



## Modification of Jordanian Zeolitic Tuff Using Cationic Surfactants and Their Capacity for Phenols Removal

IBRAHIM A. BAZBAZ<sup>1</sup>, RUSHDI I. YOUSEF<sup>2</sup> and SALEM M. MUSLEH<sup>1,\*</sup>

<sup>1</sup>Applied Science Department, Prince Abdullah bin Ghazi Faculty of Science and Information Technology, Al-Balqa Applied University, Al-Salt 19117, Jordan

<sup>2</sup>Department of Chemistry, Faculty of Arts and Sciences, Petra University, Amman 11196, Jordan

\*Corresponding author: Fax: +962 5 3530462; E-mail: smusleh@lycos.com

(Received: 23 June 2010;

Accepted: 10 February 2011)

AJC-9610

Zeolites have large cation exchange capacities, which enable them to be modified by cationic surfactants. Native zeolitic tuff was treated with different cationic surfactants, *viz.*, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, and octadecyltrimethylammonium bromide. The unmodified as well as the surfactant modified zeolites were characterized by powder X-ray diffraction, X-ray fluorescence, and infrared spectroscopy techniques. The chain length of the surfactant plays a significant role in determining the amount of surfactant loaded on zeolite surface. The total organic carbon analyses of surfactant modified zeolites revealed that hexadecyltrimethylammonium bromide has the highest affinity to be adsorbed on zeolite surface, whereas the octadecyltrimethylammonium bromide has the lowest affinity due to the possible hydrocarbon chain coiling. The surfactant modified zeolite samples were employed to study the influence of the different surfactants on the uptake of phenol, 4-chlorophenol and 4-nitrophenol onto the zeolitic tuff. It was found that there is a correlation between the chain length of the surfactant tail and the uptake of phenols on zeolite. However, the uptake of phenols at pH 9.3 was found to follow the order 4-nitrophenol > 4-chlorophenol > phenol.

**Key Words:** Surfactant modified zeolite, Jordanian zeolitic tuff, Cationic surfactants, Phenols uptake, Total organic carbon.

### INTRODUCTION

Zeolites are hydrated aluminosilicate materials having cage-like structure with internal and external surface areas of up to hundred square meters per gram and cation exchange capacities of up to several meq/kg<sup>1</sup>. Zeolites may be modified chemically in a number of different ways. Among other methods, the chemical modifications include changing the exchangeable ions, changing the Si/Al ratio by direct synthesis under different conditions, decationation to produce hydrogen zeolites and dealumination through acid treatment. The simplest and the most commonly applied modification method is the ion-exchange<sup>2</sup>.

Due to the permanent negative charges on their surfaces, zeolites can be modified with cationic surfactants. Such modification increases the sorption capability of zeolite towards non-polar hydrophobic organic contaminants and also to sorb oxyanions. It was observed that the longer the tail group of the cationic surfactant, the more stable the surfactants retained on the surface<sup>3</sup>. At very low concentration, the surfactant molecules in aqueous solutions exist as monomers. When the surfactant concentration exceeds the critical micelle concentration (CMC) the sorbed surfactant on zeolite forms bilayers (Fig. 1b)<sup>4</sup>.

When the surfactant concentration exceeds the critical micelle concentration (CMC) the sorbed surfactant on zeolite forms bilayers (Fig. 1b)<sup>4</sup>.

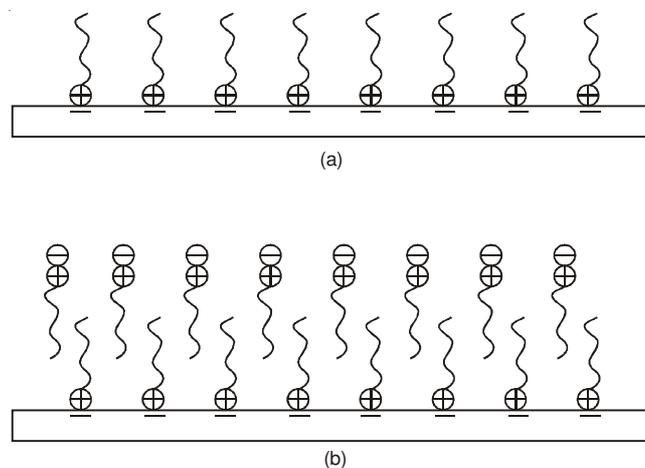


Fig. 1. Sorption of surfactant molecules as a monolayer (a) and bilayer (b) on zeolite surfaces [Ref. 4]

Surfactant modified zeolites (SMZ) are considered both physically and chemically stable sorbents<sup>5</sup>. Many recent studies on the properties of surfactant modified zeolites indicated that they are effective sorbents for multiple types of contaminants<sup>6,7</sup>. They can simultaneously remove organics such as benzene, toluene, phenol, xylene and aniline<sup>1,8,9</sup>, perchloroethylene<sup>10</sup>, dehydroabiatic acid<sup>11</sup>, fulvic acid<sup>12</sup> and inorganic cations and anions<sup>13-15</sup> from contaminated water and air.

Jordanian zeolitic tuff was discovered in Jordan at many parts of the country in 1987<sup>16</sup>. This local tuff has been chemically modified by different organic materials, *viz.*, urea and thiourea<sup>17</sup>, acetamide and N,N-dimethylformamide<sup>18</sup>, oxalic acid and salicylic acid<sup>19</sup>.

In this work, the Jordanian zeolitic tuff was chemically modified by four cationic surfactants having different chain lengths *viz.*, dodecyltrimethylammonium bromide (DDTMA-Br, 12 carbon atoms), tetradecyltrimethylammonium bromide (TDTMA-Br, 14 carbon atoms), hexadecyltrimethylammonium bromide (HDTMA-Br, 16 carbon atoms), and octadecyltrimethylammonium bromide (ODTMA-Br, 18 carbon atoms). Their capabilities to uptake phenol, 4-chlorophenol and 4-nitrophenol from water were investigated.

## EXPERIMENTAL

**Sample preparation:** Reddish zeolitic tuff from Tulul Al-Shahba in Northeast of Jordan was crushed by Jaw crusher (LECO) and sieved using vibrating sieving shaker (Retsch) to different meshes. The fraction of 0.25-0.50 mm was washed with distilled deionized water (conductivity = 0  $\mu\text{s}/\text{cm}$ ) several times until no suspended materials were observed in the leachate. The washed sample was dried in an oven at 110 °C and labeled Z.

**Surfactant modification:** Different cationic surfactants, *i.e.* dodecyltrimethylammonium bromide (DDTMA-Br, 98 %, from Sigma), tetradecyltrimethylammonium bromide (TDTMA-Br, 99 %, from Sigma), hexadecyltrimethylammonium bromide (HDTMA-Br, 96 %, from Fluka) and octadecyltrimethylammonium bromide (ODTMA-Br, from Aldrich) were used in the modification of zeolitic tuff. A 3.0 g sample of zeolitic tuff was mixed with 9 mL of 67 mM solution of the surfactants and shaken in a thermostatic shaker (Kuhner/ISF-1-W) at 25 °C for 8 h (150 rpm). Then the surfactant modified zeolite (SMZ) samples were washed thrice with 50 mL of distilled deionized water and dried overnight in an oven at 50 °C<sup>20</sup>. The resulting DDTMA-Br, TDTMA-Br, HDTMA-Br and ODTMA-Br modified zeolitic samples were kept in a desiccator and labeled DZ, TZ, HZ and OZ, respectively.

**Sample characterization:** Samples zeolitic tuff (Z), DZ, TZ, HZ and OZ were characterized using powder X-ray diffraction (XRD), X-ray fluorescence (XRF) and infrared spectroscopy (FT-IR) techniques, besides determining their total organic carbon (TOC) content. The XRD data were recorded with X'pert instrument powder diffractometer equipped with a cobalt anode (X-ray photons with  $\lambda = 1.78897 \text{ \AA}$ ). The XRF data were recorded with Diano-2023 X-ray fluorescence instrument. The infrared spectra were obtained using a double beam FTIR instrument (Jascow FTIR, 410). The TOC content was determined using a total organic carbon analyzer (LECO, 600-800).

**Phenols uptake:** A 0.4 g sample of zeolite (Z, DZ, TZ, HZ and OZ) were independently mixed with 10 mL of 100 ppm of phenol solution (phenol, 4-chlorophenol or 4-nitrophenol) buffered at pH 9.3 (using  $\text{NaCO}_3/\text{NaHCO}_3$  buffer solution). The SMZ/phenol mixtures<sup>8</sup> were shaken (150 rpm) at 25 °C for 24 h. After decantation, the clear supernatants were analyzed for their phenols equilibrium concentration using UV/Vis spectrophotometer (Jasco, V-530) at  $\lambda_{\text{max}} = 270, 280$  and 399 nm for phenol, 4-chlorophenol and 4-nitrophenol, respectively.

## RESULTS AND DISCUSSION

**Mineral content:** The X-ray diffraction analyses for raw zeolitic tuff (Z) and surfactant modified zeolite samples (DZ, TZ, HZ and OZ) are tabulated in Table-1. The mineral content of raw sample of zeolitic tuff was found to be anorthite (feldspar) as a major constituent, phillipsite (zeolite) and augite (pyroxene) as minor constituents, and hematite as a trace. The modification by the considered surfactants showed an increase of the phillipsite content, which may be due to the separation of zeolite from other minerals<sup>21</sup>. However, the chemical treatment of zeolite by the four cationic surfactants revealed that there are no significant structural changes. Janks and Cadena<sup>22</sup> reported that the only major effect of the surfactant treatment of zeolite was a change in the type of the exchangeable cations.

TABLE-1  
MINERAL CONTENT OF UNMODIFIED ZEOLITE (Z) AND THE SURFACTANT MODIFIED ZEOLITES (DZ, TZ, HZ AND OZ)

Sample	Phillipsite	Anorthite	Augite	Hematite
Z	Minor	Major	Minor	Trace
DZ	Major	Minor	Minor	Trace
TZ	Major	Minor	Minor	Trace
HZ	Major	Minor	Minor	Trace
OZ	Major	Minor	Minor	Trace

**Chemical composition:** In order to investigate the chemical composition, the X-ray fluorescence (XRF) analyses for raw zeolitic tuff (Z) and the surfactant modified zeolites samples (DZ, TZ, HZ and OZ) were performed. The results are shown in Table-2.

The loss on ignition (LOI) in surfactant modified zeolite (SMZ) samples was increased relative to raw zeolitic tuff due to the presence of surfactant loaded on zeolite surface. Consequently, the amounts of the surfactant loaded on zeolite may be estimated to follow the order HZ (1.91 %) > TZ (0.77 %) > OZ (0.17 %) ~ DZ (0.08 %).

The oxides' percentages shown in Table-2 reveal some changes in the chemical compositions of the SMZ samples, which can be attributed to the cation exchange that occurred between surfactants and exchangeable cations on the external surface of zeolite. The values of corrected percentages of surfactant modified zeolite samples showed that, the contents of  $\text{Fe}_2\text{O}_3$ , MnO, CaO,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  were decreased due to replacement of exchangeable cations by cationic surfactants as proposed by Erosy and Çelik<sup>23</sup>. The contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and MgO were increased due to the increase of phillipsite mineral content in the SMZ samples, as observed by XRD results.

TABLE-2  
CHEMICAL COMPOSITIONS (%) FOR RAW ZEOLITE (Z) AND  
THE SURFACTANT MODIFIED ZEOLITES (DZ, TZ, HZ AND OZ)

	Z	DZ	DZ <sup>a</sup>	TZ	TZ <sup>a</sup>	HZ	HZ <sup>a</sup>	OZ	OZ <sup>a</sup>
SiO <sub>2</sub>	37.94	38.77	38.80	38.68	38.98	37.54	38.27	38.75	38.82
Al <sub>2</sub> O <sub>3</sub>	13.30	13.59	13.60	13.64	13.79	13.23	13.49	13.53	13.55
Fe <sub>2</sub> O <sub>3</sub>	11.91	11.26	11.27	10.88	10.96	11.20	11.42	11.25	11.27
MnO	0.173	0.162	0.162	0.156	0.157	0.162	0.165	0.163	0.163
CaO	9.216	8.919	8.962	8.825	8.893	8.961	9.135	8.919	8.934
MgO	4.502	4.692	4.696	4.558	4.59	4.661	4.752	4.694	4.702
K <sub>2</sub> O	3.463	3.472	3.475	3.588	3.616	3.438	3.505	3.475	3.481
Na <sub>2</sub> O	2.383	2.119	2.121	2.090	2.106	2.004	2.043	2.114	2.118
TiO <sub>2</sub>	2.304	2.179	2.181	2.100	2.116	2.155	2.197	2.180	2.184
P <sub>2</sub> O <sub>5</sub>	0.900	0.850	0.851	0.822	0.828	0.840	0.856	0.843	0.844
Loss of ignition	13.90	13.98		14.67		15.81		14.07	

<sup>a</sup>Corrected for deposited amount of DDTMA-Br (0.08 %), TDTMA-Br (0.77 %), HDTMA-Br (1.91 %) and ODTMA-Br (0.17 %) calculated on the assumption of constant water content of 13.90 % as in Z.

**Total organic carbon (TOC):** In order to estimate the loaded amount of cationic surfactants on the surface of zeolite, the total organic carbon (TOC) technique for Z, DZ, TZ, HZ, and OZ samples was employed. As shown in Table-3, the total organic carbon contents (meq/100 g) in the zeolitic samples decrease in the following order HZ (0.15) > TZ ~ DZ (0.13) > OZ (0.09) > Z (0.00). The zeolitic tuff sample Z was found to have no organic carbon, which is expected because natural zeolite minerals are normally low in organic carbon content<sup>20</sup>. The highest carbon content was found in the zeolitic tuff sample modified by hexadecyltrimethylammonium bromide (HDTMA-Br) which is in a good agreement with the loss on ignition results. The HDTMA surfactant, which consists of 16-carbon atoms, showed a greater loading on zeolite surface than TDTMA (14-carbon atoms) and DDTMA (12-carbon atoms) due to the higher number of carbon atoms in the monoalkyl chain. It was reported in literature<sup>23</sup> that the amount of surfactants loaded on zeolite follows the trend HDTMA > TDTMA > DDTMA.

TABLE-3  
TOTAL ORGANIC CARBON (TOC) IN RAW  
ZEOLITE (Z) AND THE SURFACTANT MODIFIED  
ZEOLITES (DZ, TZ, HZ AND OZ)

Sample	Surfactant loading (meq/100 g)
Z	0.000
DZ	0.131
TZ	0.132
HZ	0.150
OZ	0.094

At very low concentration, the surfactant molecules exist as monomers in aqueous solutions. When the surfactant concentration exceeds the critical micelle concentration

(CMC), the sorbed surfactant on zeolite forms bilayers (Fig. 1b). The first layer retained by cation exchange whereas the second layer by hydrophobic bonding and stabilized by counterions<sup>3</sup>. However, the amounts of surfactants used for modifying zeolite, in this work, were selected to form bilayer coverage on the zeolite surface<sup>20</sup>. The octadecyltrimethyl ammonium bromide (ODTMA-Br) surfactant showed the lowest loaded amount among other surfactants, which indicates a monolayer loading of ODTMA rather than a bilayer. Such different behaviour may be attributed to that the hydrocarbon chain of surfactant when exceeds 16 carbon atoms tends to coil upon itself.

**Infrared spectroscopy (FT-IR):** The infrared absorption bands for the studied pure surfactants, raw zeolite (Z), and the surfactant modified zeolites (DZ, TZ, HZ and OZ) were measured. Some characteristic peaks are given in Table-4. As shown in Table-4, the symmetric stretching vibration bands of CH<sub>2</sub> moiety ( $\nu_{\text{sy}}[\text{CH}_2]$ ) show no significant shifts (2850 cm<sup>-1</sup>). The asymmetric stretching vibration bands of CH<sub>2</sub> moiety ( $\nu_{\text{as}}[\text{CH}_2]$ ) in pure surfactants were shifted to lower frequencies (ca. 10 cm<sup>-1</sup>) when sorbed on zeolite surface. This shift in  $\nu_{\text{as}}$  values between the pure surfactants and the SMZ's is attributed to the interaction between the surfactants and the zeolite surface. The two characteristic bands for zeolite (phillipsite), which appears at 1647 cm<sup>-1</sup> [ $\beta(\text{H}_2\text{O})$ ] and 1031 cm<sup>-1</sup> ( $\nu_{\text{as}}[\text{Si-O-Si(Al)}]$ ) showed no significant shifts due to that the sorption of surfactants occurs only on the external surface of the zeolite. Thus, the inner channel water as well as the aluminosilicate framework of phillipsite did not suffer a remarkable change by surfactant modification.

**Phenols uptake:** The phenols concentration data were used to calculate the distribution coefficient,  $K_d$  (mL/100 g), according to eqn. 1<sup>29</sup>:

TABLE-4  
INFRARED ABSORPTION OF SOME CHARACTERISTIC BANDS (cm<sup>-1</sup>) OF SURFACTANTS (DDTMA Br, TDTMA Br, HDTMA Br AND ODTMA Br), RAW ZEOLITE (Z) AND THE SURFACTANT MODIFIED ZEOLITES (DZ, TZ, HZ AND OZ)

Z	DDTMA Br	DZ	TDTMA Br	TZ	HDTMA Br	HZ	ODTMA Br	OZ	Assignment <sup>a</sup>
-	2930s	2921m	2931s	2921m	2932s	2920m	2930s	2919m	$\nu_{\text{as}}[\text{CH}_2]$ at 2926 <sup>24</sup> , 2920 <sup>25</sup>
-	2850s	2852m	2848s	2852m	2850s	2851m	2848s	2850m	$\nu_{\text{sv}}[\text{CH}_2]$ at 2853 <sup>24,26,27</sup>
1647m	-	1649m	-	1649m	-	1647m	-	1647m	$\nu[\text{H}_2\text{O}]$ of Ph at 1650 <sup>28</sup>
1031vs	-	1034vs	-	1033vs	-	1033vs	-	1033vs	$\nu_{\text{as}}[\text{Si-O-Si(Al)}]$ of Ph at 1025-1050 <sup>29</sup>

<sup>a</sup> $\nu_{\text{as}}$  = Asymmetric stretching vibration,  $\nu_{\text{sv}}$  = Symmetric stretching vibration,  $\beta$  = Bending, Ph = Phillipsite.

$$K_d = \frac{[V_{\text{spike}} \times (C_{\text{spike}} - C_{\text{final}})]}{C_{\text{final}} \times 100 \times m_{\text{smz}}} \quad (1)$$

where  $C_{\text{spike}}$  is the phenol concentration in the spike solution before the addition of the sequestering agent ( $\text{mg L}^{-1}$ ),  $C_{\text{final}}$  is the phenol concentration in the solution after contact with the sequestering agent ( $\text{mg L}^{-1}$ ),  $m_{\text{smz}}$  is the sequestering agent mass (g) and  $V_{\text{spike}}$  is the volume of the spike solution (mL).

The results of the efficiency, expressed by the distribution coefficients ( $K_d$ ), of the raw-zeolite (Z) as well as the surfactant modified zeolites (SMZ) for removal of phenol, 4-chlorophenol and 4-nitrophenol from aqueous solutions are shown in Table-5.

Sample	K <sub>d</sub> (mL/100 g)		
	Phenol	4-Chlorophenol	4-Nitrophenol
Z	0.006	0.192	0.061
DZ	0.133	0.451	0.529
TZ	0.282	1.016	4.266
HZ	0.313	1.118	5.374
OZ	0.171	0.143	0.238

According to Table-5, the raw zeolite sample (Z) shows low  $K_d$  values for the three types of phenols relative to the surfactant modified zeolites (SMZ). The ability of zeolite to uptake phenol from aqueous solution was increased by the replacement of its inorganic exchangeable cations with organic cationic surfactants, which is in agreement with the literature<sup>30</sup>. Moreover, it has been reported that the longer the hydrocarbon chain of the tail group, the more stable is the surfactant molecules on clay minerals surfaces and the more efficient is the removal of organic contaminants from aqueous solutions<sup>4,31</sup>. In this study, the results of phenols uptake showed a clear dependence of uptake on the number of carbon atoms in the monoalkyl chain of the surfactant as shown in Fig. 2. Up to 16-carbon atoms chain length, the  $K_d$  values were increased with increasing the chain length. The hexadecyltrimethylammonium-zeolite (HZ) sample showed the most efficient sorbent among other surfactant modified zeolite samples, which is in agreement with the literature<sup>23</sup>.

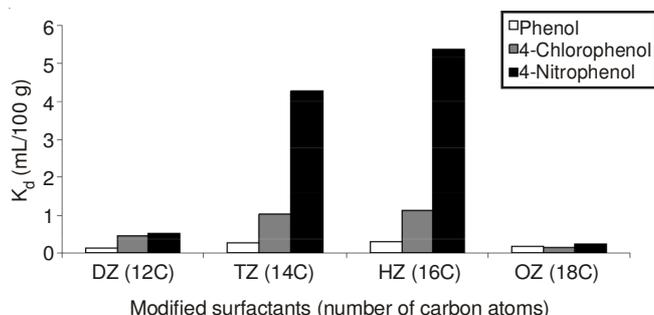
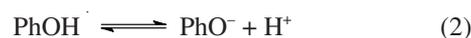


Fig. 2. Relationship between the  $K_d$  values for phenol, 4-chlorophenol, and 4-nitrophenol uptake on surfactant modified zeolites (DZ, TZ, HZ and OZ) and the number of carbon atoms of the surfactant's monoalkyl chain

In aqueous solutions, phenol exists in a pH-dependent equilibrium as represented in eqn. 2.



The uptake of phenols by surfactant modified zeolites (SMZ) in this work was performed at pH 9.3 (SMZs are often chemically stable at a wide range of pH 3-10)<sup>32</sup>. The pKa values for phenol, 4-chlorophenol and 4-nitrophenol are 9.89, 9.20 and 7.15, respectively<sup>33</sup>. At pH 9.3, phenol exists mainly in a molecular form (PhOH), whereas the 4-chloro and 4-nitrophenols are mainly in anionic phenolate forms (PhO<sup>-</sup>). Therefore, neither substituted phenols (chloro- and nitrophenols) nor unsubstituted phenol are expected to be sorbed on the negatively charged surface of raw zeolite sample (Z). On the other hand, the uptake of phenols on surfactant modified zeolite samples (DZ, TZ and HZ) was found to follow the order: 4-nitrophenol > 4-chlorophenol > phenol. This can be attributed to the extent of the corresponding phenolate anions for each phenol at pH 9.3 (which is in the same order 4-nitrophenol > 4-chlorophenol > phenol). Thus, the more the amount of phenolate anions in solution the more the interaction of these anions with the positively charged surfactant bilayer (Fig. 1b) loaded on zeolite surface.

The zeolite modified by octadecyltrimethylammonium bromide (OZ) showed a low phenols uptake (low  $K_d$  values) due to the coiling of the hydrocarbon chain (18 carbon atoms) of the surfactant, which prevents the formation of the positively charged surfactant bilayer.

## Conclusion

The type of the cationic surfactant used for modification of zeolite did not change the mineral content of the zeolitic tuff, which was clear from the XRD and FTIR results. This is because the surfactant loading was occurred only on the zeolite surface. The loss of ignition and total organic carbon results revealed that the most loaded cationic surfactant on zeolite surface is the hexadecyltrimethylammonium bromide. The  $K_d$  values for the phenols uptake, at pH 9.3, were found to follow the order: 4-nitrophenol > 4-chlorophenol > phenol, which reflects the interaction between the corresponding phenolate anions in solution and the positively charged surfactants bilayers on zeolite surface.

## ACKNOWLEDGEMENTS

The authors would like to thank the Natural Resources Authority for using their analytical facilities and to Dr. Khalil Khader, The Hashemite University for total organic carbon analyses.

## REFERENCES

- M. Ghiaci, A. Abbaspur, R. Kia and F. Seyedeyn-Azad, *Sep. Purif. Technol.*, **40**, 217 (2007).
- R.M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London (1978).
- Z. Li, I. Anghel and R.S. Bowman, *J. Dispersion Sci. Technol.*, **19**, 843 (1998).
- Z. Li and R.S. Bowman, *Environ. Sci. Technol.*, **31**, 2407 (1997).
- R.S. Bowman, Z. Li, S.J. Roy, T. Burt, T.L. Johnson and R.L. Johnson, in eds.: J.A. Smith and S.E. Burns, *Pilot Test of a Surfactant-Modified Zeolite Permeable Barrier for Groundwater Remediation*, In *Physico-chemical Groundwater Remediation*, Kluwer Academic/Plenum Publishers (2001).

6. P. Zhang, D.M. Arudzega and R.S. Bowman, *J. Environ. Qual.*, **36**, 1069 (2007).
7. X.-W. Wu, H.-W. Ma, J.-H. Li, J. Zhang and Z.-H. Li, *J. Colloid Interface Sci.*, **315**, 555 (2007).
8. Z. Li, T. Burt and R.S. Bowman, *Environ. Sci. Technol.*, **34**, 3756 (2000).
9. Y. Liu, X. Liu and J. Wang, *Huanjing Huaxue*, **22**, 373 (2003).
10. Z. Li and R.S. Bowman, *Environ. Sci. Technol.*, **32**, 2278 (1998).
11. S.C. Bouffard and S.J.B. Duff, *Wat. Res.*, **34**, 2469 (2000).
12. S. Wang, Z. Luan, B. Gao, Q. Yue and L. Yao, *Huanjing Huaxue*, **23**, 659 (2004).
13. M. Majdan, O. Maryuk and A. Gladysz-Plaska, *Przem. Chem.*, **84**, 755 (2005).
14. G.M. Haggerty and R.S. Bowman, *Environ. Sci. Technol.*, **28**, 452 (1994).
15. E. Popovici, C. Hristodor, G. Burtica, R. Pode, M. Petruc and A. Hanu, *Environ. Eng. Manage. J.*, **1**, 557 (2002).
16. I.M. Dwairi, A Chemical Study of the Palagonitic Tuffs of the Aritain Area of Jordan with Special Reference of Nature, Origin and Industrial Potential of the Associated Zeolite Deposites. Ph.D. Thesis, Hull University, UK (1987).
17. R.I. Yousef, M.F. Tutanji, G.A.W. Derwish and S.M. Musleh, *J. Colloid Interface Sci.*, **216**, 348 (1999).
18. S.M. Musleh, R.I. Yousef and A.A. Amro, *Asian J. Chem.*, **21**, 6833 (2009).
19. S.M. Musleh, R.I. Yousef and A.A. Amro, *Ultra Science*, **17**, 365 (2005).
20. Z. Li, D. Alessi and L. Allen, *J. Environ. Qual.*, **31**, 1106 (2002).
21. H. Lee, Y.S. Park, T.S. Kim, Y. Lee and K.B. Yoon, *Chem. Mater.*, **14**, 3260 (2002).
22. J.S. Janks and F. Cadena, The 66th Annual and Technical Conference and Exhibition, Society of Petroleum Engineers: TX, USA (1991).
23. B. Erosy and M.S. Çelik, *Clays Clay Miner.*, **51**, 172 (2003).
24. A. Suetsugu, T. Miyazaki and M. Nakano, *Soil Sci. Soc. Am. J.*, **65**, 1129 (2001).
25. J.M. Mellott, W.A. Hayes and D.K. Schwartz, *Langmuir*, **20**, 2341 (2004).
26. W.A. Hayes and D.K. Schwartz, *Langmuir*, **14**, 5913 (1998).
27. H.W. Marel and H. Beutelspacher, Atlas of Infrared Spectroscopy of Clay Minerals, Elsevier Scientific, Amsterdam (1976).
28. J.A. Gadseden, Infrared Spectra of Minerals and Related Inorganic Compounds, Butterworths, London (1975).
29. ASTM-American Society for Testing & Materials, Standard Test Method for 24-h Batch-Type Measurement of Contamination Sorption by Soils and Sediments, (Designation: D 4646-87), ATSM, Philadelphia, pp. 125-128 (1993).
30. P. Zhang and D.L. Sparks, *Soil Sci. Soc. Am. J.*, **57**, 340 (1993).
31. Z. Li, *Langmuir*, **15**, 6438 (1999).
32. Z. Li, S.J. Roy, Y. Zou and R.S. Bowman, *Environ. Sci. Technol.*, **32**, 2628 (1998).
33. T.W.G. Solomons, Organic Chemistry, John Wiley & Sons Inc., USA, edn. 6 (1996).