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Nanocrystalline Zeolite Y: Synthesis and Heavy Metal Removal

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Abstract

Lead (Pb) and chromium (Cr) are common groundwater contaminants at industrial installation. Zeolites are widely use as an adsorbent in heavy metal removal. Nanocrystalline zeolite Y has been synthesised from a clear solution at 150^0C by using aluminum isopropoxide ($Al(OiPr)_3$ and Ludox LS as alumina and silica source, tetramethylammonium hydroxide (TMAOH) and tetramethyl ammonium bromide (TMABr) as first and second organic template, respectively. The products were characterised by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to identify the structure and particle sizes. After 48 hours synthesis time, nanocrystalline zeolite Y samples were obtained with approximately average particle sizes of 268 and 119 nm for one and two organic templates, respectively. The synthesized nanocrystalline zeolite Y was applied for some metal adsorption including Pb(II) and Cr(III) and the results show that the nano crystal samples have good performance. The removal efficiency for Pb and Cr could be up to 88.97% depending on the initial concentration and temperature. The adsorption isotherms of Cr and Pb were determined from the Langmuir and Freundlich equations. The equilibrium sorption capacities (Q_e) from the Langmuir equation were 270.27 mg/g and 204.08 mg/g at 30^0C for Pb and Cr, respectively. Kinetic adsorption analysis of nanozeolite Y shows that the pseudo second order kinetics would be better for fitting the dynamic adsorption of both Cr and Pb cations.

Key words: adsorption isotherms, kinetic adsorption analysis, nanocrystalline zeolite Y

1. Introduction

Heavy metal ions are one of the most important pollutants in water, wastewater and any other environmental sources. Pb^{2+} and Cr^{3+} are heavy metal ions which are playing as common groundwater contaminants at industrial installation and causing numerous diseases (Erdem *et al*., 2004). Zeolites are widely used for many applications such as separations, catalysis, ion exchange and adsorption (Song *et al.*, 2005). It is widely accepted that zeolite which has porous structure is an effective heavy metal adsorbent. By using natural zeolite (clinoplitolite), Inglezakis *et al*. (2007) found that the removal efficiency of lead (Pb^{2+}) could be up to 55%. Further, 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, 2003).

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 nano zeolite Y (FAU, channel dimension: <111>**12** 7.4 x 7.4 Å ***), which was identified as crystal alumina silicate within intermediate ratio of Si/Al (Tosheva and Valtchev, 2005). 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^oC. Mintova (2003) recorded that the particle sizes of 60-70 nm of zeolite Y could be obtained at 90^oC 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).

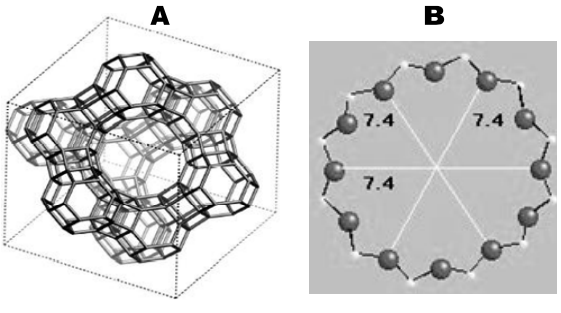

Figure 1. Zeolite Y Framework (A) and Channel Dimension (B)

This article reports experimental studies on nanocrystalline zeolite Y synthesis following the general procedure described by Holmberg *et al*. (2003). Si/Al ratio of 6.38 and a higher temperature (150^oC) with different synthesis

time were used. In this experiment, synthesis has been done from a clear solution which contains specific reactant such as tetramethyl ammonium (TMA) cations as an organic template, aluminum tri-isopropoxide ($Al(OiPr)_3$) as aluminum sources and Ludox LS as silica sources. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to characterise the nano crystalline products. Moreover, further study of heavy metal (Pb and Cr cations) removal by using synthesized nanozeolite Y was conducted.

2. Methodology

2.1 Synthesis Nano Zeolite A

In the preparation stage, the appropriate amounts of distilled water, tetramethyl ammonium 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 synthesis solution which uses second template, tetramethyl ammonium 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 which has molar composition of aAl_2O_3 : $bSiO_2$: $c(TMA)_2O(2OH^-)$: $d(TMA)_2O(2Br^-)$: eNa_2O : fH_2O with Si/Al ratio of 6.38. 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 temperature of 150°C 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°C for 24 hours and then calcined at temperature of 550°C for 3 hours. Table 1 summarizes the synthesis conditions.

2.2 Characterisation of Nanozeolite A

X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to identify the synthesised product (structure and size). The XRD patterns were recorded using Cu-radiation (40kV, 30mA) over a two–theta angular range of 5-70° at 0.04°/2s. SEM (Philips XL30) was used to obtain a visual approximation of crystal sizes.

2.3 Heavy Metal Ion Adsorption

For the adsorption study, 25 mg of zeolites was added into 125 ml solution of the heavy metal with varying concentrations of 10-80 ppm. A shaker (Certomat R Shaker from B. Braun) at 100 rpm and temperatures of 30°C were adopted. Sample (1 ml) was taken periodically at different times, diluted and then measured using Atomic Adsorption Spectrometer (SpectrAA110, Varian). Adsorption capacity of the zeolite at equilibrium (Q_e, mg/g) was calculated by using the following equation (Eq. 1).

$$Qe = \frac{(C_0V_0 - C_eV_e)}{m} \quad (1)$$

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.

Adsorption Isotherms

In this experiment, two adsorption isotherms were selected. They are the Langmuir and Freundlich isotherms. The Langmuir isotherm

Table 1. Detail of the synthesis of nanocrystalline zeolite Y at 150°C

Sample	mH_2O (g)	TMAOH (g)	TMABr (g)	$Al(OiPr)_3$ (g)	Ludox LS (g)	TMABr/TMAOH Ratio	nSi/nAl (syn. sol)	tc (day)	Product (g)
FAU-1	70	20	0	4	25	-	6.38	1	nd
FAU-2	70	20	0	4	25	-	6.38	2	0.0786
FAU-3	70	20	0	4	25	-	6.38	3	0.1203
FAU-4	70	20	3	4	25	0.15	6.38	1	0.0535
FAU-5	70	20	3	4	25	0.15	6.38	2	0.0902
FAU-6	70	20	3	4	25	0.15	6.38	3	0.1722
FAU-7	70	20	3	4	25	0.15	6.38	4	0.6344
FAU-8	70	20	3	4	25	0.15	6.38	5	0.6403

has an assumption that the adsorption occurs within adsorbent at specific homogeneous sites (Wang *et al.*, 2006). The following equation (Eq. 2) is the linear form of the Langmuir equation (Zhang and Bai, 2003).

$$\frac{Ce}{Qe} = \frac{1}{KL Q_{\max}} + \frac{1}{Q_{\max}} Ce \qquad (2)$$

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). The linear form equation of the Freundlich isotherm is listed as follows (Frimmel and Huber, 1996):

$$\log Qe = \log KF + \frac{1}{n} \log Ce \qquad (3)$$

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 equation plots.

Adsorption Kinetics

The adsorption kinetics of Pb^{2+} and Cr^{3+} was determined by using the first and second order equations (Eqs. 4 and 5).

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

$$\frac{t}{Q_t} = \frac{1}{k_2 . Qe^2} + \frac{1}{Qe} t \qquad (5)$$

Where Q_e and Q_t are ion of heavy metal 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.

3. Results and Discussion

3.1 Characterisation of Nanozeolite A

Throughout XRD observation, it is identified that the synthesis process has obtained zeolite Y (FAU). Figure 1 shows the XRD pattern of the product. Sharp measured diffraction patterns of the curve mean that the sample is kind of crystalline material. It can also be obviously seen that peaks of these products indicated similar pattern to zeolite Y (interpreted using the database of the PDF #88-2290/Appendix 12, Jade6.0 and CSM search/match software). It also can be expressed that these products have nearly the same characteristics as zeolite Y. This result indicates that synthesis conditions such as temperature of 150°C, 24 hours crystallization times (by adding second organic template, TMABr) and 6.38 Si/Al ratios of initial reactants are an effective method.

It was recorded that the product of nanocrystalline zeolite Y increases with increasing crystallization time (Table 1). For crystallisation time of 24 hours without adding of TMABr, no crystals were obtained but on the other hand by adding TMABr, 0.0535 gram yield could be obtained. It means synthesis time would be longer without TMABr to obtain the product. Further, at the same synthesis time (48 hours) the yield increases from 0.0786 gram to 0.0902 gram by adding TMABr.

The SEM measurements show that the nano size particles have been obtained. Figure 3

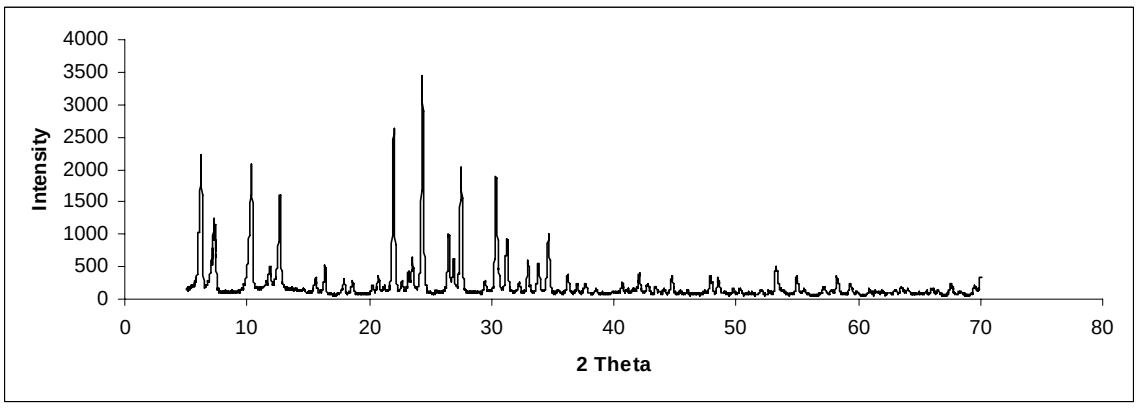

Figure 2. XRD Patterns of Nanozeolites Y

shows the size of the crystals of the nanozeolite Y synthesized at temperature 150°C for 48 hours (2 days). It was observed that by adding TMABr the crystal size decrease from approximately 268 nm to 119 nm. From these result it can be mention that by adding TMABr as second organic template, crystal sizes would be decrease, the product would be increase and the synthesis times would be shorter. This result is similar to the investigations reported by other researchers (Holmberg *et al*., 2003).

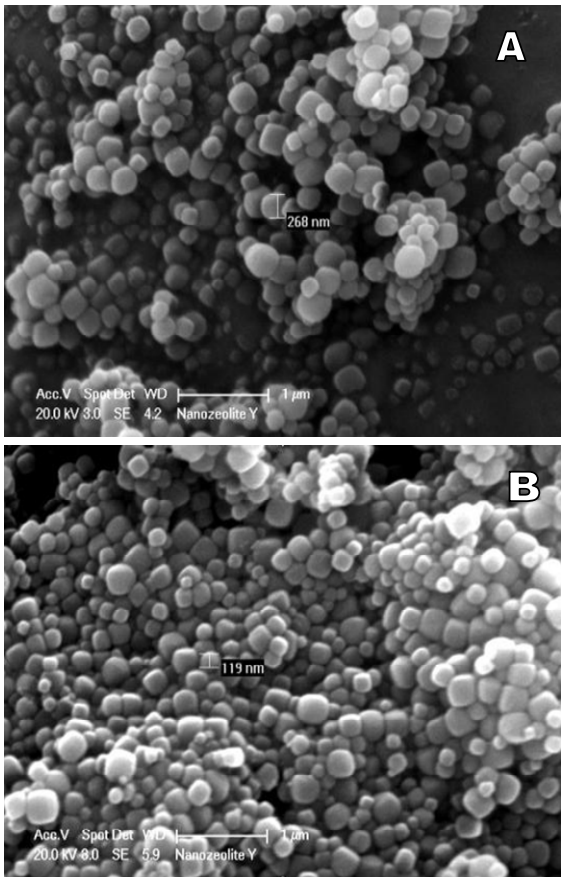

Figure 3. SEM images of zeolites Y nano crystals synthesized at 150°C and 48 hours crystallization time. With TMABr (A), Without TMABr (B)

3.2 Heavy Metal Ion Adsorption

Figure 4 illustrates the dynamic adsorption of Pb and Cr on nanozeolite Y. It is observed that, at temperature 30°C, adsorption of Pb^{2+} tends to increase up to the time around 216 hours (Figure 4A). The lowest adsorption capacity (Qt) is recorded at the concentration of 10 ppm (23.56 mg/g). The highest adsorption is recorded at 80 ppm (231.45 mg/g) at the equilibrium. For the adsorption of Cr^{3+}, the lowest value is recorded at 5 ppm (31.85 mg/g) and the highest is at 80 ppm (147.37 mg/g) (Figure 4B).

Figure 5 shows the effect of temperature on adsorption capacity (Qt) of Pb^{2+} and Cr^{3+}. It can be seen that Qt of Pb^{2+} and Cr^{3+} tends to increase following the increase of temperatures due to the increase in surface area and pore volume of adsorbent. For instance from Figure 5A, Qt of Pb^{2+} increases from 181.02 mg/g (30°C) to 219.24 mg/g (45°C) at equilibrium, or increases 21.12%. Similar condition can also be seen from Figure 5B for Qt of Cr^{3+}. The values increase from 109.75 mg/g to 138.015 mg/g or 25.75%.

All of adsorption capacities of Pb^{2+} and Cr^{3+} tend to increase following the increase of times, initial concentrations and temperatures due to the availability of greater surface area and pore volume of the adsorbent. It is also shown that the adsorption capacity of Pb^{2+} is higher than Cr^{3+} for both nanozeolite Y and natural zeolite. In addition, Erdem *et al*. (2004) mentioned that by using adsorbent of natural zeolite, other researchers found similar experimental results tendency.

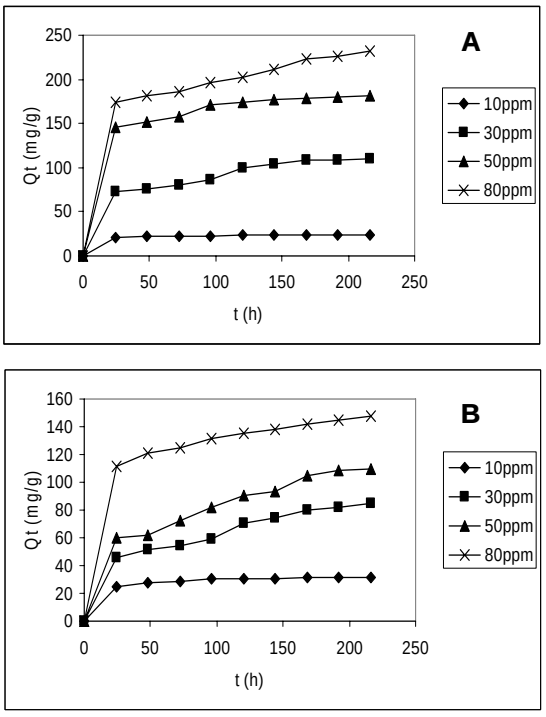

Figure 4. Dynamic adsorption of heavy metal cations at 30°C , Pb^{2+} (A) and Cr^{3+} (B)

In comparison between nanozeolite Y (NNY) and natural zeolite (NTZ, particle sizes 75 µm). Figure 6 describes that nanozeolite Y has better adsorption capacity than natural zeolite (for instance at 30°C and 50 ppm).

Table 2. Adsorption isotherm parameters of Cr^{3+} and Pb^{2+} on nanozeolite Y at 30^0C

Heavy Metal Cations	*Langmuir isotherm*			*Freundlich isotherm*		
	Qe_{max} (mg/g)	K_L (l/mg)	R^2	K_F	n	R^2
Pb^{2+}	270.27	0.108	0.9886	32.21	1.85	0.983
Cr^{3+}	204.08	0.045	0.9893	14.94	1.693	0.9738

Table 3. Kinetic parameter of Pb and Cr adsorption on nanozeolite A at 50 ppm

Cation	*Temp*	*Pseudo 1st order*			*Pseudo 2nd order*			Q_e *Experiment*
	(^{0}C)	$k_1(h^{-1})$	Q_e(mg/g)	R^2	k_2(g/mg.h)	Q_e(mg/g)	R^2	(mg/g)
Pb^{2+}	30	0.0242	112.93	0.9657	0.00081	185.19	0.9987	181.0193
	45	0.0254	104.032	0.9469	0.00113	222.22	0.9995	219.2393
Cr^{3+}	30	0.0185	122.38	0.8868	0.000331	114.94	0.9672	109.7477
	45	0.0196	120.60	0.8969	0.000502	140.85	0.9889	138.0153

The highest adsorption capacity of Pb^{2+} on NNY is 181.02 mg/g. It is better than NTZ, 148.29 mg/g. Similarly for Cr^{3+}, the highest adsorption capacity recorded is 109.75 mg/g (NNY) and it is also better than 85.65185 mg/g (NTZ).

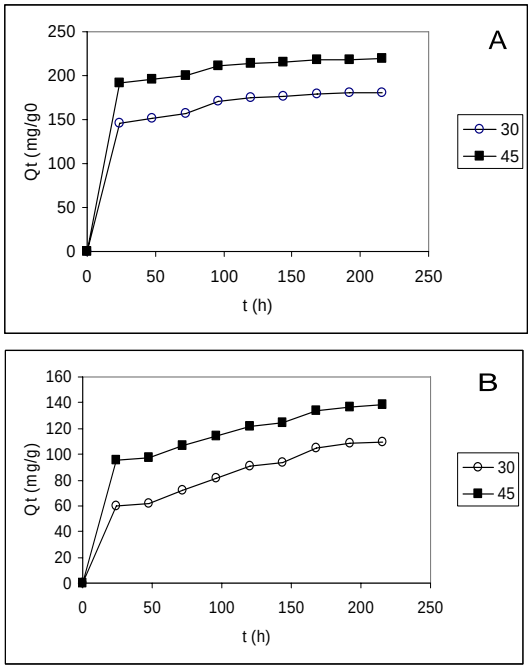

Figure 5. Effect of temperature on adsorption capacity, Pb^{2+} (A) and Cr^{3+} (B)

The performance of the nanozeolite Y for metal removal can also be measured in terms of removal efficiency. The removal efficiency of Pb^{2+} and Cr^{3+} increases concurrently with the increase of time as depicted in Figure 7A. From 24 hours to 216 hours, the removal efficiency of Pb^{2+} increases from 54.17% up to 67.51%, and Cr^{3+} increases from 24.12% to 44.35%.

This experimental study also indicates that the efficiency strongly depends on the initial concentration as depicted in Figure 7B. The increase of concentration tends to decrease the efficiency. For instance, increasing the initial concentration from 10 ppm up to 80 ppm will reduce the efficiency of Pb^{2+} about 44.63% (from 88.97% decrease to 49.26%). Similarly, for Cr^{3+}, the efficiency decreases from 62.54% to 36.88%.

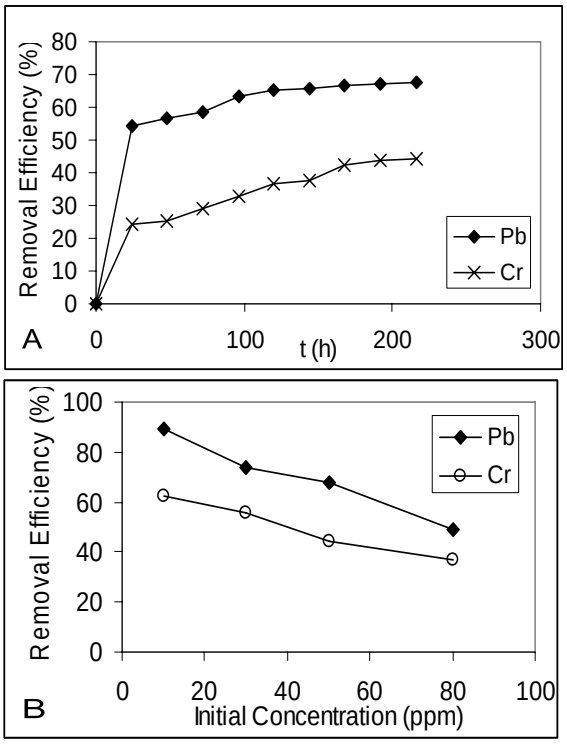

Figure 7. Removal efficiency, effect of times (A), effect of initial concentration (B)

In more detail, the increase of temperature significantly influences the efficiency as depicted in Figure 8. For 216 hour, the efficiency of Pb^{2+} increases from 67.51% up to 76.53% following the increase of temperature from 30^oC to 45^oC (Figure 8A).

Similarly, for Cr^{3+}, the efficiency increases from 44.35% up to 54.34% (Figure 8B).

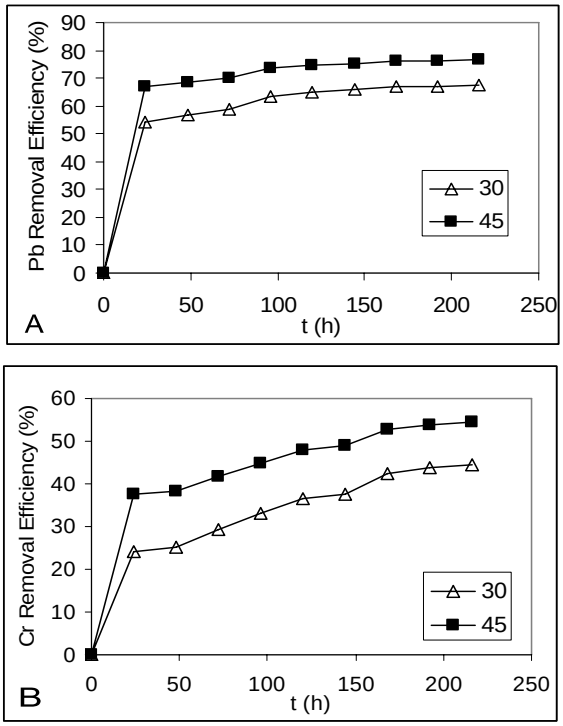

Figure 8. The effect of temperatures on removal efficiency, Pb^{2+} (A), Cr^{3+} (B)

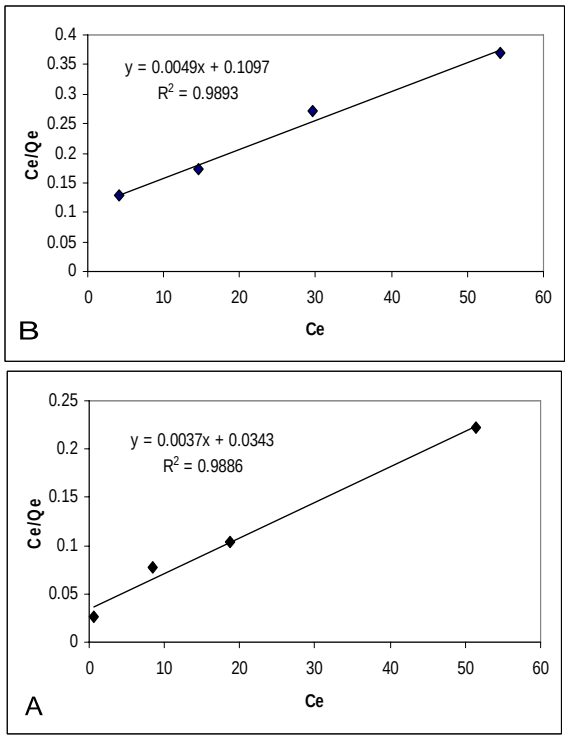

Figure 9. Adsorption isotherm at 30^0C, Langmuir isotherm of Pb (A), Langmuir isotherm of Cr (B)

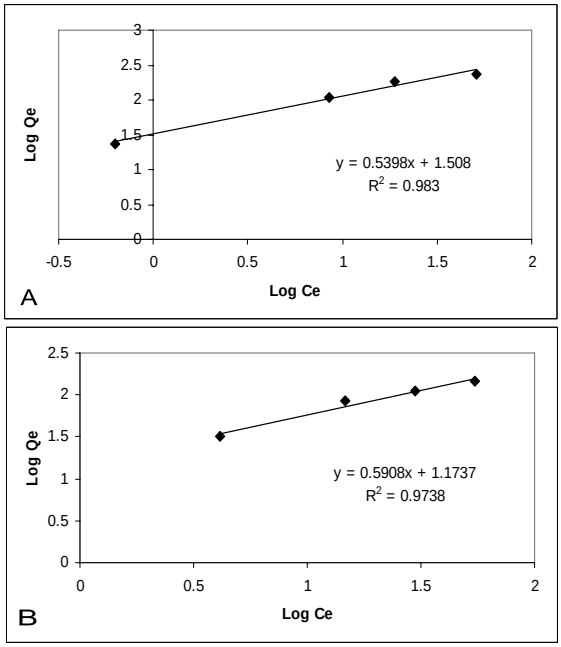

Figure 10. Adsorption isotherm at 30^0C, Freundlich isotherm of Pb^{2+} (A) Freundlich isotherm of Cr^{3+} (B)

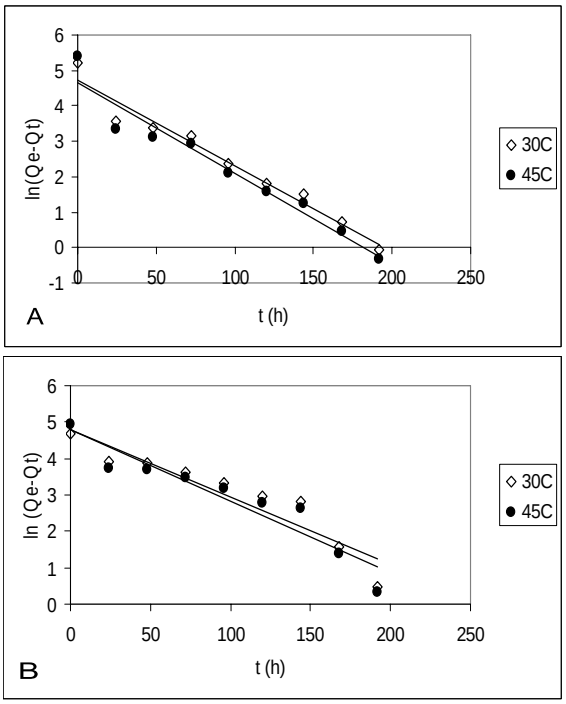

Figure 11. The pseudo first order kinetics of metal adsorption on nanozeolite A at 50 ppm, cation Pb^{2+} (A) and cation Cr^{3+} (B)

3.3 Adsorption Isotherm

Referring to Eq. (2) and Eq. (3), the adsorption isotherm models are examined.

The results can be seen in Table 2, Figure 9, and Figure 10. It can be seen from the tables and figures that the Langmuir and Freundlich models are all good for simulation of experimental data. Both Langmuir and Freundlich models show that Pb^{2+} is favourably adsorbed by nanozeolite Y than Cr^{3+}. The regression coefficients (R^2) indicate that the Langmuir isotherm model is better in fitting the adsorption of Pb^{2+} and Cr^{3+}.

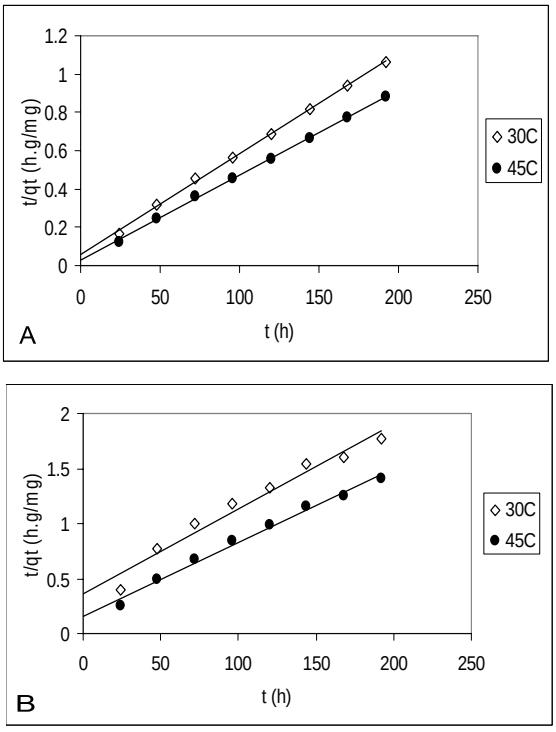

Figure 12. The pseudo second order kinetic of metal adsorption on nanozeolite A at 50 ppm, cation Pb^{2+} (A) and cation Cr^{3+} (B)

3.4 Adsorption Kinetics

Referring to Eq. (4) and Eq. (5) kinetic calculation as depicted in Table 3, Figures 11 and 12 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 second order reveals closer results to experimental data. Moreover, a regression coefficient of the pseudo second order kinetics also shows a better result in simulation.

4. Conclusion

Nanocrystalline zeolite Y can be successfully synthesised at a temperature of 150°C, 1-5 days crystallisation and 6.38 of initial Si/Al ratio. By adding TMABr as second organic template the higher product can be obtained while the particle sizes and crystallization times tend to decrease. The nanocrystalline zeolite Y achieves a significant result on removing heavy metal compounds (Pb^{2+} and Cr^{3+}), which gives better results than natural zeolite. During adsorption, several parameters such as initial concentration, time and temperature influence adsorption capacity and adsorption efficiency. The Langmuir and Freundlich models have been proved as suitable models explaining the phenomena of adsorption isotherm. The equilibrium sorption capacities of Pb^{2+} and Cr^{3+} on nanozeolite Y are 270.27 mg/g and 204.08 mg/g, respectively. The adsorption kinetic of the heavy metals could be better described by the second order equation.

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