Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1091748

57 (2016) 18286–18292
August

Taylor & Francis
Taylor & Francis Group

A study on adsorptive removal of DMAZ from aqueous solutions by ZSM-5, NaY zeolites, and activated carbon: kinetic and isotherm

Shahram Ghanbari Pakdehi, Behzad Vaferi*

Department of Chemical Engineering, Malek-Ashtar University of Technology, Tehran, Iran, email: sh_ghanbari73@yahoo.com (S. Ghanbari Pakdehi); Tel. +98 7136135904; Fax: +98 7136473687; email: behzad.vaferi@gmail.com (B. Vaferi)

Received 12 June 2015; Accepted 1 September 2015

ABSTRACT

The adsorptive removal of dimethyl amino ethyl azide (DMAZ) from aqueous solution by hydrothermally synthesized ZSM-5 and NaY zeolites as well as commercial activated carbon (AC) was studied. The effects of various parameters like the initial concentration of DMAZ, contact time, and adsorbent dosage on the DMAZ sorption yield were examined and the optimum experimental conditions were determined. The DMAZ adsorption efficiency of 60, 23, and 45% were obtained by ZSM-5, NaY zeolites, and AC, respectively. The experimental equilibrium data were analyzed by Langmuir and Freundlich isotherms. The Langmuir isotherm represented equilibrium data for NaY and ZSM-5 zeolites with regression coefficients (R^2) of 0.974 and 0.971, respectively. The Freundlich isotherm revealed a better correlation for the commercial AC ($R^2 = 0.97$). The experimental kinetic data were analyzed through pseudo-second-order model. It was observed that 15.04, 50.75, and 41.35 g of DMAZ could be removed by a unit mass of NaY zeolite, ZSM-5 zeolite, and AC, respectively.

Keywords: DMAZ adsorption; ZSM-5 and NaY zeolites; Parametric study; Kinetic model; Isotherm study

1. Introduction

Adsorption, as a surface-based process, adheres adsorbate (molecules, atoms, or ions from a fluid or dissolved solid) to the surface of a highly porous solid, namely, the adsorbent [1]. The difference between adsorbate concentrations in solid and fluid phase provides the driving force for its movement towards the adsorbent surface. The movement of adsorbate to the solid surface terminates as soon as this driving force is vanished, leading to equilibrium condition (adsorbent saturation). This process is extensively run in many applications like water purification [2], wastewater treatment [3–9], and air conditioning [10]. Zeolites are one of the most important collectives of adsorbents. They are microporous, aluminosilicate/silicate crystalline materials which have wide range of practical and industrial applications in wastewater treatment [11], fuel purification [12], gas storage [13], ion exchange [14,15], membrane technology [16], catalysis synthesis [17,18], the capture of carbon dioxide in fluidized bed systems [19], and catalytic cracking of the gas oil [20].

In order to synthesize a specific type of zeolite, an appropriate ratio of its ingredients should be applied and special attention should be devoted to both temperature and crystallization time [21]. The effect of synthesis parameters on the particulate properties and

---

*Corresponding author.

crystallization pathway of the zeolite [22], the synthesis method of zeolites [23], and activation mechanism [24] are some of the most popular aspects of zeolites in scientific literatures.

2-Dimethylaminoethylazide (DMAZ) is a new liquid fuel which has contributed to significant progress in the development of bi/mono propellant rocket engines [25,26]. It is noncarcinogenic [27] but, toxic [26,28] like most chemicals. The synthesis process produces an aqueous phase containing this liquid fuel [26]. It has been reported that water may have undesirable effects on the performance of liquid fuel DMAZ and increase its spontaneous explosion significantly [26]; therefore, the separation of DMAZ from aqueous solution seems to be the interesting subject. Although there are proposals on oxidation processes for amine wastewaters [29], it is important to separate these groups by adsorption method because of some next probable dangers. Adsorption and membrane technologies [25,26,30] are some of the appropriate processes to be run for the considered task.

2. Materials and methods

In this study, the NaY ($10SiO_2$-$Al_2O_{3–4}$·$6Na_2O$-$180H_2O$) and ZSM-5 ($TiO_{2–0}$·25 $Al_2O_{3–40}SiO_{2–7}$·44 TPA (OH)-$216H_2O$) zeolites were synthesized hydrothermally. Operating conditions and the molar ratio of the consumed ingredients for zeolite synthesis are tabulated in Table 1.

The source and specifications of the materials consumed during hydrothermal synthesis of both ZSM-5 and NaY zeolites are tabulated in Table 2.

Table 1
Experimental procedure of synthesizing of the utilized zeolites

Zeolite	Property	Value	Unit
NaY	SiO_2/Al_2O_3	10	–
	Na_2O/Al_2O_3	4.6	–
	H_2O/SiO_2	18–42	–
	Mixing temperature	80–110	°C
	Reaction time	5–12	h
	Drying temperature	100	°C
ZSM-5	SiO_2/Al_2O_3	160	–
	H_2O/SiO_2	5.4	–
	$TPA(OH)/TiO_2$	7.44	h
	Mixing temperature	120–170	°C
	Reaction time	1	h
	Drying temperature	100	°C

3. Results and discussion

3.1. Parametric study

The effects of some key parameters on the separation of DMAZ from aqueous solution are investigated experimentally. Adsorbent type, initial concentrations of DMAZ, adsorbent dosage, and contact time were the parameters affected on the adsorption process. The DMAZ reacts with acid and produces salt, deactivates the adsorbent. Moreover, addition of a base reagent (such as NaOH) to the solution removes the N_3 group from DMAZ and decomposes it. It is obvious that the solution should be neutral. In all experiments of this study, the solution pH was kept in the range of 8–9.

3.1.1. The effect of initial concentrations of DMAZ

The experimental values of adsorbed DMAZ on NaY and ZSM-5 zeolites as well as on the commercial activated carbon (AC) at various initial concentrations of DMAZ are illustrated in Fig. 1. It is clear that the adsorption of DMAZ increases with the increase in its initial concentration. Moreover, it is obvious that by increasing the initial concentration of DMAZ, the number of its free molecules increase, promoting their availability for adsorption on the active surface of the adsorbents.

The effect of adsorbent type on the DMAZ separation yield was investigated (Fig. 1). It is observed that ZSM-5 zeolite demonstrates the best performance for the considered task with the highest adsorption capacity. In this process, 50 mg of initial DMAZ is separated by a unit mass of ZSM-5 zeolite. This can be attributed to the surface characteristic of ZSM-5 zeolite and the amount of available active sites in it for the adsorption of DMAZ molecules.

3.1.2. The effect of adsorbent dosage

The influence of mass dosage of adsorbents on DMAZ adsorption capacity was studied experimentally. The amount of separated DMAZ from the aqueous solution by different mass ratios of adsorbents/solution is presented in Fig. 2. That the amount of adsorbed DMAZ is reduced by an increase in the mass dosage of the adsorbents (adsorbent/solution mass ratio) is implied in this figure. The complex behavior of adsorbent particles, such as agglomeration which reduces the total surface area and the number of active adsorption sites of the adsorbent may be responsible for the decrease in the amount of DMAZ separation.

Table 2
Source and purity of the consumed materials for synthesizing of zeolites

Material	Chemical formula	Purity (%)	Company	Country
Tetraethyl orthosilicate	$Si(OC_2H_5)_4$	99.9	Merck	Germany
Sodium aluminate	$Na_2O·Al_2O_3$	99	Riedel	Germany
Sodium silicate solution	SiO_2	28	Merck	Germany
Sodium hydroxide	NaOH	99.9	Merck	Germany
Double distilled water	H_2O	–	Pars Tajhiz	Iran
Aluminium isopropoxide	$Al(OC_3H_7)_3$	99.95	Aldrich	Germany
Erapropyl ammonium hydroxide	TPAOH	40	Alfa	Germany
Titanium tetra butoxide	$Ti(OC_4H_9)_4$	99.9	Alfa	Germany
Isopropyl alcohol	C_3H_7OH	99	Mokarrar	Iran
Hydrochloric acid	HCl	0.2 N	Merck	Germany

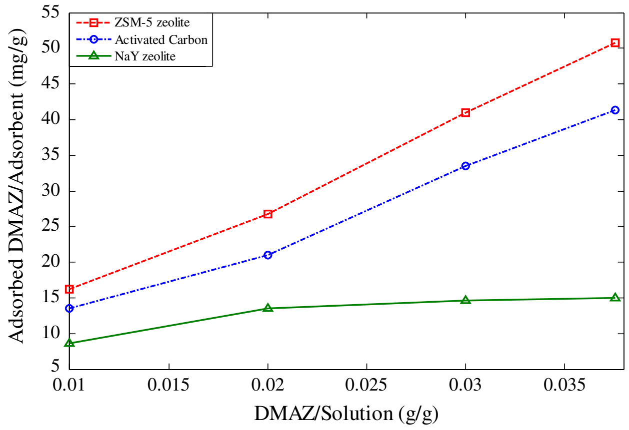

Fig. 1. Variation of DMAZ adsorption capacity for various adsorbents.

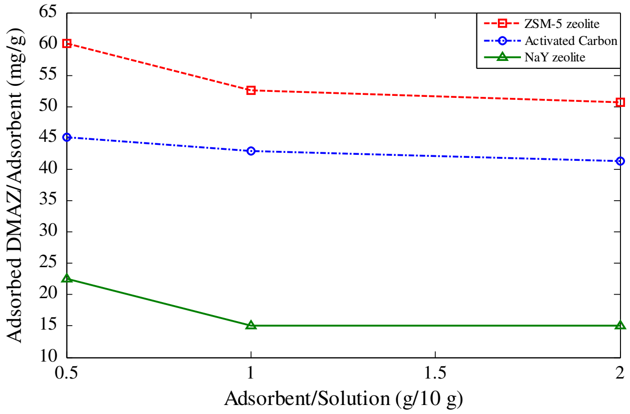

Fig. 2. Effect of adsorbents dosage on their capacity for DMAZ adsorption.

That the DMAZ adsorption ability of the ZSM-5 zeolite is higher than those of the two other adsorbents in the entire operating conditions is clearly demonstrated in Fig. 2.

3.1.3. The effect of contact time

As previously described, the contact time is one of the key parameters in the adsorption process which has an influence on the amount of transferred adsorbate from fluid to solid. The capacity of different adsorbents for the separation of DMAZ from aqueous solution under various operating conditions is shown in Fig. 3. It is observed that the amount of adsorbed DMAZ on the considered adsorbents increases with an increase in solid–fluid contact time. The excellent early time capacity of the ZSM-5 zeolite for DMAZ separation from aqueous solution is concluded in Fig. 3.

The saturation time of various adsorbents can also be observed in Fig. 3, where the AC is saturated after 60 min, while the saturation time of the ZSM-5 and NaY zeolites occur after 50 and 30 min, respectively.

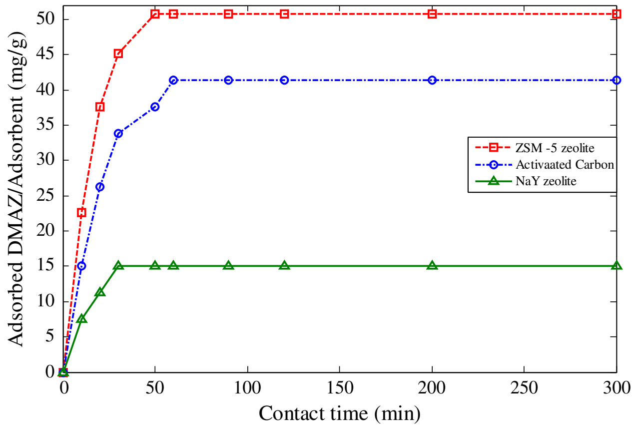

Fig. 3. Effect of contact time on the adsorbents capacity for DMAZ adsorption.

3.2. Kinetics study

The analysis of kinetic data is very important for the adsorption process. Various kinetic models have been proposed for analyzing the various adsorbent–fluid systems [4]. The parameters of the kinetic models should be determined through the experimental data. In this study, the best match for experimental data was obtained by the pseudo-second-order kinetic model [31]. The presented experimental data in Table 3 were utilized for the evaluation of the parameters of this kinetic model. Kinetic experimental data (q_t) is the amount of the adsorbed DMAZ in the unit mass of adsorbent (mg/g) in time t.

3.2.1. Pseudo-second-order kinetic model

The kinetic model of pseudo-second-order [31] is expressed mathematically by Eq. (1):

$$\frac{t}{q_t} = \frac{t}{Q} + \frac{1}{K Q^2} \tag{1}$$

where K and Q are the constants. It is clear that the plot of t/q_t vs. t is a straight line with a $1/Q$ slope and a $1/KQ^2$ intercept. Therefore, the values of the constants for the kinetic model (K and Q) can be evaluated in accordance with the slope and intercept of this plot. The values of the coefficients for this kinetic model in the considered adsorbent–DMAZ system are tabulated in Table 4.

The kinetic experimental data as well as the data which are estimated by the pseudo-second-order kinetic model for all adsorbent–DMAZ systems are presented in Fig. 4. The observed regression coefficients (R^2), tabulated in Table 4, justify the good agreement between the experimental and estimated kinetic data.

3.3. Equilibrium study

The mathematical analysis of equilibrium behavior for various adsorbent/adsobate systems is usually accomplished through isotherms [32]. The isotherms are special equations which correlate the amount of the adsorbate in the adsorbent body to its dosage in the fluid at constant temperature. Freundlich and Langmuir are the most well-known isotherms [32].

The following experimental data are used to determine the coefficients of these isotherms for three different adsorbent–DMAZ systems. In Table 5, q_e is an equilibrium amount of adsorbed DMAZ in the unit mass of adsorbent, and C_e is its equilibrium concentration in the fluid phase.

3.3.1. Freundlich isotherm

As the Freundlich isotherm was being developed, the assumption was that the adsorbent materials are not homogenous and have different adsorption capabilities [31]. This isotherm can be expressed mathematically as Eq. (2):

$$\log q_e = \frac{1}{n} \times \log C_e + \log K_f \tag{2}$$

where n and K_f are the coefficients of the Freundlich isotherm.

The log–log plot of q_e vs. C_e leads to a straight line with a $1/n$ slope and a $\log K_f$ intercept. Therefore, the

Table 3
Kinetic experimental data for various adsorbents

Time (min)		0	10	20	30	50	60	90	120
NaY zeolite	q_t (mg/g)	0	7.52	11.28	15.04	15.04	15.04	15.04	15.04
ZSM-5 Zeolite	q_t (mg/g)	0	22.56	37.59	45.11	50.75	50.75	50.75	50.75
Activated Carbone	q_t (mg/g)	0	15.04	26.32	33.84	37.59	41.35	41.35	41.35

Table 4
Developed pseudo-second-order kinetic model and value of its coefficient for various systems

	Coefficients of kinetic model			
Adsorbent type	K	Q	R^2	Kinetic model
NaY zeolite	0.0132	15.625	0.986	$\frac{t}{q_t} = 0.064\,t + 0.3103$
ZSM-5 zeolite	0.0022	58.823	0.964	$\frac{t}{q_t} = 0.017\,t + 0.1314$
Activated Carbon	0.0018	47.619	0.977	$\frac{t}{q_t} = 0.021\,t + 0.2450$

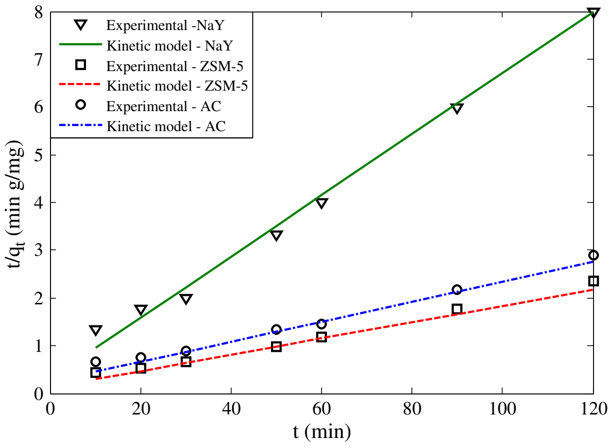

Fig. 4. Kinetic experimental data and the estimated value by pseudo-second-order kinetic model for various systems, AC represents the activated carbon.

coefficients of the Freundlich isotherm (K_f and n) can be obtained from the slope and intercept of this log–log plot. The developed Freundlich isotherm and its coefficients for various adsorbent–DMAZ systems are tabulated in Table 6.

The experimental equilibrium data as well as those equilibrium values which are obtained by the developed Freundlich isotherms are illustrated in Fig. 5. This figure and the calculated R^2 in Table 6 confirm that the derived Freundlich isotherm is in a good agreement with the experimental equilibrium data.

3.3.2. Langmuir isotherm

Langmuir is another well-known isotherm, often employed to correlate the adsorbate dosage in solid and fluid phases. This isotherm can be defined by the following equation [32]:

$$\frac{1}{q_e} = \frac{1}{a\,b} \times \frac{1}{C_e} + \frac{1}{a} \tag{3}$$

where a and b are the coefficients of the Langmuir isotherm often estimated from experimental data. The

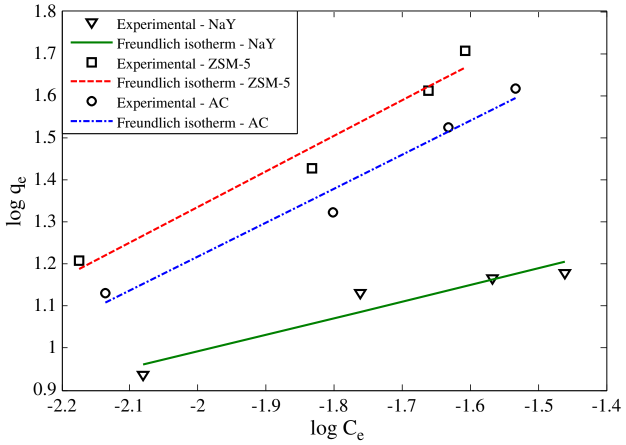

Fig. 5. Experimental data and estimated value by the Freundlich isotherm for various systems.

Table 5
Results of DMAZ adsorption by various adsorbents

	NaY		ZSM-5		Activated carbon	
DMAZ/Solution (g/g)	q_e (mg/g)	C_e (mg/L)	q_e (mg/g)	C_e (mg/L)	q_e (mg/g)	C_e (mg/L)
0.01	8.647	0.0083	16.165	0.0067	13.534	0.0073
0.02	14.661	0.0173	26.692	0.0147	21.053	0.0158
0.03	13.533	0.0271	40.977	0.0218	33.459	0.0233
0.0376	15.038	0.0346	50.752	0.0247	41.353	0.0293

Table 6
Developed Freundlich isotherm and the value of its coefficients for various systems

	Coefficients of Freundlich isotherm			
Adsorbent type	n	K_f	R^2	Freundlich isotherm
NaY zeolite	2.5387	60.223	0.911	$\log q_e = 0.394 \times \log C_e + 1.78$
ZSM-5 zeolite	1.1818	1064.1	0.969	$\log q_e = 0.846 \times \log C_e + 3.03$
Activated Carbon	1.2424	673.0	0.970	$\log q_e = 0.805 \times \log C_e + 2.83$

Table 7
Developed Langmuir isotherm and the value of its coefficients for various systems

Adsorbent type	Coefficients of Langmuir isotherm		R^2	Langmuir isotherm
	a (mg/g)	b (L/mg)		
NaY zeolite	21.155	85.356	0.974	$\frac{1}{q_e} = \frac{0.00055}{C_e} + 0.0473$
ZSM-5 zeolite	128.568	21.027	0.971	$\frac{1}{q_e} = \frac{0.00037}{C_e} + 0.0078$
Activated Carbon	88.028	24.227	0.962	$\frac{1}{q_e} = \frac{0.00047}{C_e} + 0.0114$

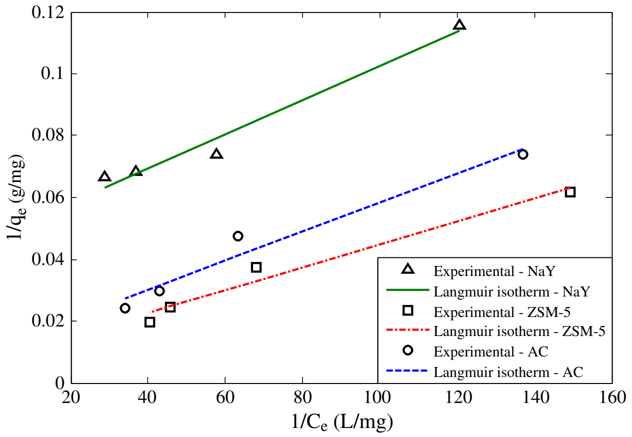

Fig. 6. Experimental data and estimated value by the Langmuir isotherm for various systems.

$1/q_e$ plot vs. $1/C_e$ is a straight line with a slope of $1/ab$ and an intercept of $1/a$. The coefficient of Langmuir isotherm (a and b) can be estimated from the slope and intercept of this plot for various adsorbent–DMAZ systems. The derived Langmuir isotherm and the value of its coefficients (a and b) for all the considered adsorbent–DMAZ systems are tabulated in Table 7.

Experimental equilibrium data as well as the predicted values by the developed Langmuir isotherm are presented in Fig. 6, where a good agreement is observed between the experimental data and the estimated ones. The comparison of the presented R^2 values in Tables 6 and 7 make it clear that the Langmuir isotherm demonstrates better performance for modeling the equilibrium data for NaY and ZSM-5 zeolites, while the Freundlich isotherm shows better performance for modeling the AC–DMAZ system.

4. Conclusions

The synthesized ZSM-5 and NaY zeolites as well as commercial AC were studied experimentally for adsorptive removal of DMAZ from aqueous solution. The theoretical aspects of the considered adsorbent–DMAZ systems were studied by equilibrium as well as kinetic models. Results indicated that the amount of DMAZ increases as its initial concentration increases. The DMAZ sorption capacity of the considered adsorbents reduces as their dosages increase. Moreover, the amount of the adsorbed DMAZ increases when the contact time increases. Among the adsorbents, ZSM-5 demonstrated the best efficiency for DMAZ adsorption under different experimental conditions. The pseudo-second-order model represented the kinetic experimental data better than the other models. The Langmuir isotherm represented better experimental equilibrium data for NaY and ZSM-5 zeolites than the Freundlich isotherm; while, Freundlich isotherm presented better experimental equilibrium data for the AC than the Langmuir isotherm.

References

[1] S. Chang, C. Lu, K.Y.A. Lin, Comparisons of kinetics, thermodynamics and regeneration of tetramethylammonium hydroxide adsorption in aqueous solution with graphene oxide, zeolite and activated carbon, Appl. Surf. Sci. 326 (2015) 187–194.
[2] K. Yu, J. Ho, E. McCandlish, B. Buckley, R. Patel, Z. Li, N.C. Shapley, Copper ion adsorption by chitosan nanoparticles and alginate microparticles for water purification applications, Colloids Surf., A Physicochem. Eng. Aspects 425 (2013) 31–41.
[3] A. Mittal, Use of hen feathers as potential adsorbent for the removal of a hazardous dye, Brilliant Blue FCF, from wastewater, J. Hazard. Mater. 128(2–3) (2006) 233–239.
[4] A. Mittal, Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers, J. Hazard. Mater. 133(1–3) (2006) 196–202.
[5] A. Mittal, L. Kurup, Column operations for the removal and recovery of a hazardous dye 'Acid Red-27' from aqueous solutions, using waste materials—Bottom ash and de-oiled soya, Ecol. Environ. Conserv. 12(2) (2006) 181–186.
[6] G. Sharma, M. Naushad, D. Pathania, A. Mittal, G.E. El-desoky, Modification of *Hibiscus cannabinus* fiber by graft copolymerization: Application for dye removal, Desalin. Water Treat. 54(11) (2015) 3114–3121.

[7] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies, Desalin. Water Treat. 53(1) (2015) 214–220.

[8] H. Feather, A remarkable adsorbent for dye removal, in: J. Mittal, A. Mittal, Chapter 11 of the Book "Green Chemistry for Dyes Removal from Wastewater" (2015) 409–857 by Dr S.K. Sharma (Eds.), Publisher: Scrivener Publishing LLC, USA (ISBN: 978-1-118-72099-8).

[9] M. Kragović, A. Daković, Živko Sekulić, M. Trgo, M. Ugrina, J. Perić, G.D. Gatta, Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite, Appl. Surf. Sci. 258 (2012) 3667–3673.

[10] Y. Zhong, T. Fang, K.L. Wert, An adsorption air conditioning system to integrate with the recent development of emission control for heavy-duty vehicles, Energy 36 (2011) 4125–4135.

[11] W. Wang, Q. Feng, K. Liu, G. Zhang, J. Liu, Y. Huang, A novel magnetic 4A zeolite adsorbent synthesised from kaolinite type pyrite cinder (KTPC), Solid State Sci. 39 (2015) 52–58.

[12] S. Ghanbari, B. Vaferi, Experimental and theoretical investigation of water removal from DMAZ liquid fuel by an adsorption process, Acta Astronaut. 112 (2015) 19–28.

[13] Z. Yang, Y. Xia, R. Mokaya, Enhanced hydrogen storage capacity of high surface area zeolite-like carbon materials, J. Am. Chem. Soc. 129 (2007) 1673–1679.

[14] J. Hou, J. Yuan, R. Shang, Synthesis and characterization of zeolite W and its ion-exchange properties to K^+ in seawater, Powder Technol. 226 (2012) 222–224.

[15] M. Naushad, A. Mittal, M. Rathore, V. Gupta, Ion-exchange kinetic studies for Cd(II), Co(II), Cu(II), and Pb (II) metal ions over a composite cation exchanger, Desalin. Water Treat. 54(10) (2015) 2883–2890.

[16] B. Soydaş, A. Çulfaz, H. Kalipçilar, Effect of soda concentration on the morphology of mfi-type zeolite membranes, Chem. Eng. Commun. 196 (2008) 182–193.

[17] N. Popovych, P. Kyriienko, S. Soloviev, S. Orlyk, S. Dzwigaj, Catalytic properties of AgAlBEA and AgSiBEA zeolites in H2-promoted selective reduction of NO with ethanol, Microporous mesoporous mater. 203 (2015) 163–169.

[18] J.M. Müller, G.C. Mesquita, S.M. Franco, L.D. Borges, J.L. de Macedo, J.A. Dias, S.C.L. Dias, Solid-state dealumination of zeolites for use as catalysts in alcohol dehydration, Microporous Mesoporous Mater. 204 (2015) 50–57.

[19] F. Raganati, P. Ammendola, R. Chirone, CO_2 capture performances of fine solid sorbents in a sound-assisted fluidized bed, Powder Technol. 268 (2014) 347–356.

[20] P.G. Smirniotis, E. Ruckenstein, Catalytic cracking of gas oil: Effect of the amount of zeolite in composite catalysts, Chem. Eng. Commun. 116 (1992) 171–191.

[21] X.D. Liu, Y.P. Wang, X.M. Cui, Y. He, J. Mao, Powder Technol. 243 (2013) 184–193.

[22] X. Zhang, D. Tang, M. Zhang, R. Yang, Synthesis of NaX zeolite: Influence of crystallization time, temperature and batch molar ratio SiO_2/Al_2O_3 on the particulate properties of zeolite crystals, Powder Technol. 235 (2013) 322–328.

[23] A.J.J. Koekkoek, C.H.L. Tempelman, V. Degirmenci, M. Guo, Z. Feng, C. Li, E.J.M. Hensen, Hierarchical zeolites prepared by organosilane templating: A study of the synthesis mechanism and catalytic activity, Catal. Today 168 (2011) 96–111.

[24] T. Tunç, A. Şükran, Demirkıran, The effects of mechanical activation on the sintering and microstructural properties of cordierite produced from natural zeolite, Powder Technol. 260 (2014) 7–14.

[25] T.S. Kokan, J.R. Olds, J.M. Seitzman, P.J. Ludovice, Characterizing high-energy-density propellants for space propulsion applications, Acta Astronaut. 65 (2009) 967–986.

[26] B. Mellor, A preliminary technical review of DMAZ: A low toxicity hypergolic fuel, 2nd International Conference on Green Propellants for Space Propulsion, European Space Agency, Italy, (2004) 967–986.

[27] G. Reddy, J. Song, M.S. Mecchi, M.S. Johnson, Genotoxicity assessment of two hypergolic energetic propellant compounds, Mutat. Res. Genet. Toxicol. Environ. Mutagen. 700(1–2) (2010) 26–31.

[28] C.J. Meyers, B.M. Kosowski, Dimethylamino ethylazide—A replacement of hydrazine derivatives in hypergolic fuel applications, Int. Annu. Conf. ICT 177 (2003) 1–4.

[29] R.N. Goyal, A. Kumar, A. Mittal, Oxidation chemistry of adenine and hydroxyadenines at pyrolytic graphite electrodes, J. Chem. Soci., Perkin Trans. 2 II(9) (1991) 1369–1375.

[30] S. Satyanarayana, P. Bhattacharya, Pervaporation of hydrazine hydrate: Separation characteristics of membranes with hydrophilic to hydrophobic behaviour, J. Membr. Sci. 238 (2004) 103–115.

[31] N. Passe-Coutrin, S. Altenor, D. Cossement, C. Jean-Marius, S. Gaspard, Comparison of parameters calculated from the BET and Freundlich isotherms obtained by nitrogen adsorption on activated carbons: A new method for calculating the specific surface area, Microporous Mesoporous Mater. 111 (2008) 517–522.

[32] F. Li, L. Song, L. Duan, X. Li, Z. Sun, A frequency response study of thiophene adsorption in zeolite catalysts, Appl. Surf. Sci. 253 (2007) 8802–8809.