedom ΔH= 468.8347 KJ mol $^{-1}$, ΔG=1.2913 KJ mol^{-1}K^{-1}, and ΔS= 1.3631KJ mol^{-1}K$^{-1,}$ respectively. The process of adsorption-fluidization is spontaneous process and the type of isotherm adsorption-fluidization is the Freundlich isotherm with Freundlich constant K = -1.3482 mg/l.

Acknowledgements
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