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Research Article

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Grafting of chitosan as adsorbent Cr(VI) from water with adsorption-fluidization method

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ABSTRACT

The study of kinetic and thermodynamic properties of adsorption-fluidization on Cr(VI) ions were performed using chitosan grafting, which was called as carboxy methyl chitosan-benzaldehyde (CMChi-B). This compound was synthesized from chitosan which was grafting with chloroacetic acid. The product was carboxy methyl chitosan (CMChi) and was characterized by FTIR spectrophotometer. CMChi which was grafted with a benzaldehyde solution produced CMChi-B and was characterized by FTIR spectrophotometer. Adsorption-fluidization of Cr(VI) ions has been done with the variation of times, temperatures and pHs. Fluidization bed was filled in 200 ml solution of Cr(VI) ions. The results revealed that the adsorption capacity of CMChi-B yield 96.19% or 38.48 mg/g at operation conditions. With the same condition, adsorption capacity of blend silica gel-CMChi-B yield 92.70%. The adsorption-fluidization was not spontaneous process, but it was a regularity process which the type of Langmuir isotherm adsorption with 2^{-1} as the order rate of adsorption.

Keywords*:* Kinetic, Thermodynamic, Adsorption-fluidization, Carboxymethyl chitosan- benzadehyde, Cr(VI)

INTRODUCTION

Chitin is the abundant material of biopolymer/polysaccharides after the cellulose. Chitin can be obtained from low organism; insect's shell; arthropods, like crustacean (shrimp, crabs, lobster); fungi cell wall; yeast and rodulus mollusks; and cephalopods, including octopuses and squids [1-4]. Chitin can be transformed to chitosan. Chitosan was solved in dilute acetic acid and aqueous solution on pH< 6,5, and then it was dissolved in N-metil morfolin-N-oxide/HOH [5]. Chitosan grafting with chloroacetic acid produced CMChi, and CMChi can be used in biomedical, pharmaceutical, environmental, veterinary, and metal ions adsorbent [6-14].

The availability of clean water is very important for human health, especially for drinking and cooking. High concentration of heavy metal in water is very dangerous for human health. Toxic chemicals effect is caused the physiological changing in humans immediately or cumulatively [15]. For examples, the toxicity effects of chromium (Cr) are caused headache, nausea, vomeeting, carcinogenic and diarrhea [16]. The conventional methods for removal Cr ions from water are reverse osmoses, chemical reactions, and activated carbon adsorption. These methods are high cost, inefficiency, and ineffectively for concentration less than 100 mg/l [17-20]. Cr(VI) waste water removal with membrane or electro dialysis is expensive [21-22], whereas photo catalysis Cr(VI) removal is need a long time [23,24]. The other conventional methods are reduction, hydroxides sedimentation, and ion exchange [25].

Some industries which resulting Cr(VI) in the waste water are galvanizing industry, petroleum complex, stainless steel, waste water from chromium plating, and acid cleaning [25]. The maximum international standard WHO for using of water domestic is 0.05 mg/l, whereas the limit standard concentration for drinking ground water is rejected in 0.05 ppm [15, 26]. CMChi could form chelate with metal ions, whereas, chitosan was used as metal chelating agent, and the harmful metal ions could be removed by the formation of a chelating polymer [14, 27-34]. Grafting on chitosan increases its efficacy and selectivity to metal ions via forming of a chelate-metal ions complex [34-39].

Fluidization is a process when fine particles are converted to fluid by contacted fine particles with liquid or gas [40, 41]. Fluidization is occurred from solid particles, thereby liquid or gas flows from the bottom of fluidized bed. In the solid-liquid-gas system, with certain gas rate, solid particles were carried by gas flow and apart from others. Circulation experiment was continuing flow from the bottom to the top of the bed, and the flow returned to the bottom of the bed. The good contact of solid particles with solution increases the adsorption capacity of metal ions.

EXPERIMENTAL SECTION

This research was using commercial chitosan with degree of deacethylation 79,56% and relative mass average 5,52599 x 10^5 g/mole . The reagents for this research were used pro analyzed grade. The instruments, which used in this research, were FTIR, AAS and SEM.

Synthesis carboxymethyl chitosan (CMChi) carried out by Chen-Park's method [42]: a 500 ml Beaker glass was filled in 10 g of chitosan, 100 ml acetic acid 2% and it was stirred until chitosan soluble. 13.50 g NaOH was added to the Beaker glass. The Beaker glass was put in the water bath at 50^{o}C during 1 hour, and 15 g chloroacetic acid in 20 ml isopropanol was added in dropwise solution. The next step, Beaker glass was refluxed for 4 hours at 50^{o}C. The reaction was finished with adding of 200 ml of 70% ethanol. The obtaining precipitate was dried at room temperature, and the product was characterized by FTIR spectrophotometer (Shimadzu).

Synthesis carboxymethyl chitosan-benzadehyde (CMChi-B) was conducted by modified Guinesi-Cavalheiro's method [43]: 20 g CMChi was diluted in 400 ml aquadest and the solution was filled in a 1000 ml three neck round bottom glass. 10 ml of benzaldehyde solution in ethanol (1:1) was filled in separation funnel. Benzadehyde-ethanol was added by drop wise to CMChi solution and the mixture compound was refluxed at 60^{o}C for 5 hours. The obtaining precipitate was CMChi-B and it was filtered with Buchner funnel. Finally, it was washed with ethanol and it was dried in the oven. The product was characterized by FTIR spectrophotometer (Shimadzu).

Adsorption-fluidization step**:** 200 ml of Cr(VI) solution with initial concentration of 100 ppm was filled in to the fluidization bed, then 0.5 g of (CMChi-B) was added. Air was flowed from the bottom of the column with the pump and it led to adsorption-fluidization process. Optimum condition was obtained from variation of times, temperatures and pHs. After adsorption-fluidization process, the concentration of Cr(VI) which was remaining in solution was determined by AAS (Zeenit 700), and morphology of CMChi-B was evaluated by SEM (Zeis EVO MA 10).

RESULTS AND DISCUSSION

Determination of adsorption capacity

The adsorption capacity of CMChi-B to Cr(VI) ions at various times, temperatures and pHs were calculated with formula

p = [(Ci – Ca) / Ci] x 100 %...... (1)

or equation

p = V (Ci – Ca) / m…........(2) [34],

where p is the adsorption power (% or mg/g), Ci and Ca are concentration of Cr(VI) metal before and after adsorption (mg/l), m is mass of adsorbent (g), and V is volume of solution Cr(VI) in liter. The adsorption capacity of CMChi-B to Cr(VI) ions at various times, temperatures, and pHs and time are shown in Table 1.

The CMChi product of synthesis was analyzed with FTIR spectrophotometer and its spectra was compared with the reference. The carboxyl group was indicated by wave number band at 2927 cm^{-1}, and the reference was showed in 3000-2500 cm^{-1}. In addition, the CMC has two C-O-C group bands at 1072 cm^{-1}, while the reference wave number band was 1150-1040 cm^{-1}. The width of the reference was 34.922, which was higher than C-O-C chitosan area, 33.662. The FTIR spectrum for CMChi-B showed that the wave number of C=NH group was 3400 cm^{-1} and aromatic ring wave number was 1635 cm^{-1}. The structure CMChi-B can be showed in Figure 1. Adsorption capacity of Cr(VI) ions was increased because of the extended surface on CMChi-B which were bumpy, peaks, and valley morphology (Figure 2).

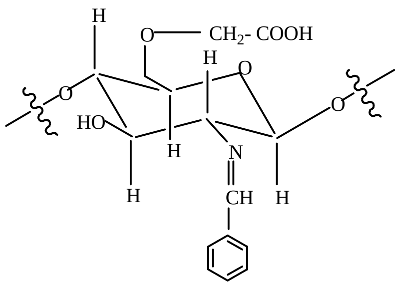


Figure 1. The Structure of CMChi-B

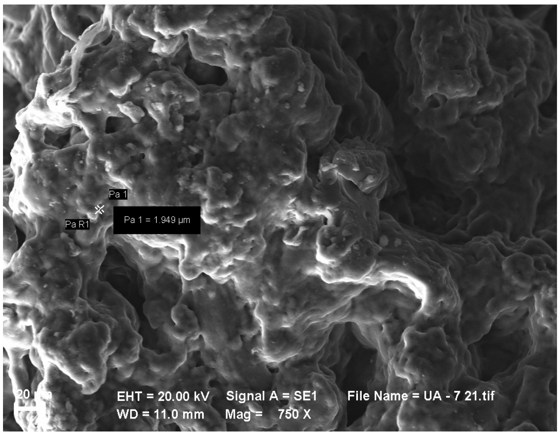


Figure 2. The Morphology of CMChi-B

Table 1. The adsorption capacity of CMCB to Cr (VI) ions at various times, temperatures, and pH with Ci = 100 mg/l, m=500 mg and V=200 ml

Time (minute)	: 30	45	60	75	90
Adsorption capacity (%)	: 91,17	91,13	91,28	91,49	90,88
Temperature (°C)	: 30	50	70	85	90
Adsorption capacity (%)	: 91,17	91,43	91,43	91,69	91,22
pH	: 4	5	6	7	8
Adsorption capacity (%)	: 91,20	90,28	90,79	79,82	90,92

The optimum condition of the adsorption-fluidization was 75 minutes, 85°C and pH 4. From Table 1 and Figure 3, these were showed that time played the main role in the adsorption of Cr(VI) ions. The capacity of CMChi-B adsorption was increased equivalent with the increasing of time. It happened because in the long time range, the interaction between CMChi-B and Cr(VI) ions is excellent. The resultant of the maximum adsorption was observed at 75 minutes. This curve related to the setting of equilibrium between adsorption and desorption on the adsorbent at its active sites, especially when the adsorption-fluidization was at 75 minutes. Table 1 was showed that CMChi-B presented saturation at 75 minutes, but at 90 minutes the adsorption capacity of CMChi-B was decreased. At this condition, the adsorbent was over saturated, thus the adsorbent was not able to absorb of Cr(VI) ions.

Table 1 shows that adsorption effected by pH. The increasing of pH would decrease the adsorption Cr(VI) ions to CMChi-B, which in the highest acidic medium (pH =4) chelate complex was formed by 5 atoms from CMChi-B-Cr(VI) interaction. The chelate has similar conformation with furan ring of sucrose, very stable, because of the low stereo-hindrance effect. The hypothesis of the mechanism of chelate complex formation by CMChi-B-Cr(VI) interaction in the acidic medium is presented at Figure 3.

Table 1 shows that optimum condition on adsorption-fluidization is at 75 minute, 85 °C and pH=4. The adsorption of 500 mg CMChi-B to 200 ml solution Cr(VI) with adsorption-fluidization method at optimum conditions resulted Ca=3,807 mg/l. The adsorption power was calculated with equations (2) and (1), so the resultant p= [(100-3.807)/100] x100% = 96.19% or p = 0,2 (100 - 3.807) : 0.5 = 38.48 mg adsorbate/g adsorbent.

The equation to determinate rate of adsorption [44] is $Ca^{-(n-1)} = (n-1)akt + Ci^{-(n-1)}$ ...... (3), where Ci and Ca are concentration of Cr(VI) before and after adsorption and k is rate of adsorption constant, *n* is order of rate adsorption, while t is time.

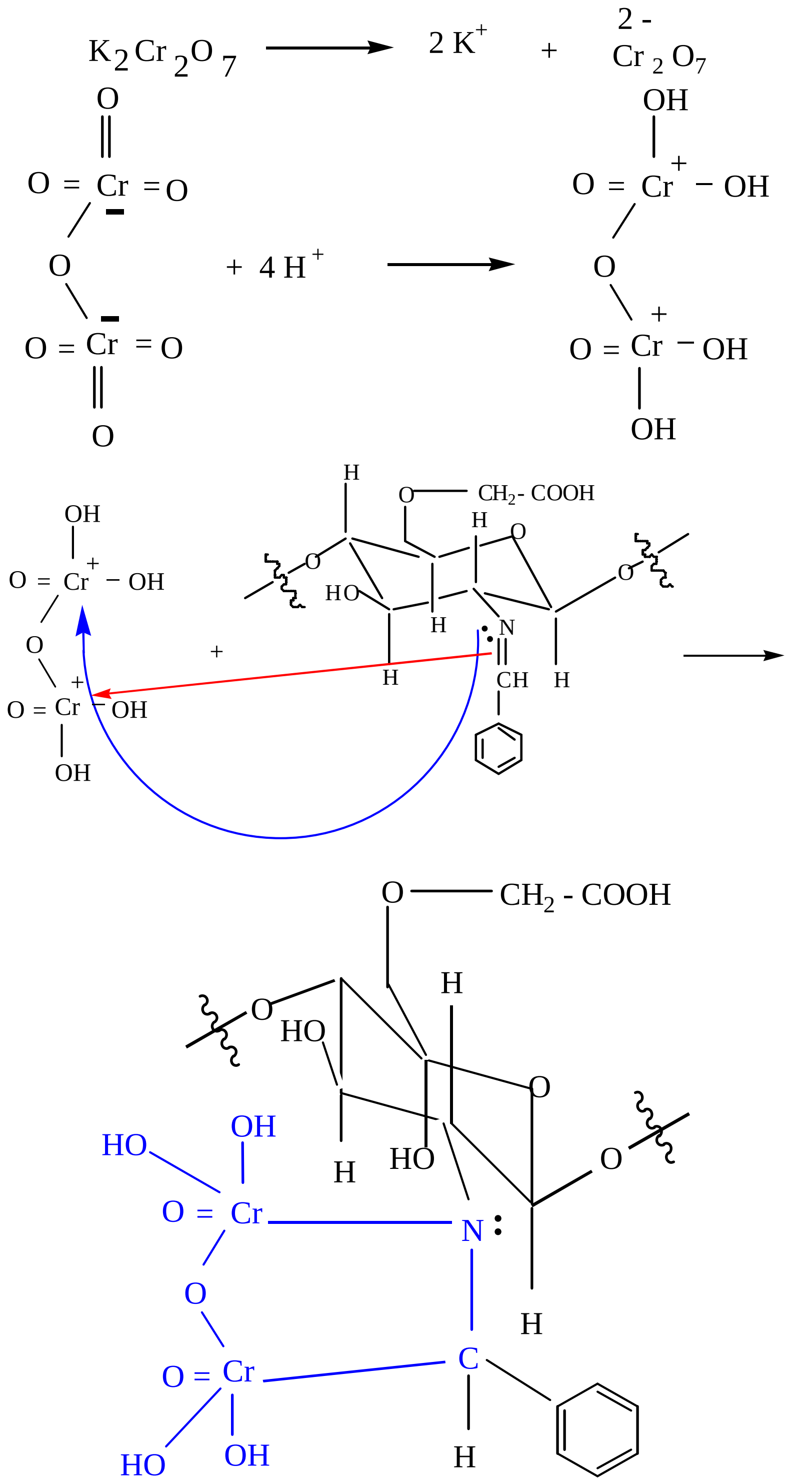


Figure 3. Mechanism hypothesis of chelate complex by interaction CMCB-Cr(VI)

Table 2. Correlation of time and Ca for various rate adsorption order

Time(min)	Ca(mg/l)	orde 0	orde 0,5	orde1	orde1,5	orde 2
		Ca	$Ca^{0,5}$	lnCa	$Ca^{-0,5}$	Ca^{-1}
30	8,83	8,83	2,9715	2,1781	0,3365	0,1132
45	8,87	8,87	2,9782	2,1826	0,3357	0,1127
60	8,72	8,72	2,9529	2,1656	0,3386	0,1146
75	8,51	8,51	2,9172	2,1412	0,3428	0,1175
90	9,12	9,12	3,0199	2,2104	0,3311	0,1096

The plot of Ca, $Ca^{0,5}$, ln Ca, $Ca^{-0,5}$ and Ca^{-1} vs t resultant regression with value of square correlation coefficient R^2 are shown in Table 3 and the highest value of R^2 is 0.7893 (Figure 4), so the adsorption rate order is 2^{-1}. Entalphy can obtain from slope of curve ln K vs 1/T, therefore:

ln K=ln[(x/m):Ca]......(4), where x is amount of adsorbate which adsorpted by adsorbent, m is mass of adsorbent. The curve lnK vs 1/T resultant equation y = 114.17x – 5.7949 with R^2 = 0.9481 is shown in Figure 5.

Table 3. Correlation coefficient for various rate adsorption order

Rate adsorption order	: 0	0,5	1	1,5	2
Square of Corr.coeficient	: 0,7890	0,7893	0,7885	0,7842	0,7857

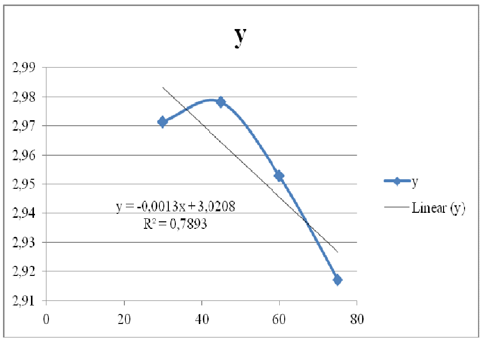


Figure 4. The curve $Ca^{0,5}$ vs t for adsorption- fluidization

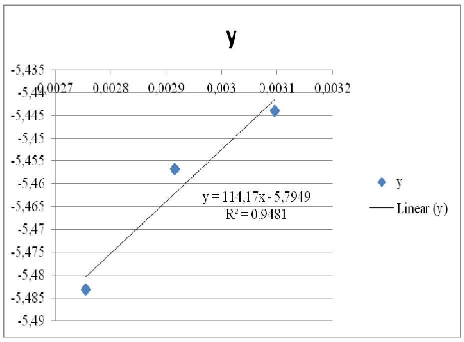


Figure 5. The curve ln K vs 1/T for adsorption-fluidization

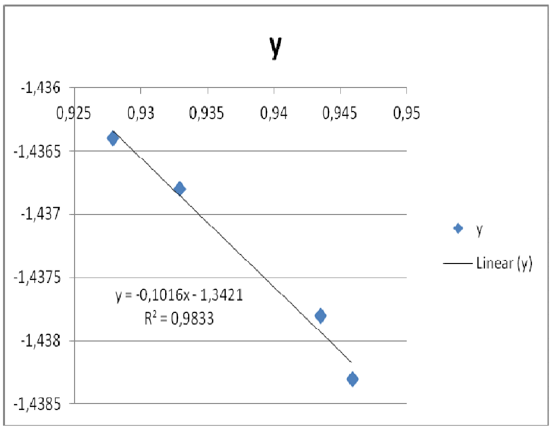
The slope is (-ΔH/R) = 114.170 K, while R is constant general for gas = 8,314 J mol^{-1} K^{-1}, and -ΔH= 114.17 K x 8.314 J $mol^{-1}K^{-1}$, thus entalphy ΔH= -949.21J mol^{-1} adsorbate (exothermic adsorption). Degree of freedom ΔG = $-nRTlnK_{ads}$, whereas n is mol of adsorbate. At the optimum condition (85°C), amount of adsorbate is x/m = 0.03667, and m = 500 mg, thus x =500(0.03667) mg or n = (500 x 0.03667 mg) / Mr Cr(VI) = 3.52664 x 10^{-4} mol. If this data was inserted in equation, the degree of freedom ΔG=-nRTlnK =5.693 J for 0.000352664 mol adsorbate or ΔG =16142.5695 J mol^{-1} and ΔS= (ΔH-ΔG)/T= -47.7424J $mol^{-1}K^{-1}$. Because of ΔH and ΔS were negative and ΔG was positive, the equation is ΔG = ΔH - TΔS. From this result, we can conclude that T must be high. Degree of freedom ΔG was positive, it means that the process of adsorption-fluidization was not spontaneous but regularly, as shown in Table 1. The adsorption capacity was gradually increased from 30°C to 85°C and the maximum of adsorption capacity take place at high temperature, 85°C.

The plot log x/m vs log Ca [45] was using data in Table 4. The result of Freundlich isotherm which expressed in equation is y= -0.1016x – 1.3421 and value of square correlation coefficient is R^2 = 0.9833, as presented at Figure 6. Langmuir isotherm can obtain from curve [Ca:(x/m)] vs Ca [45], with data in Table 4, resultant curve equation was y = 30.131x – 23.866 and R^2 = 0.9999, as presented at Figure 7. The linear form of the Langmuir isotherm is [Ca:(x/m)] = [1/ Kp_m]+[Ca/p_m] ....(5), 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 p_m is the maximum adsorption capacity of the monolayer which was formed in the adsorbent (mg/g) [34,46]. Figure 7 shows that [1: Kp_m] = -23.866 and [1: p_m] = 30.131 so K = - 1.26206 mg/L. Because R^2 Langmuir higher than R^2 Freundlich, the adsorption type for this adsorption-fluidization was Langmuir isotherm monolayer with Langmuir constant K = -

1.26206 mg/L.

Table 4.value of 1/T and lnK for m = 500 mg

T(K)	10^{-3} x (1/T)	Ca(mg/l)	x/m	[(x/m) : Ca]10^{-3}	lnK
303	3,3000	8,83	0,03645	4,1279	-5.48997
323	3,0959	8,47	0,03610	4,3223	-5.44397
343	2,9155	8,57	0,03657	4,2674	-5.45678
358	2,7933	8,31	0,03667	4,4127	-5.42325
363	2,7548	8,78	0.03649	4.1560	-5.48319



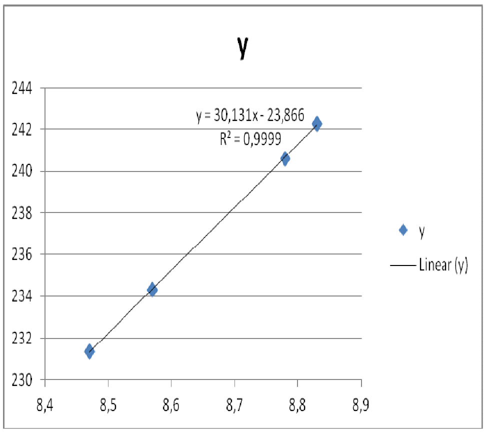


Figure 6. The Curve of log x/m vs log Ca for adsorption-fluidization Figure 7. The Curve of [Ca: (x/m)] vs Ca for adsorption-fluidization

CONCLUSION

Carboxymethyl chitosan-benzadehyde (CMChi-B) can be synthesized from chitosan and adsorb of Cr(VI) ions by adsorption-fluidization method with adsorption capacity was 96.19 % or 38.48 mg adsorbate/g adsorbent. The kinetic properties of adsorption-fluidization in this research was showed by the rate of adsorption order was 2^{-1}. The thermodynamic parameter properties of adsorption-fluidization in this research were entalphy, entrophy, and degree of freedom which were respectively ΔH= -949.21 KJ mol^{-1}, ΔG= 5.693 KJ mol^{-1} K^{-1}, and ΔS= - 2.6673 KJ mol^{-1} K^{-1}. The process of adsorption-fluidization was exothermic and was not spontaneous, but regularly process. Regularly process happened with the increasing of temperature. The type of adsorption-fluidization was the Langmuir isotherm monolayer with Langmuir constant K = - 1.26206 mg/L.

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REFERENCES

[1] YS Puvvada; S Vankayalapati; S Sukhavasi, *International Current Pharmaceutical Journal*, **2012**, 1(9), 258-263.
[2] RAA Muzzarelli, *Cellular and Molecular Li fe Sciences*, **1997**, 53(2), 131–140, in L Xiaosong; M Min; N Du; Y Gu; T Hode; M Naylor; D Chen; E Robert; and WR Chen, *Clinical and Developmental Immunology*, **2013**, 1-8.
[3] L Xiaosong; M Min; N Du; Y Gu; T Hode; M Naylor; D Chen; E Robert; and WR Chen, *Clinical and Developmental Immunology*, **2013**, 1-8.
[4] R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[5] DW Jenkins; SM Hudson; ed Czekaj C, Chitin and Chitosan: Encyclopedia of Polymer Science and Technology, 3rd Edition, Wiley Interscience, New York, 2001, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.

[6] DK Singh; AR Ray, *J. Macromol Sci. Rev. Macromol Chem Phys.*, **2000**, 40, 69–83, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[7] KC Gupta; MNV Ravi Kumar, *J. Macromol Sci. Rev. Macromol Chem Phys.*, **2000**, 40, 273–308, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[8] K Kurita, *Prog. Polym. Sci.*, **2001**, 26, 1921–71, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[9] E Khor; LY Lim, *Biomaterials*, **2003**, 24, 2339–2349, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[10] MNV Ravi Kumar; RAA Muzarelli; A Muzzarelli; H Sashiwa; AJ Domb, *Chem. Rev.,* **2004**, 104, 6017–6084, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[11] Sashiwa H and Aiba SI, *Prog. Polym. Sci.*, **2004**, 29, 887–908, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[12] C Valenta, *Adv. Drug Deliv. Rev.*, **2005**, 57, 1692–712, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[13] M Prabaharan; JF Mano, *Carbohydr. Polym.*, **2006**, 63, 153–166, in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[14] L Zhou; Y Wang; Z Liu; Q Huang, *Acta Phys-chi Sin.*, **2006**, 22, 1342-1346 in R Jayakumar; M Prabaharan; SV Nair; S Tokura; H Tamura; N Selvamurugan, *Progress in Materials Science*, **2010**, 55, 675–709.
[15] HM Dix, Enviromental Pollution, John Wiley & Sons, Chichester, New York, Brisbane, Toronto, **1981**, 168-172.
[16] S Babel and TA Kurniawan, **2003**. Various treatment technologies to remove arsenic and mercury from contaminated groundwater: an overview. In: Proceedings of the First International Symposium on Southeast Asian Water Environment, Bangkok, Thailand, 24–25October, pp. 433–440 in MA Barakat, *Arabian Journal of Chemistry*, **2011**, 4, 361–377.
[17] G Tiravanti; D Pertluzzelli; R Passino, *Water Sci. Technol.*, **2006**, 36, 197-207 in E Malkoc; Y Nuhuglu; *Chem. Eng. Sci.*, **2006**, 61, 4363-4372.
[18] Y Sag; Y Aktay, *Process Biochemistry*, 2001, 36(12), 1187-1197 in E Malkoc; Y Nuhuglu; *Chem. Eng. Sci.*, **2006**, 61, 4363-4372.
[19] G Rojas; J Silva; JA Flores; A Rodriguez; M Ly; H Maldonado, *Separation and Purif. Technol.* , 2005, 44, 31-36, in E Malkoc; Y Nuhuglu; *Chem. Eng. Sci.*, **2006**, 61, 4363-4372.
[20] V Sarin, PP Pant, *Biorest, Technol.*, 2001, 97(1), 15-20, in E Malkoc; Y Nuhuglu; *Chem. Eng. Sci.*, **2006**, 61, 4363-4372.
[21] TA Kurniawan, GYS Chan, WH Lo, S Babel, *Chem. Eng. J.*, **2006**, 118, 83–98, in MA Barakat, *Arabian Journal of Chemistry*, **2011**, 4, 361–377.
[22] T Mohammadi; A Mohebb; M Sadrzadeh; A Razmi, *Sep. Purif. Technol,* **2005**, 41, 73–82, in MA Barakat, *Arabian Journal of Chemistry*, **2011**, 4, 361–377.
[23] MA Barakat, *Arabian Journal of Chemistry*, **2011**, 4, 361–377.
[24] P Kajitvichyanukula; J Ananpattarachaia; S Pongpom, *Sci. Technol. Adv. Mater.***,** **2005**, 6, 352–358, in MA Barakat, *Arabian Journal of Chemistry*, **2011**, 4, 361–377.
[25] Kurita, Kurita Hand Book of Water Treatment, **1985**, 208.
[26] D Hendricks, Water Treatment Unit Processes, Taylor and Francis, Boca Raton, London, New York, **2006**, 26.
[27] HK No; SP Meyers, *Rev. Environ. Contam. Toxicol*., **2000**, 163(1), in AR Cestari; EFS Veiera; JDS Matos; DCS dos Anjos, *J. of Colloid and Interface Science*, **2005,** 285, 288-295.
[28] RS Juang; FC Wu; RL Tseng, *Biores. Tech*., **2000**, 80, 187, in AR Cestari; EFS Veiera; JDS Matos; DCS dos Anjos, *J. of Colloid and Interface Science*, **2005,** 285, 288-295.
[29] OAC Monteiro Jr; C Airoldi, *J. of Colloid Interface Sci*., **1999,** 212, in AR Cestari; EFS Veiera; JDS Matos; DCS dos Anjos, *J. of Colloid and Interface Science*, **2005,** 285, 288-295.
[30] AR Cestari; EFS Veiera; JDS Matos; DCS dos Anjos, *J. of Colloid and Interface Science*, **2005,** 285, 288-295.
[31] M Rinaudo, *Prog. Polym. Sci*., **2006**, 31, 603-632, in R Laus; TG Costa; B Szpoganicz; VT Favere, *J. of Hazard. Mat*., **2010**, 183, 233-241.
[32] AJ Varma; SV Deshpande; JF Kennedy, *Carbohydr. Polym.*, **2004**, 55, 77-93, in R Laus; TG Costa; B Szpoganicz; VT Favere, *J. of Hazard. Mat*., **2010**, 183, 233-241.
[33] T Becker; M Schlaak; H Strasdeit, *React Funct. Polym.*, **2000**, 44, 289-298 in R Laus; TG Costa; B Szpoganicz; VT Favere, *J. of Hazard. Mat*., **2010**, 183, 233-241.
[34] R Laus; TG Costa; B Szpoganicz; VT Favere, *J. of Hazard. Mat*., **2010**, 183, 233-241.
[35] S Sun; A Wang, *Separation and Purifcatiotion Technology*, **2006**, 49, 197-204.
[36] S Sun; A Wang, *J of Hazardous Materials*, **2006**, 131, 103-111.

[37] ST Lee; FL Mi; YJ Shen; SS Shyu, *Polymer*, **2001**, 42, 1879-1892, in S Sun; A Wang, *J of Hazardous Materials*, **2006**, 131, 103-111.
[38] CA Rodriguez; MC Laranjeira; VT Favere; E Stadler, *Polymer*, **1998**, 39, 5121-5126, in S Sun, A Wang, *J of Hazardous Materials*, **2006**, B131, 103-111.
[39] K Inone; K Yoshizuka; K Ohio, *Anal. Chim. Acta*, **1999**, 388, 209-218, in S Sun; A Wang, *J of Hazardous Materials*, **2006**, 131, 103-111.
[40]D Kunii; O Levenspil, Fluidization Engineering, 2nd Edition, Butterworth-Heinemann, Boston, London, Singapore, Sydney, Toronto, Wellington, **1991**, 1-3.
[41] LG Gibilaro, Fluidization Dynamics, Butterworth Heinemann, Oxford, Auckland, Boston, Johanesburg, Melbourne, New Delhi, **2001**, 1.
[42] XG Chen; HJ Park, *Carbohydrate Polymer*, **2003**, 53, 355-359, in S Sun; A Wang, *J of Hazardous Materials*, **2006**, 131, 103-111.
[43] LS Guinesi; ETG Cavalheiro, *Carbohydr.Polym.*, **2006**, 65, 557-561 in HK Jiao; Y Zhou; JX Zhou; L Gao; YY Xing; XH Li, *Iranian Polymer Journal*, **2011**, 20(2), 123-136.
[44] F Wilkinson, Chemical Kinetics and Reaction Mechanism, von Nostrand Company, Molly, Millans Lane, Wokinghan, Berkshire, England, **1980**, 24.
[45] PW Atkins, Physical Chemistry, 4th Edition, Oxford University Press, Oxford, Melbourne, Tokyo, **1990**, 885-889.
[46] KC Justi; VT Favere; MCM Laranjeira; A Neves; RA Peralta, *Colloid Interface Sci.*, **2005**, 2369-374, in R Laus; TG Costa; B Szpoganicz; VT Favere, *J.Hazard. Matr.* **2010**, 183, 233-241.