



Heavy Metal Removal from Wastewater Using Synthesized Silicate-1 Nanocrystal

Syaifullah Muhammad^{1,2}, Edy Syahputra^{2,3}, Nasrullah¹, Suraiya¹
Shaobin Wang² and Moses O. Tade²

¹ Chemical Engineering Department, Faculty of Engineering,
Syiah Kuala University, Darussalam, Banda Aceh

² Curtin University of Technology Western Australia

³ Department of Chemical Engineering, Riau University, Pekanbaru28293, Indonesia
E-mail: s.muhammad@postgrad.curtin.edu.au

Abstract

Particle size reduction of zeolite to the nanometer scale leads to substantial changes in the properties of zeolite which make them promising materials for many applications including adsorption. Zeolite silicate-1 Nanocrystal was synthesized at temperatures of 80°C, 120°C and 150°C by adding tetrapropylammonium hydroxide (TPAOH) into silica sources. The synthesis mixtures are 2TPAOH: 0.15Na₂O: 4.5Si: 382H₂O: 51EtOH (TEOS as silica source) and 2TPAOH: 0.15Na₂O: 6SiO₂: 532H₂O: 51EtOH (Ludox LS as silica source). X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to characterize the synthesised products. The nanosilicate-1 particle size were obtained in range of 119 nm – 1678 nm. This research also confirmed that TEOS can make smaller particle size up to 36.43 % than Ludox LS due to an average hydrodynamic diameter of 4 nm of TEOS smaller than Ludox LS of 15-19 nm. In the heavy metal adsorption study, it was found that the adsorption capacity indicated by Q_{max} (Langmuir) and K_F (Freundlich) shows higher Pb²⁺ adsorption than Cr³⁺. The maximum adsorption capacities of Pb and Cr at 30°C are 131.58 mg/g and 129.87 mg/g, respectively. Further, it can also be seen that the K_L values in the Langmuir isotherm indicate the higher selectivity of Pb on silicate-1 zeolite than Cr.

Keywords : Adsorption capacity, Heavy metal, Isotherm, Silicate-1 nanocrystal

1. Introduction

There are three steps in nanozeolite synthesis i.e. induction, nucleation and crystallization. Nucleation is the step where germ nuclei are obtained from very small aggregates of precursor and become larger with the time. Crystallization is initiated with engaging the germ nuclei from the nucleation step and other components of the reaction mixture. This process is influenced by several factors which can be modified during the synthesis procedure. These factors are the presence of cations in the reaction solution, OH⁻ concentration, SiO₂/Al₂O₃ ratio, H₂O content, temperature, pH, time, aging, stirring of the reaction mixture, order of mixing and other factors (Malherbe, 2007).

Tosheva and Valtchev (2005) reviewed that nanozeolite crystals can be synthesized from clear solution or gel system and also by confined space synthesis method. Zeolite nanocrystals are usually synthesized under hydrothermal condition using clear aluminosilicate solution, usually in the presence of organic compounds as templates such as tetramethyl- ammonium (TMA) and tetrapropyl- ammonium (TPA) (Zhan, et al. 2001). Further, Cundy and Cox

(2004) reported aluminosilicate zeolites synthesized under hydrothermal condition from reactive gels in alkaline media at temperature of about 80°C and 200°C and most high Si/Al ratio of zeolites (>10) are synthesized using organic templates, which have to be removed from the zeolites structure by calcinations. However, Corkery and Ninham (1997) synthesized nano crystal of silicate-1 at low temperature of 35°C and 1 atmosphere pressure despite very long synthesis time of about 40 months. According to this report, precipitated silica nanocrystal entered to the solution through slow depolymerization.

Many other researchers reported the success of zeolite nanocrystal synthesis. The main concept of nanozeolite synthesis is to terminate the synthesis process while the zeolite crystals are still in the nano size range and to prohibit further crystal growth. Base on this concept, nanozeolites should be synthesized at low temperatures and ambient pressure. Unfortunately, low temperature in this process will result in low product yield and long synthesis time. However, Song et al. (2005) reported a method achieving high yield for nano-crystalline zeolite synthesis by periodically removing nanocrystal from synthesis

solution and recycling unused chemicals including organic template.

This article reports experimental studies on synthesis of nanocrystalline zeolite silicate-1. Moreover, further study of heavy metal (Pb and Cr cations) removal by using synthesised nanozeolite silicate-1 was conducted.

2. Methods

2.1 Synthesis of Nanozeolite Silicate-1

Synthesis solution was made by adding tetrapropylammonium hydroxide (TPAOH, 1 M solution in water, Sigma Aldrich) into silica sources (Ludox LS or TEOS) and followed by strong mixing. The solution was then added by distilled water and ethanol (99.99% analytical reagent). If the silica source is TEOS (tetraethyl orthosilicate, 99.99% Sigma-Aldrich), the synthesis solution was shaken for 12 hours on a shaker (Certomat R Shaker from B. Braun). The synthesis mixtures with molar composition 2TPAOH: 0.15Na₂O: 4.5Si: 382H₂O: 51EtOH (TEOS as silica source) and 2TPAOH: 0.15Na₂O: 6SiO₂: 532H₂O: 51EtOH (Ludox LS as silica source, 30 wt.%, Sigma-Aldrich) were obtained. In the next step, the synthesis mixture was transferred to the crystallization vessel and heated in an oven at temperatures of 80°C, 120°C and 150°C. After a certain synthesis time, the product was separated from mother liquor by centrifuge (Heraeus Multifuge 1s Kendro) at 4700 rpm for 2 hours. The solid phase was then rinsed by using ultra pure water up to 5 times and filtered. After that, the product was dried at 120 °C for 24 hours and then calcined at temperature of 600°C for 3 hours. The temperatures of 80°C and 120°C were used for two stages synthesis period with varying of temperatures where 3, 4 and 5 days synthesis time were used at 80°C as the first stage and another 1 day was used at 120°C as the second stage.

2.2 Characterization of Nanosilicate-1

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° at 0.04°/2s. The measured diffraction patterns were interpreted by using the PDF Database sets

1-52, Jade6.0 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 conducted by using the software of Image pro plus version 4.1.0.0 onto the SEM images.

2.3 Heavy Metal Removal

For the adsorption study, 10, 25 and 50 mg of zeolites were added into 125 ml synthetic wastewater solution of the heavy metal (Pb²⁺ and Cr³⁺) with varying concentrations of 10-80 mg/L. Controlling of pH was done by using NaOH 1M and H₂SO₄ 1M. A shaker (Certomat R Shaker from B. Braun) at 100 rpm and temperatures of 30 °C and 45°C were adopted. Sample (1 ml) was taken periodically at different times, diluted and then measured using Atomic Adsorption Spectrometer (AAS, SpectrAA110, Varian) at λ = 217.0 nm for lead and λ=357.9 nm for chromium. AAS checking is started with preparing a standard solution of Pb(NO₃)₂ and Cr(NO₃)₃ with concentration in range of 1-30 mg/L for lead and 1-15 mg/L for chromium. The standard solution is then checked by AAS to obtain calibration curve which indicating correlation between concentration and AAS absorbance. The linear equation of calibration curve is used to convert AAS absorbance into samples concentration.

2.4 Adsorption Capacity

Adsorption capacity of the zeolite at equilibrium (Q_e , mg/g) was calculated by using the following equation (Eq.1)

$$Q_e = \frac{(C_0 V_0 - C_e V_e)}{m} \quad (1)$$

Where C_0 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 (Wang & Zhu, 2006).

The Langmuir isotherm model uses the following linear form equation (Eq.2)

$$\frac{C_e}{Q_e} = \frac{1}{K L Q_{\max}} + \frac{1}{Q_{\max}} C_e \quad (2)$$

Where Q_e is adsorption capacity at equilibrium (mg/g), Q_{\max} is the maximum adsorption capacity (mg/g), C_e (mg/l) is the

solution concentration at equilibrium, and K_L is the Langmuir constant (l/mg) (Zhang & Bai, 2003). The linear form equation of the Freundlich isotherm is listed as follows (Eq.3)

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where Q_e is adsorption capacity at equilibrium (mg/g), C_e is the concentration at equilibrium (mg/l), K_F and n are the Freundlich constants. The value of K_F can be taken as a relative indicator of adsorption capacity while $1/n$ is indicative of the energy or intensity of reaction. The values of Q_{max} , K_L (Eq.2), K_F and n (Eq.3) are calculated from the intercepts and slopes of the equations plots.

The adsorption kinetics of Pb^{2+} and Cr^{3+} was determined by using the first and second order equations, respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (5)$$

Where Q_e and Q_t are adsorbate per mass unit of adsorbent (mg/g) at equilibrium and specific times, k_1 (h^{-1}) and k_2 (g/mg h) are the rate constants of the first and second order kinetics (Juang et al, 2000; Chang & Juang, 2005).

3. Results and Discussion

3.1 Synthesis of Nanozeolite Silicate-1

In this research, it was found that synthesis of silicate-1 nanocrystal takes longer crystallization time than crystalline zeolite A and Y. The silicate-1 nanocrystal product can be obtained after 5-day crystallization while Zeolite A and Y can be synthesized within 1-2 days (Tosheva & Valtchev, 2005). In this report abbreviation SIL is used to describe silicate-1 nanocrystal products such as SIL-1, SIL-2, SIL-3 etc. The focuses on the effect of time, temperature (80°C, 120°C and 150°C), silica source (Ludox LS and TEOS) and two-stage synthesis will be elaborated further.

Effect of crystallization time and temperature

It is well known that synthesis time and temperature directly affect the crystalli-

zation process. Higher product yield and bigger particle size will be obtained at longer synthesis time and higher temperature. This tendency could be found based on samples of SIL-9, SIL-10, SIL-11 and SIL-12 which were synthesised at 120°C by using Ludox LS as silica source. XRD patterns of the samples are shown in Figure 1 (well corresponding with PDF card of #44-696 Jade 6.0 match software).

The yields of SIL-9, SIL-10, SIL-11 and SIL-12 are 0.4065 g, 0.6263 g, 0.8028 g and 0.9957 g, respectively, with the particle sizes of 119.94 nm, 276.68 nm, 992.17 nm and 1678.54 nm. It can be seen that increase of crystallization time increases silicate-1 nanocrystal yields. And also similar trend regarding the average particle size with crystallization time can be seen from Figure 2, which shows the SEM image of silicate-1 nanocrystal at 30,000 magnifications.

Further, the effect of temperature on synthesis can also be seen in Figure 2. At 9-day crystallization the silicate-1 product weights are 0.9077 g, 0.9957 g and 0.5267 g for temperature of 80°C, 120°C and 150°C, respectively. Similar trend can also be found for crystallization time less than 9 days. At temperature of 150°C it seems the products are lower than others. The reason is due to the less amounts of reactants such as TPAOH, Ludox LS, distilled water and ethanol compared with those to other temperatures. At temperature of 150°C only half amount of the reactants were used compared with 80°C and 120°C. The less reactants in the synthesis mixture result in the lower products of silicate-1 crystals. However, if the yield is calculated relative to the amount of used silica, it will get yields of 30.26 %, 33.19 % and 35.11 % for 80°C, 120°C and 150°C, respectively, after 9 day, which means an increasing yield with increasing temperature. Other information can be retrieved from Figure 3 is that no silicate-1 nanocrystal yield can be obtained at 80°C and 5-day crystallization time while 0.4065 g (13.55%) and 0.2155 g (14.37%) yields could be obtained at 120°C and 150°C, respectively. The yields of silicate-1 obtained in this experiment are quite low. The highest percentage of yield based on silica used is 35.11 % which is much lower than 61.45 % reported by Li et al (2000). The reason is probably the difference of molar composition of synthesis solution. Li et al (2000) used the molar composition of 9TPAOH: 0.13Na₂O: 25SiO₂: 595H₂O: 100EtOH while this experiment used the

molar composition of 2TPAOH: 0.15Na₂O: 6SiO₂: 532H₂O: 51EtOH.

Effect of silica sources

The use of Ludox LS and TEOS as silica sources affects yield and average particle size. It is found that by using TEOS, the nucleation is faster and the particle size is

smaller (Persson et al, 1994). However, in this research it is found that the yields of silicate-1 crystal are lower if Ludox LS was used as silica source. For instance, SIL-13 (TEOS as silica source) has 0.2169g yield or 16.07 % based on Si used. This is lower than SIL-9 (Ludox LS as silica source) which has 0.4065g or 29.46 % yield.

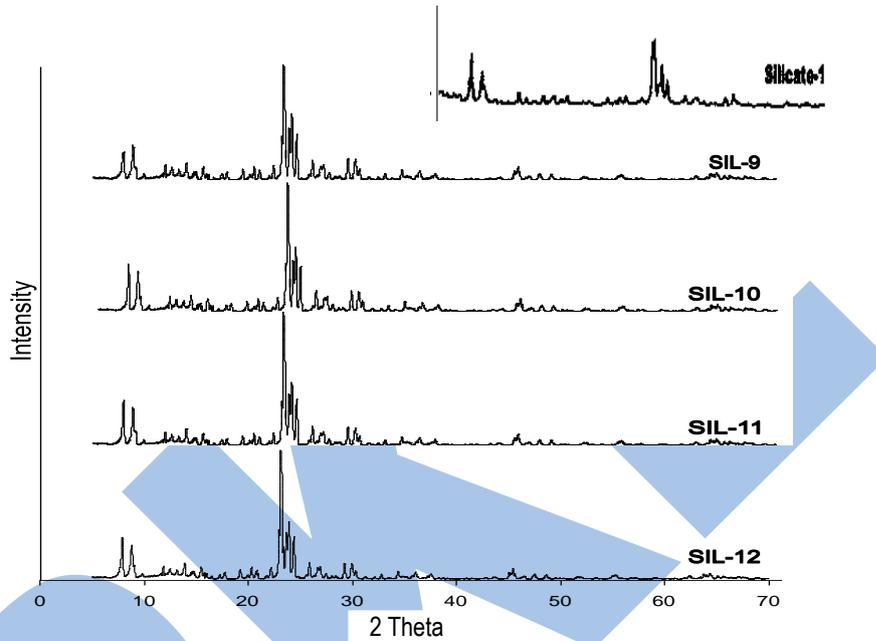


Figure 1. XRD patterns of silicate-1 crystals with insert of silicate-1 XRD pattern standard

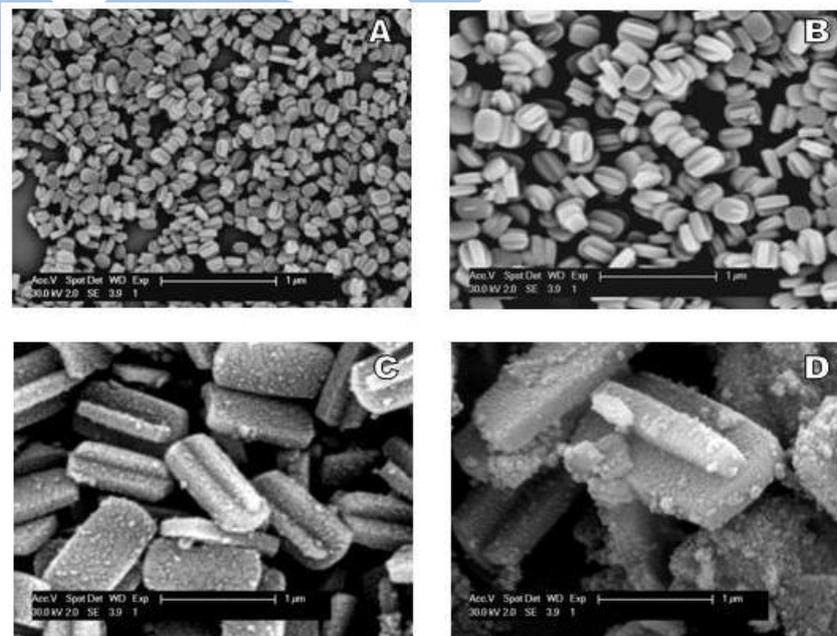


Figure 2. SEM images of silicate-1 nanocrystal at 120°C, SIL-9, 5 days (A), SIL-10, 6 days (B), SIL-11, 7 days (C) and SIL-12, 9 days (D)

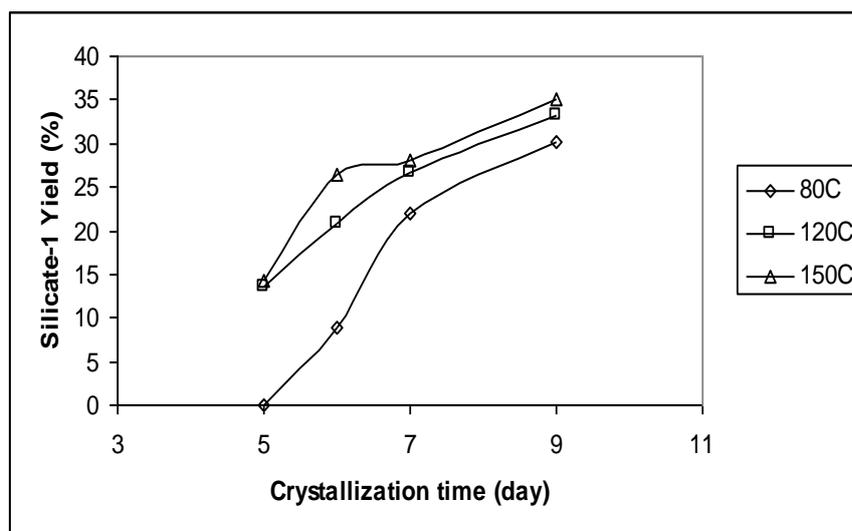


Figure 3. Correlation of crystallization time, temperature and silicate-1 yield

Similar results can also be found at SIL-2 (Ludox LS) and SIL-6 (TEOS) which were synthesised for 6 days at 80°C and they have 19.38% and 18.19% yields based on Si used, respectively. Furthermore, by using TEOS, 0.0745 g silicate-1 sample with average particle size of 50.26 nm (SIL-5) can be obtained after 5 days at 80°C. On the other hand no product can be obtained at the same condition by using Ludox LS. It can be meant that TEOS makes shorter nucleation and crystallization time than Ludox LS.

The smaller average particle size by using TEOS compared with Ludox LS can be shown from SIL-9 and SIL-13 samples which were synthesised at 120°C and 5-day crystallization and also other samples such as SIL-12 and SIL-16 at the same temperature and 9-day crystallization. The average particle size of SIL-9 and SIL-13 are 119.94 nm and 76.25 nm, respectively. It means, at the same conditions using TEOS can reduce 36.43 % of average particle size. Similar trend also can be seen for SIL-12 and SIL-16 which have average particle size of 1678.54 nm and 524.10 nm, respectively.

For SIL-9 and SIL-12 samples which were synthesised at 5 and 9 days using Ludox LS, the average particle size is increased from 119.94 nm to 1678.54 nm. On the other hand, the particle size of SIL-13 and SIL-16 which were synthesised using TEOS at 5 and 9 days is increased from 76.25 nm

to 524.10 nm. Thus, it is confirmed that TEOS can make smaller particle size than Ludox LS. Visualization of SEM image at 30.000 of magnification can be seen in Figure 4. The main reason that TEOS produces smaller crystal size is due to an average hydrodynamic diameter of 4 nm of TEOS smaller than Ludox LS of 15-19 nm (Li et al, 2000). Mintova and Valtchev (2002) also found similar results that the fast nucleation period and smaller particle size will be occurred if using TEOS. Li et al (2000) also reported the average crystal size could be reduced up to 66 % by using TEOS compared with Ludox LS. Further, at 100°C crystallization temperature, Ludox LS gave a little bit higher yield than TEOS (60.6 % yield for TEOS and 61.45 % for Ludox LS)

Two stage synthesis

The two stage synthesis procedure involves synthesis at 80°C and then 120°C for a certain times. In this research, it is found that the two-stage synthesis has shorter crystallization time. For instance, samples SIL-25 (0.2613 g yield) and SIL-28 (0.0821 g) could be obtained in 4-day crystallization (3 days at 80°C and 1 day at 120°C). This result is better than any other samples synthesised at 80°C, 120°C and 150°C, 5 days crystallization. However, the average particle size produced in the two stage synthesis is bigger than that in one stage synthesis. XRD patterns and SEM images of the samples are presented in Figure 5. It can be seen that the samples SIL 30 and SIL-10 have the average particle size of 292.87 nm and 276.68 nm, respectively.

This result is different from the observation reported by Li et al (1999). They found the same average particle size but a higher yield of silicate-1 in two stage synthesis. Further, this investigation shows that the effect of silica source on particle size using the two-stage synthesis is much similar to that in one stage synthesis, where TEOS gives smaller particle size while Ludox LS gives higher yield. This tendency can be reflected from samples SIL-27 and SIL-30 which used Ludox LS and TEOS as silica source, respectively.

3.2 Dynamic Adsorption on Synthesized Zeolite Silicate-1 Nanocrystals

Synthesized zeolite silicate-1 which was used in adsorption process in this research is SIL-24 sample. The SIL-24 has the average particle size of 920.26 nm which was synthesized by using TEOS as silica source at temperature of 150°C for 9- day crystallization. Due to free alumina in the zeolite sample, the adsorption ability on heavy metal removal on silicate-1 is observed lower than other nanozeolite such as zeolite A, zeolite Y and ZSM-5. Some factors influencing adsorption such as contact time, temperature and initial of

heavy metal concentration will also be discussed further.

Effect of time and initial heavy metal concentration

Figure 6 shows correlation between contact time, initial heavy metal concentration and adsorption capacity (Q_t) at 30°C by using SIL-24 sample as adsorbent. It can be seen from the figure that adsorption capacities increase with increasing contact time. For instance, at concentration of 50 mg/L adsorption capacity of Pb ion increases from 36.29 mg/g at 24 hour to 99.95 mg/g at 216 hour. Similar to concentration of 80 mg/L, adsorption capacity of Pb increases from 65.57 mg/g to 99.98 mg/g (Fig.6A). Further, a similar trend can also be found on Cr ion removal. The adsorption capacity of Cr increases from 41.07 mg/g at 24 hour to 69.46 mg/g at 216 hour for 50 mg/L and from 44.99 mg/g at 24 h to 85.97 mg/g at 216 h for 80 mg/L of initial heavy metal concentration as described in Figure 8B. In the same time, it can also be seen that adsorption capacity of Pb ion is higher than Cr ion on silicate-1 zeolite.

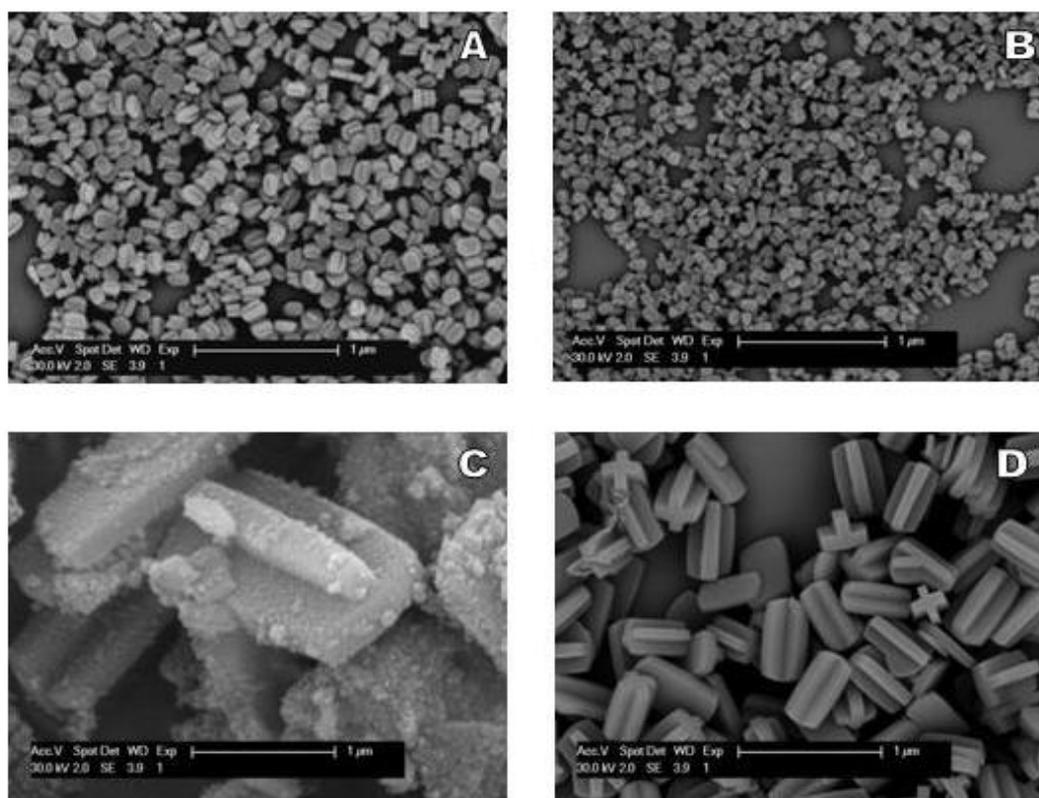


Figure 4. SEM images of silicate-1 nanocrystal at 120°C, SIL-9, Ludox LS (A), SIL-13, TEOS (B), SIL-12, Ludox LS (C) and SIL-16, TEOS (D)

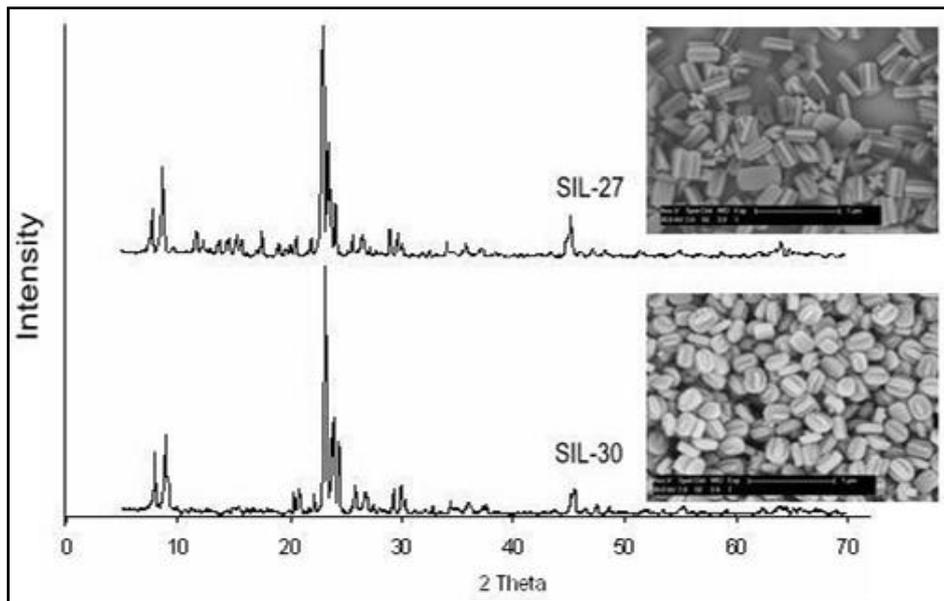


Figure 5. XRD patterns and SEM image of silicate-1 crystal at two-stage synthesis

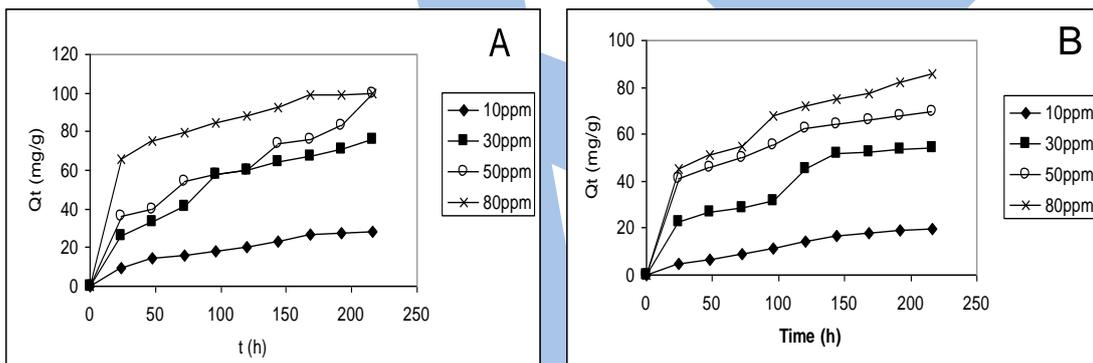


Figure 6. Effect of treatment time and initial concentration on adsorption capacities by using SIL-24 sample, (A) Pb^{2+} , (B) Cr^{3+}

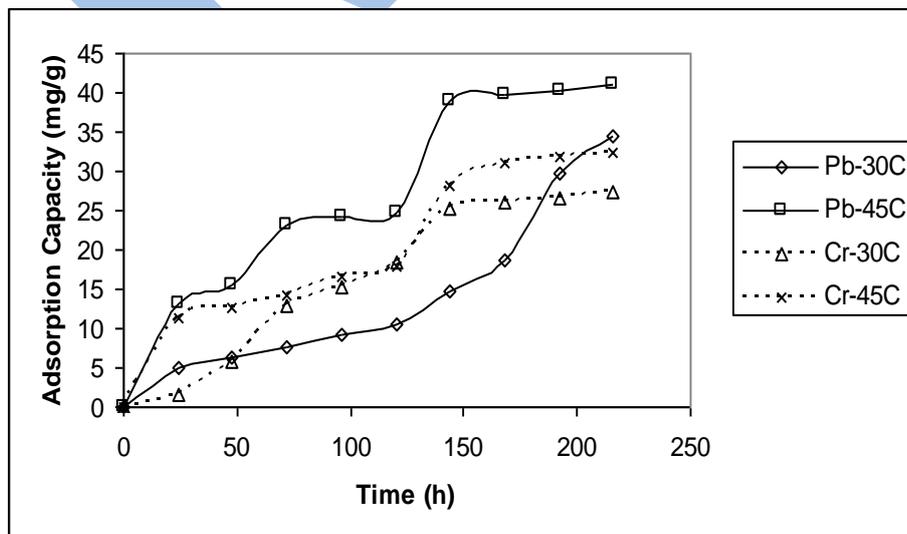


Figure 7. Effect of treatment temperature on adsorption capacities of Pb and Cr by using SIL-24 sample

Effect of temperature

The effect of temperature on Pb and Cr removal by using silicate-1 zeolite can be observed from Figure 7. It can be seen that adsorption of both Pb and Cr increases with increasing of temperature. For example at contact time 216 h, adsorption capacities of Pb at 30°C and 45°C are 34.47 mg/g and 40.98 mg/g or increased by 18.9 %. At the same time, adsorption capacities of Cr are 27.28 mg/g and 32.49 mg/g at 30°C and 45°C, respectively, or increased by 19.1 %. The increase of adsorption capacity as temperature increasing indicates that diffusion of Pb and Cr cation on silicate-1 is endothermic reaction.

Adsorption isotherm

Langmuir and Freundlich isotherm parameters are depicted in Table 1, and Figures 8. As seen that the Langmuir and Freundlich isotherm models are all good for the simulation of experimental data. The Langmuir isotherm presents slightly better in regression coefficients (R^2). The adsorption capacity indicated by Q_{max} (Langmuir) and K_F (Freundlich) shows higher Pb^{2+} adsorption than Cr^{3+} on SIL-24. The maximum adsorption capacities of Pb and Cr at 30°C are 131.58 mg/g and 129.87 mg/g, respectively. Further, it can also be seen that the K_L values in the Langmuir isotherm indicate the higher selectivity of Pb on silicate-1 zeolite than Cr.

Table 1. Isothermal parameter of Pb and Cr on SIL-24 zeolite at 30°C

Adsorbate	Langmuir isotherm			Freundlich isotherm		
	Q_{max} (mg/g)	K_L (l/mg)	R2	K_F	1/n	R2
Pb	131.58	0.1	0.9815	12.07	0.54	0.9402
Cr	129.87	0.0297	0.9852	6.5133	0.59	0.9738

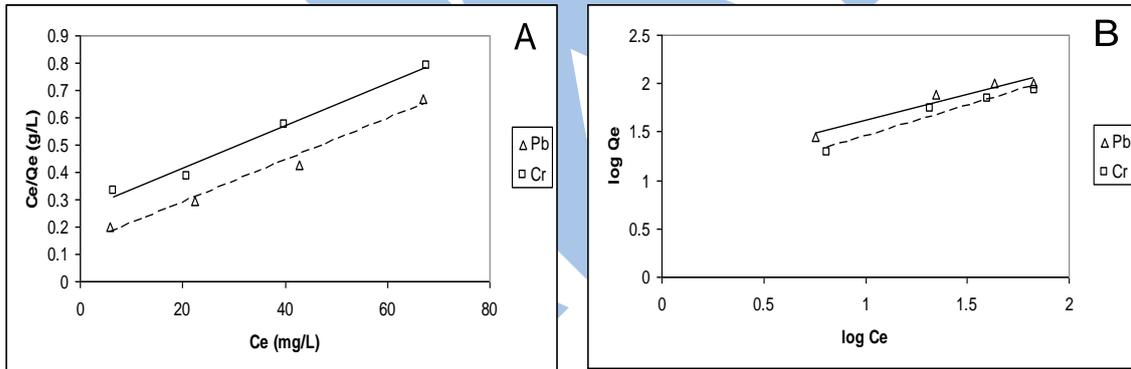


Figure 8. Adsorption isotherm on SIL-24 at 30°C, (A) Langmuir, (B) Freundlich

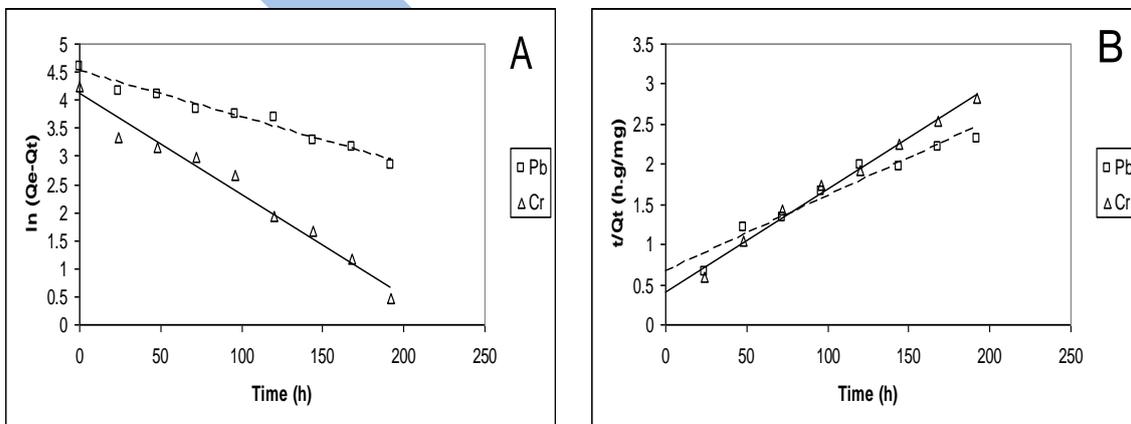


Figure 9. Adsorption kinetics of Pb and Cr on SIL-24 with initial concentration of 50 mg/L at 30°C and 45°C, (A) First order, (B) Second order

Table 2. Kinetics parameter of Pb and Cr adsorption on silicate-1 zeolite

Cation	Cont. (mg/L)	1st order			2nd order			Q_{exp} (mg/g)
		k_1 (h^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg.h)	Q_e (mg/g)	R^2	
Pb	10	0.016	34.73	0.893	2.8×10^{-4}	38.91	0.9286	28.42
	30	0.0137	77.44	0.9818	1.1×10^{-4}	102.04	0.9596	75.65
	50	0.0082	89.96	0.9655	1.3×10^{-4}	107.53	0.9368	99.95
	80	0.0232	98.01	0.8931	4.1×10^{-4}	108.70	0.993	99.98
Cr	10	0.0194	31.62	0.851	1.1×10^{-4}	41.32	0.821	19.46
	30	0.0218	80.05	0.9079	1.2×10^{-4}	80.65	0.8209	54.29
	50	0.0178	60.98	0.9741	4.0×10^{-4}	78.13	0.9891	69.46
	80	0.0139	73.44	0.968	2.6×10^{-4}	96.15	0.9828	85.97

Adsorption kinetics

The Lagergren first order kinetics and the pseudo second order kinetics are used for the kinetic adsorption study. Kinetic calculation as depicted in Table 2 and Figures 9 show that the pseudo first order and pseudo second order kinetics can represent the experiment data. It can be seen from the Q_e that the first order kinetics reveals slightly closer simulation results to the experimental data (Q_{exp}).

4. Conclusions

Nanocrystalline silicate-1 can be synthesized at temperature of 80, 120 and 150 °C with molar composition of 2TPAOH: 0.15Na₂O: 4.5Si: 382H₂O: 51EtOH (TEOS as silica source) and 2TPAOH: 0.15Na₂O: 6SiO₂: 532H₂O: 51EtOH (Ludox LS as silica source). The product could be obtained after 5 days crystallization time and the yield increases by increasing temperature and crystallization time. The yields of SIL-9, SIL-10, SIL-11 and SIL-12 are 0.4065 g, 0.6263 g, 0.8028 g and 0.9957 g, respectively, with the particle sizes of 119.94 nm, 276.68 nm, 992.17 nm and 1678.54 nm. This research proved that TEOS can make smaller particle size up to 36.43 % than Ludox LS. In this research, it is found that the two-stage synthesis has shorter crystallization time. However, the average particle size produced in the two stage synthesis is bigger than that in one stage synthesis. In adsorption study, it is found that adsorption capacities of zeolite increase with increasing contact time, initial concentration of heavy metal ions, and pH. The Langmuir isotherm presents slightly better correlation of regression coefficients (R^2) for Pb cation. In the heavy metal adsorption study, it was found that the adsorption capacity indicated by Q_{max} (Langmuir) and K_F (Freundlich) shows

higher Pb²⁺ adsorption than Cr³⁺. The maximum adsorption capacities of Pb and Cr at 30°C are 131.58 mg/g and 129.87 mg/g, respectively.

Further, it can also be seen that the K_L values in the Langmuir isotherm indicate the higher selectivity of Pb on silicate-1 zeolite than Cr.

References

- Chang M. Y., Juang R. S. (2005), Equilibrium and kinetic studies on the adsorption of surfactant, organic acids and dyes from water onto natural biopolymers, *Colloid Surfaces A: Physicochemical Engineering Aspects*, 269, pp. 35-46.
- Corkery R.W., Ninham B.W. 1997, Low-temperature synthesis and characterization of a stable colloidal TPA-silicalite-1 suspension, *Zeolites*, 18, 379-386.
- Cundy C.S., Cox P.A. 2004, The hydrothermal synthesis of zeolites: History and development from the Earliest to the present time, *Chem. Rev.* 103, pp. 663-701.
- Juang R.S., Wu F.C., Tseng R.L. 2000, Mechanism of adsorption of dyes and phenols from water using activated carbons prepared from plum kernels, *Journal of Colloid Interface Science*, 227, pp. 437-444.
- Kirschhock C.E.A., Ravishankar R., Truyen K., Verspeurt F., Brober P.J., Martens J.A. 2000, Performance of tetraalkylammonium ions during the formation of zeolites from tetraethylorthosilicate, *Studies in Surface Science and Catalysis*, 129, pp. 139-146.
- Li Q., Mihailova B., Creaser D, Sterte J. 2000, The nucleation period for crystallization TPA-silicalite-1 with

- varying silica source, *Microporous and Mesoporous material*, 40, pp. 53-62.
- Malherbe R. 2007, *Adsorption and diffusion in nanoporous material*, CRC Press, United State of America.
- Mintova S., Valtchev V. 2002, Effect of the silica source on the formation of nanosized silicalite-1: an in situ dynamic light scattering study, *Microporous and Mesoporous Material*, 55, 171-179.
- Song W., Grassian, V.H., Larsen, S.C. 2005, High yield method for nanocrystalline zeolite synthesis, *Journal of The Royal Society of Chemistry, Chem. Comm.*, pp. 2951-2953.
- Tosheva L., Valtchev V.P. (2005) Nanozeolites: synthesis, crystallization mechanism, and applications, *Chem. Mater.* 17, 2494-2513.
- Wang S., Zhu Z.H. 2006, Characterization and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, *Journal of Hazardous Material*, B136, pp. 946-952.
- Zhan B.Z., White M.A., Robertson K.N., Cameron T.S., Gharghoury M. 2001, A novel, organic-additive-free synthesis of nanometer-sized NaX crystal, *Journal of The Royal Society of Chemistry (Communication)*, pp. 1176-1177.
- Zhang X., Bai R. 2003, Mechanism and kinetics of humic acid adsorption on to chitosan coated granules, *Journal of Colloid Interface Science*, 264, pp. 30-38.

ARKAT