CHROMIUM AND LEAD REMOVAL USING SYNTHESIZED NANOCRYSTALLINE ZEOLITE

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Abstract

Zeolite Y nanocrystal was synthesized from a clear solution at temperature of 80-150^{0}C with 6.38 of Si/Al molar ratio by using Aluminum isopropoxide ($Al(OiPr)_3$) and Ludox LS as alumina and silica source, Tetrametylammonium Hidroxide (TMAOH) and Tetrametylammonium Bromide (TMABr) as first and second organic template, respectively. The products were characterised by X-Ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM) to identify the structure and particle sizes. The image measurements of the particle size record that the average particle sizes of FAU-5, FAU-20 and FAU-35 are 116.46 nm, 169.33 nm and 178.12 nm, respectively. Furthermore, 0.5988 g and 0.6001 g of yields with average particle sizes of 116.46 nm and 43.76 nm can be obtained for FAU-5 (single organic template) and FAU-10 (two organic template, TMABr/TMAOH=0.15) samples, respectively. The smallest average particle size observed is 33.87 nm (FAU-15). The synthesised nanocrystalline zeolite Y was applied for Pb(II) and Cr(III) removal and the results show that the nano crystal samples have very good performance. On FAU-37 at 10 ppm, 30 ppm, 50 ppm and 80 ppm of initial concentration, the adsorption of Pb is 23.56 mg/g, 109.71 mg/g, 181.02 mg/g and 231.46 mg/g, respectively at 216 h and adsorption capacities of Cr are 23.18 mg/g, 84.94 mg/g, 109.75 mg/g and 147.37 mg/g.

Keywords: adsorption capacities, heavy metal, organic template, zeolite Y nanocrystal

1. INTRODUCTION

Nanotechnology has generated much interest in the scientific community, and it has become a very active area of research. Nano size particles such as nanocrystalline zeolites have unique properties relative to conventional micrometer sized zeolite crystals. The reduction of particle size to the nanometer scale leads to substantial changes in properties of zeolite which make them promising materials for many applications. On the other hand, Heavy metal ions are one of the most important pollutants in water, wastewater and any other environmental sources. The fact is that zeolites possess exchangeable ions making them particularly suitable for removing heavy metal ions from industrial effluent waters (Erdem *et al.*, 2004). For instance, by using natural zeolite (clinoplitolite), Inglezakis *et al.* (2007) found that the removal efficiency of lead (Pb^{2+}) could be up to 55%. Also, Basaldella *et al.*, (2007) mention that synthetic zeolite A (LTA) is an effective adsorbent for chromium removal. Nevertheless, nano scale zeolite for heavy metal removal has been less developed (Cundy and Cox, 2004).

It was reported that the particle size of nano zeolite is in the range of 10-1000 nm (Mintova, 2003). It has been developed in terms of hydrothermal condition to produce nano zeolite such as nanozeolite Y (FAU, channel dimension:<111>**12** 7.4 x 7.4 Å ***) and nanozeolite ZSM-5 ({[100]**10** 5.1x5.5 ↔ [010]**10** 5.3 x 5.6} *** (www.iza-stucture.org, retrieve: 10 August 2007). For instance, Holmberg *et al.*, (2003) reported nano zeolite Y synthesis (Si/Al ratio of initial solution of 4.3) with a size of 32-120 nm at a temperature of 100^{0}C. Mintova (2003) recorded that the

particle sizes of 60-70 nm of zeolite Y could be obtained at 90^0C and 45 hours crystallization time with SiO_2/Al_2O_3 ratio of 4.35. Figure 1 shows the framework and channel dimension of zeolite Y (FAU).

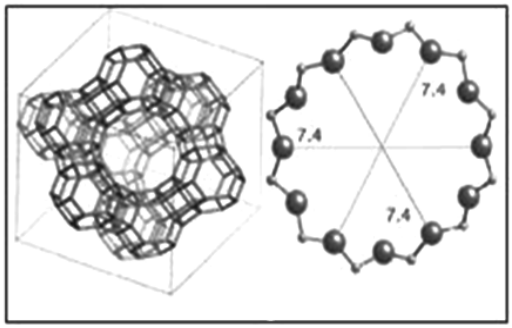

Figure 1. Zeolite Framework and Channel Dimension (Pore Opening) of Faujasite (FAU) (http://www.iza-stucture.org, Retrieved: 10 August 2007)

This article reports experimental studies on synthesis of nanocrystalline zeolite Y following the general procedure described by Holmberg *et al*., (2003) with different molar composition, temperature and synthesis time. Moreover, further study of heavy metal (Pb and Cr cations) removal by using synthesised nanozeolite Y was conducted.

2. METHODS

Synthesis of Nanozeolite Y

Appropriate amounts of distilled water, tetramethylammonium hydroxide solution (TMAOH, 25 wt. % in water, Sigma-Aldrich) and aluminum isopropoxide ($Al(OiPr)_3$, 99.99%, Sigma-Aldrich) were mixed in the polypropylene bottle by vigorous stirring until aluminum source is fully hydrolyzed and the solution is clear. Then for those synthesis solutions which use a second template, tetramethylammonium bromide (TMABr, 98 wt%, Sigma-Aldrich) was added and stirred until completely dissolved. Ludox LS colloidal silica (30 wt. %, Sigma-Aldrich) was then added to complete the synthesis solution. In this study, zeolite Y nanocrystals are synthesized at 80^0C, 120^0C and 150^0C with Si/Al ratio of 6.38 and molar compositions are shown in Table 1. The samples of FAU-5, FAU-8, FAU-9 and FAU-10 were synthesized at 80^0C, the FAU-20 and FAU-25 at 120^0C, and the others at 150^0C.

Table 1. Molar Composition of Zeolite Y Synthesis Solution

Sample	Molar Composition
FAU-5, FAU-35	$12.75SiO_2$: Al_2O_3: $0.05Na_2O$: 2.80 $(TMA)_2O$ (OH^-): $586.96H_2O$
FAU-8, FAU-9, FAU-10, FAU-36, FAU-37, FAU-38, FAU-39, FAU-40	$12.75SiO_2$:Al_2O_3:$0.05Na_2O$:$2.80(TMA)_2O(OH^-)$:$0.97(TMA)2O(Br^-)$: $586.96H_2O$
FAU-41, FAU-42, FAU-43, FAU-44, FAU-45	$12.75SiO_2$:Al_2O_3:$0.05Na_2O$:$2.80(TMA)_2(OH^-)$:$2.11(TMA)2O(Br^-)$: $586.96H_2O$
FAU-20	$12.75SiO_2$: Al_2O_3: $0.05Na_2O$: 4.2 $(TMA)_2O$ (OH^-): $629.51H_2O$
FAU-25	$12.75SiO_2$:Al_2O_3:$0.05Na_2O$:$4.2(TMA)_2O(OH^-)$:$4.87(TMA)2O(Br^-)$: $629.51H_2O$

Next, the bottle was sealed tightly and aged for 2 days at room temperature with vigorous stirring. Then, the solution was put in a stainless steel autoclave (100 mL) for crystallisation at temperatures of 80^0C, 120^0C 150^0C in an oven. After a certain synthesis time, the product was separated from solution in a centrifuge with 4700 rpm for 3 hours (Heraeus Multifuge 1s Kendro). Repeated rinsing and centrifugation for 3 times were done to purify the product and finally filtration was employed to obtain the nanocrystalline zeolite Y product. After that, the product was dried at 120^0C for 24 hours and then calcined at a temperature of 550^0C for 3 hours.

Characterization of Nanozeolite Y

X-Ray Diffraction (Siemen D501 XRD) and Scanning Electron Microscopy (SEM) were used to identify the synthesised product (structure and size). The specimens were mounted in standard plastic holder. The XRD patterns were recorded using Cu-radiation

(40kV, 30mA) over a two–theta angular range of 5-70^0 at 0.04^0/2s. The measured diffraction patterns were interpreted by using the PDF Database sets 1-52, Jade 6.0 and CSM search/match software. SEM (Philips XL30) was used to obtain a visual image of the samples with magnification in range of 30,000 to 75,000. The measurements of the particle size are done by using the software of Image pro plus version 4.1.0.0 onto the SEM images.

Heavy Metal Removal

For the adsorption study, 10, 25 and 50 mg of zeolites were added into 125 mL solution of the heavy metal (Pb^{2+} and Cr^{3+}) with varying concentrations of 10-80 ppm. Controlling of pH was done by using NaOH 1M and H_2SO_4 1M. A shaker (Certomat R Shaker from B. Braun) at 100 rpm and temperatures of 30^{0}C and 45^{0}C were adopted. Sample (1 mL) was taken periodically at different times, diluted and then measured using Atomic Adsorption Spectrometer (SpectrAA110, Varian) at λ = 217.0 nm for lead and λ=357.9 nm for chromium. Adsorption capacity of the zeolite at equilibrium (Q_e, mg/g) was calculated by using the following equation (Syaifullah *et al.*, 2009):

$$Qe = \frac{(C_0V_0 - C_eV_e)}{m}$$

Where C_o and C_e are initial and final sample concentrations (mg/L) respectively, V_0 and V_e are the initial and final volume of the sample solution and m is the weight of adsorbent added.

3. RESULTS AND DISCUSSION

Synthesis of Nanocrystalline Zeolite Y

In this study, zeolite Y nanocrystals were synthesized at 80^{0}C, 120^{0}C and 150^{0}C with Si/Al ratio of 6.38. According to 2Θ^0 peaks of XRD patterns (Figure 2), not only nanozeolite Y are present in the sample but also zeolite A nanocrystals (LTA) (PDF card of #14-298 Jade 6.0 match software). The exact composition or the percentage of zeolite Y and zeolite A nanocrystal are not detected (Quality XRD examination). However, XRD examination gives the main phase of zeolite Y or Faujasite (FAU) sample nanocrystals (well corresponding with PDF card of #38-238 Jade 6.0 match software). The presence of LTA crystals can also be seen from SEM images (Figure 3) where the presence of cubic crystals morphology are clearly shown with the particle size which are larger than others. The reason is the higher ratio of sodium to alumina which enables the formation of LTA. Schoeman *et al.* (1994) have found that 100% of zeolite Y yield could be obtained when the molar ratio of Na_2O/Al_2O_3 is 0.044, whereas at Na_2O/Al_2O_3 ratio of 0.077, 75% of zeolite Y and 25% of zeolite A would be obtained. In this investigation, the Na_2O/Al_2O_3 ratio is 0.05. Therefore, it is possible that zeolite A would be favoured to form resulting in two kinds of zeolite crystal in the samples. However, at the 0.05 of Na_2O/Al_2O_3 ratio zeolite Y is the main phase in the samples.

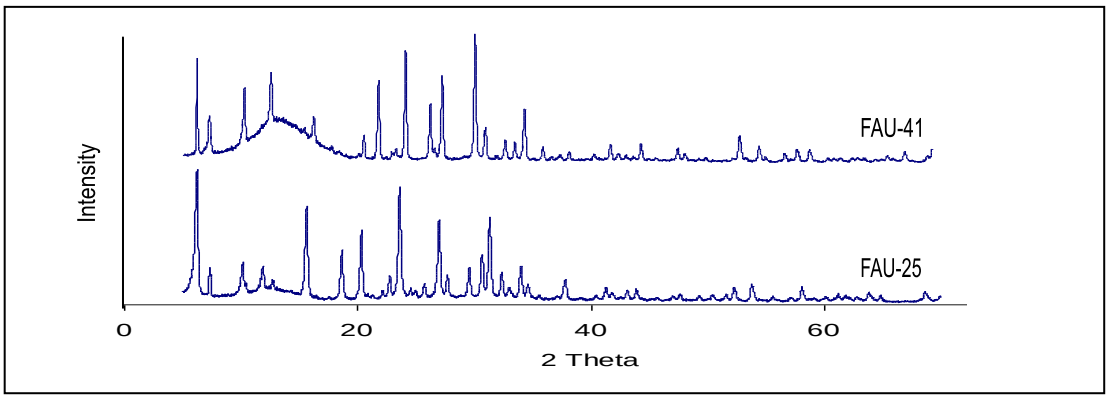

Figure 2. XRD Patterns of FAU-25 and FAU-41

From Figure 3, it is clearly seen that there are two morphologies of crystals. The cubic morphology of the crystal is LTA type of the zeolite and the other is zeolite Y crystal. It is also seen that LTA crystals have bigger particle sizes than zeolite Y. Based on the measurement of the particle sizes of the samples LTA has crystal size in range of 200-300 nm. It means, LTA crystal is growing up much faster than zeolite Y. This result is similar to the observation reported by Schoeman *et al.* (1994).

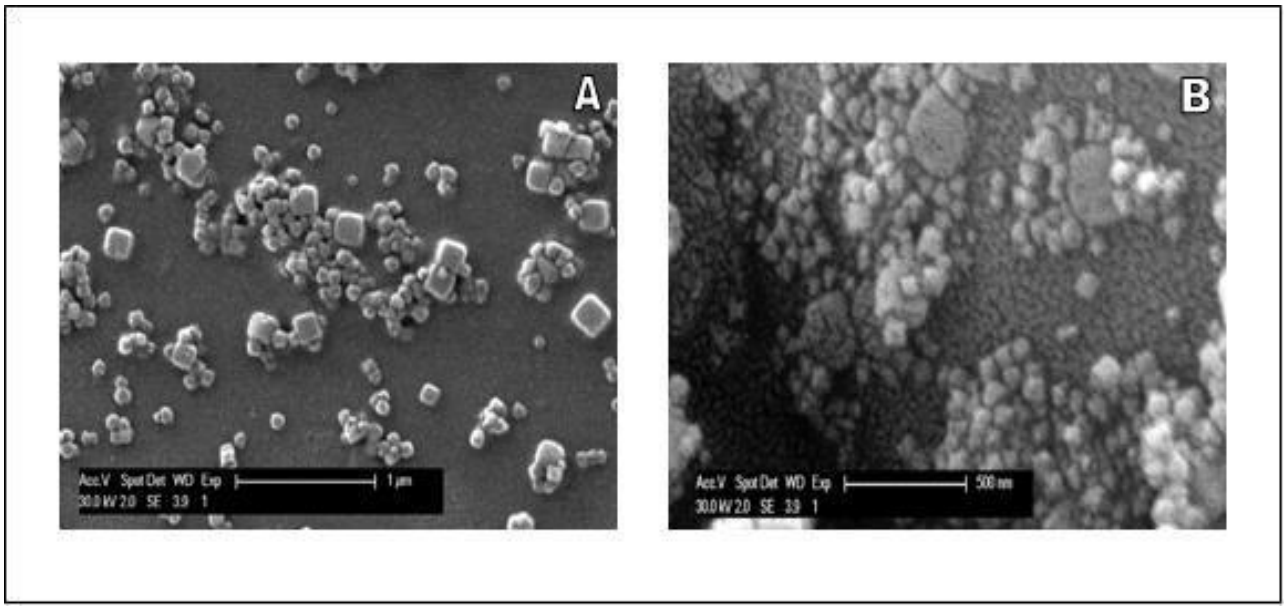

Figure 3. SEM Images which Contain FAU and LTA Nanocrystal, FAU-25 (A) and FAU-41 (B)

Comparing with zeolite A (LTA), zeolite Y nanocrystals have smaller average particle. Based on the SEM images, zeolite Y crystals are not in cubic morphology but octahedral, which can be seen from the samples of FAU-5, FAU-20 and FAU-35. The products were synthesized with single organic template (TMAOH) for 5 day at temperature of 80^0C, 120^0C and 150^0C, respectively. The image measurements of the particle size record that the average particle sizes of FAU-5, FAU-20 and FAU-35 are 116.46 nm, 169.33 nm and 178.12 nm, respectively. Figure 4 shows XRD patterns and SEM images of the three samples of zeolite Y nanocrystal.

Effect of Crystallization Time and Temperature

Similar to zeolite A, crystallization time and temperature also affect crystallization process of zeolite Y synthesis. In general, a longer time and higher temperature will produce higher product yield because time and temperature will initiate more nucleation and crystallization stage of zeolite in the synthesis process. For those samples FAU-41, FAU-42, FAU-43, FAU-44 and FAU-45, which were synthesized at 150^0C at time of 1, 2, 3, 4, and 5 days, respectively, the yields are 0.0655 g, 0.1028 g, 0.1799 g, 0.6508 g and 0.7998 g, respectively, showing an increasing trend with increasing crystallization time.

Correlation between temperature and yield can be seen from Figure 5. The samples FAU-8, FAU-9 and FAU-10 were synthesized at 80^0C with TMABr/TMAOH ratio of 0.15. On the other hand, FAU-36, FAU-37, FAU-38, FAU-39 and FAU-40 were synthesized at 150^0C with the same TMABr/TMAOH ratio. The synthesized samples at 120^0C are not compared here due to the different of TMABr/TMAOH ratio and it will be discussed later. Figure 5 shows that the zeolite-Y product could be obtained after 1 day crystallization time at 150^0C (FAU-36 and FAU-37) while at

80^0C the product could only be obtained after 3 days. At crystallization time of 3, 4 and 5 days, 0.1422 g, 0.5763 g and 0.6001 g yields were obtained at 80^0C, respectively. Moreover 0.3722 g, 0.6344 g and 0.6403 g yields were obtained at 150^0C at the same time. Similar results were also seen with TMABr/TMAOH ratio of 0.325. At 3, 4 and 5 days, the 0.1585 g, 0.6169 g and 0.8514 g of the FAU samples can be obtained at 80^0C followed by 0.1799 g, 0.6508 g and 0.85.14 g at 150^0C. It can be concluded that the FAU yields are increased with the increase of temperature at all the synthesis time.

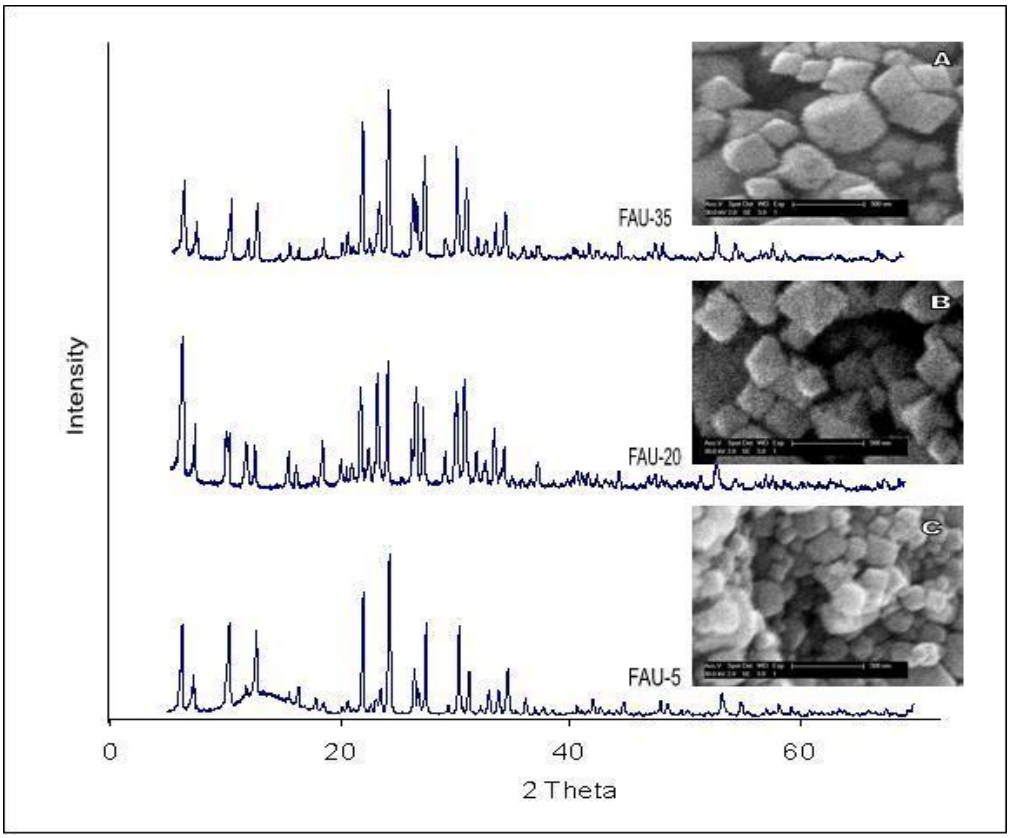

Figure 4. XRD Patterns and SEM Images of FAU Samples at 5 Day Crystallization Time and Single Organic Template

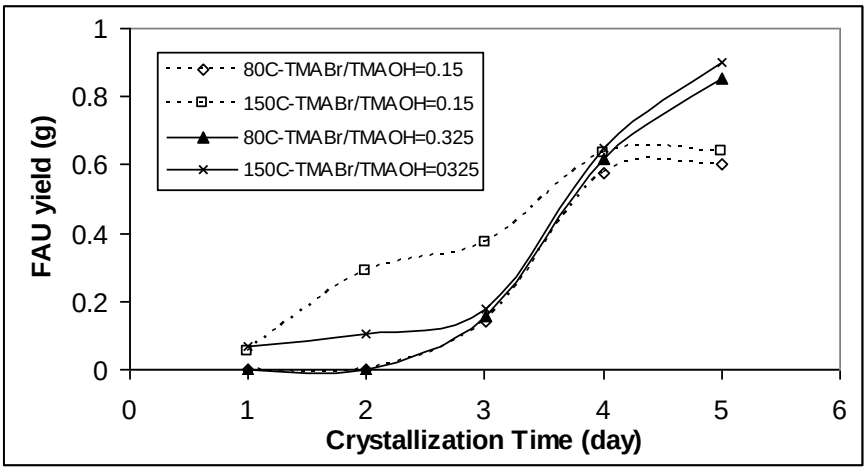

Figure 5. Effects of Crystallization Time and Temperature on Zeolite Y Nanocrystal Yield with Two Organic Templates

Meanwhile, the synthesized zeolite-Y yields by using single organic template can be seen in Table 2. It is shown that the FAU yields increase from temperature of 80^0C to 120^0C and from 80^0C to 150^0C at all of the time. However, correlation between temperature and yield seems to have a small deviation particularly from temperature of 120C to 150^0C where decreasing of yield can be found for all cases. The likely reason is the higher amount of organic template of TMAOH in solution than that at 150^0C. At 120^0C the amount of TMAOH used is 30 g while 20 g was used at 150^0C. Rakoczy and Traa (2003) reported that the high concentration of TMAOH in the synthesis mixture substantially increases the concentration of the mineralizing agent OH^-. In this way, the solubility of silicon and aluminum precursor is increased by the higher ionic strength and the necessary degree of oversaturation is reached. This condition strongly promoted the nucleation and crystallization process at a certain time.

Table 2. FAU Yields with Single Organic Template at Various Temperatures

Temperature (^{0}C)	FAU Yield (g)				
	1 day	2 day	3 day	4 day	5 day
80	0	0	0.0965	0.4273	0.5988
120	0	0.1013	0.1766	0.6832	0.9782
150	0	0.0786	0.1203	0.5023	0.6024

From Table 2 it can also be seen that no yield can be obtained within 2 day crystallization time at temperature of 80^0C. It is different compared with those at 120^0C and 150^0C. This fact means that the increase of crystallization temperature influence the acceleration of crystallization process.

Furthermore, time and temperature also directly affect the average particle size. The results show that the average particle size is increased by increasing crystallization time. For instance, it can be seen that samples of FAU-41, FAU-42, FAU-43 and FAU-45 which were synthesized at 150^0C with initial TMABr/TMAOH of 0.325 have the average particle size of 37.27 nm, 51.59 nm, 75.82 nm, 91.81 nm and 122.92 nm, respectively. Moreover, other examples FAU-5, FAU-20 and FAU-35 which were synthesized at temperature of 80^0C, 120^0C and 150^0C for 5 days have average particle size of 116.46 nm, 169.33 nm and 178.12 nm, respectively. It can be concluded that the increase of time and temperature will increase the particle size.

Effect of Second Organic Template of TMABr

It has been reported that adding TMABr as a second organic template can reduce the particle size while simultaneously increase zeolite Y yields (Holmberg *et al.*, 2003). XRD patterns and SEM images of the synthesized zeolite-Y nanocrystals with one and two organic templates are shown in Figure 6.

In this investigation, two samples of FAU-5 and FAU-10 were synthesized at 80^0C and 5-days crystallization time. FAU-5 sample is synthesized by using single organic template (TMAOH) and the other one FAU-10 was synthesized by addition of the second organic template of TMABr with 0.15 initial ratio of TMABr/TMAOH. Based on the examination and image measurement, 0.5988 g and 0.6001 g of yield with average particle sizes of 116.46 nm and 43.76 nm can be obtained for FAU-5 and FAU-10 samples, respectively. According to this result, it can be seen that the second organic template of TMABr improves slightly the yield but significantly reduce the particle size by 62.42 %. Further, if FAU-10 is compared with FAU-15 which have also the same synthesis conditions but with different of TMABr/TMAOH ratio (0.325), then it is found that the yield increases from 0.6001 g to 0.8514 or enhanced by 41.88 % and the

average particle size is decreased from 43.76 nm to 33.87 nm or 29.2 % lower. Moreover, comparison between FAU-5 and FAU-15, 42.18 % of increasing yield can be obtained and the average particle size is decreased by 70.92 %.

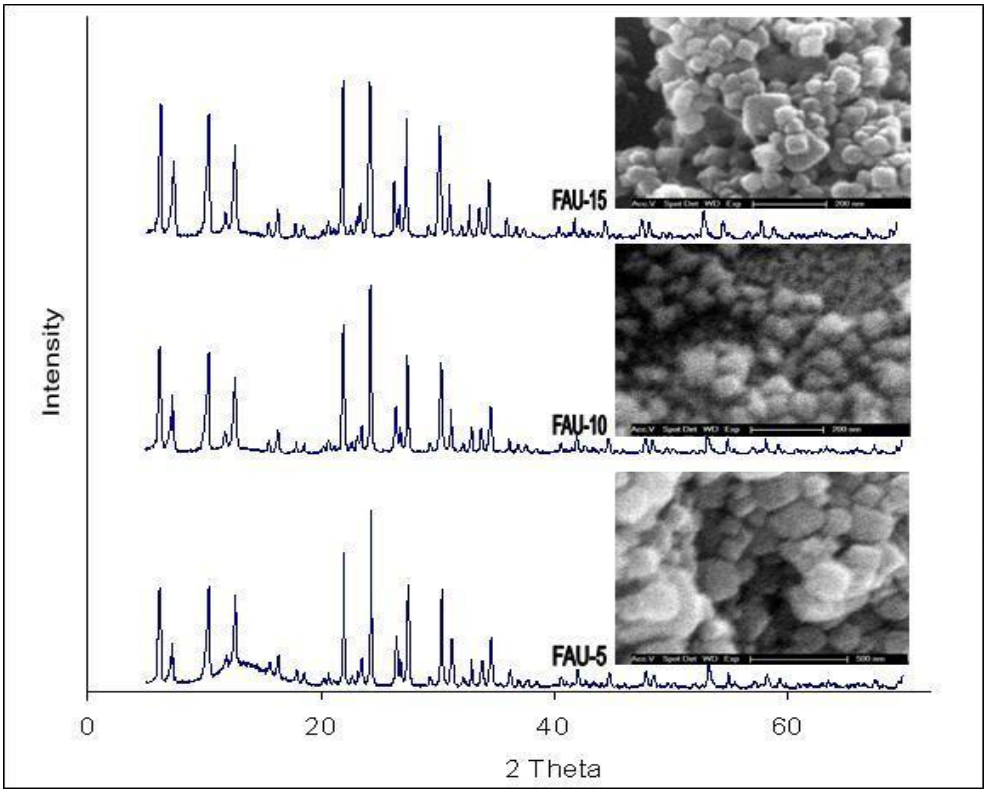

Figure 6. XRD Patterns and SEM Images of Zeolite Y Nanocrystals with One and Two Organic Templates

Chromium and Lead Removal

Synthesized zeolite Y (FAU) was used as an adsorbent in the study of heavy metal removal. The experimental result shows that the synthesized zeolite Y nanocrystals have good performance in heavy metal removal. In this research, two FAU samples were used in adsorption of heavy metals. They are FAU-35 and FAU-37. Sample of FAU-35 was synthesized at 150^0C with 5-day crystallization time and using single organic template while FAU-37 was synthesized at the same temperature by using second organic template with crystallization time of 2 days. Both FAU-35 and FAU-37 have initial Si/Al synthesis solution of 6.38. The average particle sizes of FAU-35 and FAU-37 are 178.12 nm and 108.14 nm, respectively. Some factors influencing adsorption such as contact time, temperature, initial concentration and pH will be discussed further.

Effect of Time and Initial Heavy Metal Concentration

Figure 7 shows a correlation among contact time, initial heavy metal concentration and adsorption capacity (Qt) at 30^0C by using FAU-37 sample as adsorbent. It can be seen that adsorption capacities increase by increasing contact time. On average, the adsorption equilibrium can be reached after 24 h. No significant change of adsorption capacity is observed after 24 h. At concentration of 50 ppm, adsorption capacity of Pb ion increases from 145.25 mg/g at 24 hour to 181.02 mg/g at 216 hour. Another example is at 80 ppm, adsorption capacity of Pb increases from 174.24 mg/g to 213.46 mg/g. Similar trends

can also be found on Cr ion removal as shown in Figure 7B. For the same treatment time, the adsorption capacity of Pb ion is higher than Cr ion.

Figures 7 also show the effect of initial adsorbate concentration on adsorption capacity. For instance, the adsorption of Pb at 10 ppm, 30 ppm, 50 ppm and 80 ppm are 23.56 mg/g, 109.71 mg/g, 181.02 mg/g and 231.46 mg/g, respectively at 216h (Fugure 7A). At the same treatment time and initial concentration, adsorption capacities of Cr are 23.18 mg/g, 84.94 mg/g, 109.75 mg/g and 147.37 mg/g (Figure 7B). From the curves it can also be concluded that the lower initial concentration of heavy metal the faster equilibrium could be reached.

Effect of Temperature

The effect of temperature on Pb and Cr removal by using FAU zeolite is shown in Figure 8. It can be seen that adsorption of both Pb and Cr increases by increasing temperature. For example at contact time 216 h, adsorption capacities of Pb at 30^0C and 45^0C are 181.02 mg/g and 219.24 mg/g or increased by 21.11 %. At the same time, adsorption capacities of Cr are 109.75 mg/g and 138.02 mg/g at 30^0C and 45^0C, respectively, or increased by 25.76 %. The increase of adsorption capacity by increasing temperature indicates that diffusion of Pb and Cr cation on zeolite Y (FAU) is endothermic reaction where the increase of temperature results in the increase of active surface area and pore volume which increase adsorbent ability to adsorb the heavy metals.

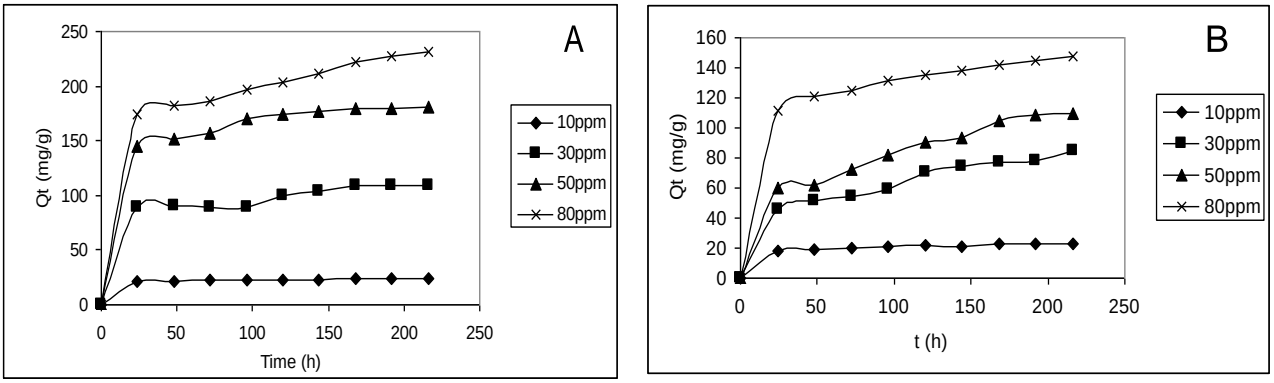

Figure 7. Effect of Treatment Time and Initial Concentration on Adsorption Capacities, Pb^{2+} (A), Cr^{3+} (B)

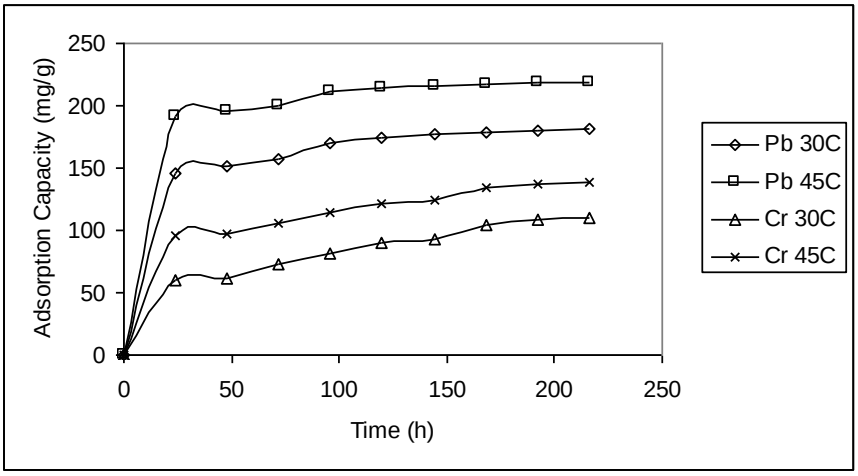

Figure 8. Effect of Treatment Temperature on Adsorption Capacities of Pb and Cr by Using FAU-37 Sample

Effect of pH

The pH effect study on heavy metal removal is carried out on FAU-35. As seen at Figure 9, the adsorption capacity of heavy metal tends to increase by increasing the pH due to the increase of hydroxyl concentration in the solution which produces surface precipitation for heavy metal cation on the adsorbent. From Figure 9A, it can be seen that at 24-72 h, adsorption capacity of Pb increases following the order of pH-4.03>pH-6.01>pH-5.02>pH-3.01 and at 92-216 h, following the order of pH-6.01 > pH-5.02 > pH-4.03 > pH-3.01. For instance at 216 h, adsorption capacities for pH of 3.01, 4.03, 5.02 and 6.01 are 165.39 mg/g, 170.37 mg/g, 204.25 and 214.93 mg/g, respectively. Figure 9B shows that adsorption capacities of Cr increase by increasing the pH. For instance, adsorption of Cr at pH of 3.01, 4.03, 5.02 and 6.01 is 59.25 mg/g, 83.81 mg/g, 106.29 mg/g and 129.64 mg/g at 24 h contact time.

This study also presents the comparison of adsorption capacity with natural zeolite (NTZ). The used NTZ is clinoplitolite type material with 75 micron of particle size. On the test of heavy metal removal together with the synthesized nanocrystalline zeolites, the adsorption capacity of Pb follows the order of zeolite A > zeolite Y > natural zeolite > ZSM-5 > silicate-1 while for Cr the order is zeolite A > zeolite Y >ZSM-5 > natural zeolite > silicate-1. For instance, adsorption capacities of Pb at 216 h are 282.02 mg/g, 264.63 mg/g, 148.29 mg/g, 128.64 mg/g and 99.94 mg/g for zeolite A, zeolite Y, natural zeolite, ZSM-5 and silicate-1, respectively. With the same contact time, the adsorption capacities of Cr are 120.45 mg/g, 107.69 mg/g, 98.28 mg/g, 85.65 mg/g and 69.46 mg/g for zeolite A, zeolite Y, ZSM-5, natural zeolite and silicate-1, respectively (Syaifullah, 2008). Better adsorption capacities of nanozeolite than natural zeolite are affected by the particle size and the composition of zeolite. Dynamic adsorption of Pb and Cr on different types of adsorbent at 30^0C with initial concentration of heavy metal of 50 ppm is shown in Figure 10.

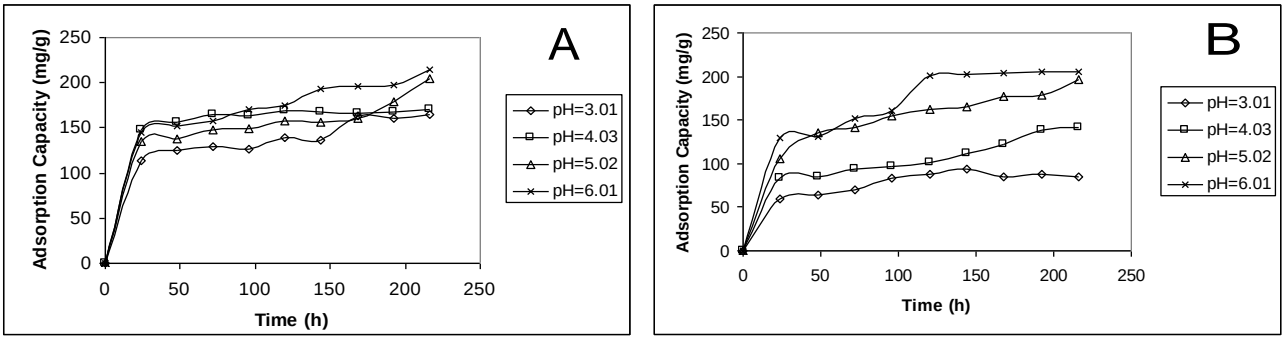

Figure 9. Effect of pH on Adsorption Capacity, Pb^{2+} (A), Cr^{3+} (B)

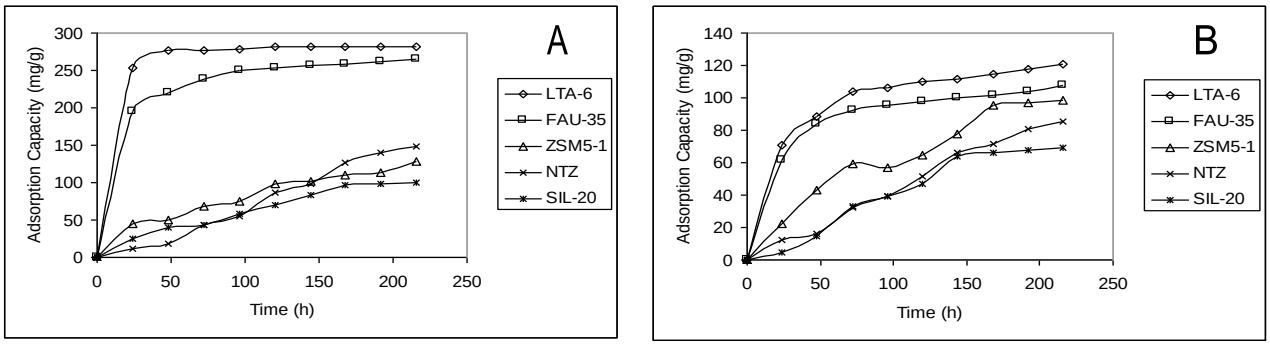

Figure 10. Dynamic Adsorption with Different Adsorbent at 30^0C and 50 ppm of Initial Concentration, Pb^{2+} (A), Cr^{3+} (B)

4. CONCLUSIONS

Zeolite Y nanocrystal can be synthesized at temperature of 80-150^{0}C with 6.38 of Si/Al molar ratio. The zeolite yields increase with increasing time and temperature. Time and temperature also influence the particle size. The image measurements of the particle size record that the average particle sizes of FAU-5, FAU-20 and FAU-35 are 116.46 nm, 169.33 nm and 178.12 nm, respectively. Further, 0.5988 g and 0.6001 g of yields with average particle sizes of 116.46 nm and 43.76 nm can be obtained for FAU-5 (single organic template) and FAU-10 (two organic template, TMABr/TMAOH = 0.15) samples, respectively. It is seen that the second organic template of TMABr improves the yield slightly but significantly reduces the particle size by up to 62.42 %. The smallest average particle size observed is 33.87 nm (FAU-15). It is found that adsorption capacities increase with increasing contact time, temperature, initial of heavy metal ions, and pH. The increase in adsorption capacity by temperature indicates that diffusion of Pb and Cr cation on zeolite nanocrystal of FAU-37 is endothermic reaction. Adsorption capacities of Pb and Cr are increased with increasing initial concentration of heavy metal ion. On FAU-37 at 10 ppm, 30 ppm, 50 ppm and 80 ppm of initial concentration, the adsorption of Pb is 23.56 mg/g, 109.71 mg/g, 181.02 mg/g and 231.46 mg/g, respectively at 214h and adsorption capacities of Cr are 23.18 mg/g, 84.94 mg/g, 109.75 mg/g and 147.37 mg/g.

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