Application of activated zeolite in the advanced treatment of potable water

Changsheng Peng and Hong Meng

ABSTRACT

The natural clinoptilolite originating from Baiyin in Gansu province was selected as filter material for the advanced treatment of potable water in this investigation. The optimal parameters for zeolite activation were obtained by a series of experiments: the concentration of $MgCl_2$ is 20%, the temperature of heating is 300°C and the contact time is 20 minutes. This kind of activated zeolite was applied in Lanzhou Railway waterworks as filter material for the advanced treatment of potable water, and its adsorption effects were observed and compared with that of activated carbon. The observed date indicated that the activated zeolite could remove hardness, iron, manganese, arsenic, anion detergent, sulfate and soluble solid effectively. As a filter material, the activated zeolite was similar to the activated carbon, but much cheaper for preparation and much easier for regeneration, so it is possible to substitute activated zeolite for activated carbon in the advanced treatment of potable water.

Key words | activated carbon, activated zeolite, advanced treatment, potable water

Changsheng Peng (corresponding author)
College of Environmental Science and Engineering,
Ocean University of China,
Qingdao 266100,
China
Tel.: +86(532)66782011
Fax: +86(532)66782012
E-mail: *cspeng@ouc.edu.cn*,
Web site: http://www2.ouc.edu.cn/huanjing/news/view.asp?id = 225

Hong Meng
School of Chemical Engineering,
Beijing University of Chemical Technology,
Beijing100029,
China

INTRODUCTION

The conventional water treatment process, mixing and flocculation → sedimentation → granular filter → disinfection with Cl_2, is still used in most waterworks in China. This conventional process is effective for the removal of turbidity and color, but ineffective for organic matter, heavy metal and bacteria, which cannot meet the demand for high quality potable water. So a unit process of activated carbon filter is added behind the conventional process in some waterworks for the advanced treatment of potable water (Zhang *et al.* 2005; Ji *et al.* 2005; Liang 2005). However, the high cost (750 ~ 1,300 USD per ton) for purchase and complicated techniques for regeneration limit the application of activated carbon in potable water treatment in most of the waterworks.

Natural zeolite, a group of crystalline aluminosilicates with the composition of SiO_2, Al_2O_3, CaO, MgO and Na_2O, has attracted increasing attention for the past two decades in the field of pollution control. Due to its specific structure and adsorption and ion-exchange abilities, natural zeolites have found applications in the field of water treatment, such as industrial wastewater purification and municipal water treatment (Meng *et al.* 2001; Xiao 2002; Trgo & Peric 2003; Farkas *et al.* 2005). But most research on the application of zeolite in water treatment are still limited to the laboratory stage, in the world, especially in China.

The price of natural zeolite is generally 50 ~ 100 USD per ton in China, and the cost of zeolite activation can also be controlled within 120 USD per ton. Moreover, it is relatively easier and cheaper to regenerate the saturated zeolite. So, substituting activated zeolite for activated carbon is attractive in the advanced treatment of potable water, but there is no information about this in China.

In this paper, the optimal parameters for a kind of zeolite activation were investigated, and the activated zeolite was applied in a waterworks as a filter material for the advanced treatment of potable water, paralleled with activated carbon. The variety of water quality before and after the process of filter by activated zeolite or activated carbon was also

doi: 10.2166/aqua.2007.003

Table 1 | The chemical composition of the natural clinoptilolite originated from Baiyin (wt%)

Composition	SiO_2	Al_2O_3	CaO	K_2O	MgO	FeO	Na_2O	TiO_2	Loss of ignition
Content	68.52	11.49	3.27	1.66	1.13	1.04	0.61	0.10	12.18

investigated, in order to estimate the feasibility of substituting activated zeolite for activated carbon.

METHODS

Zeolite material

A kind of natural clinoptilolite originated from Baiyin in Gansu province was selected here for the investigation. The apparent and real density of this black red zeolite are 1.4 g/mL and 2.5 g/mL, respectively. And its chemical composition is listed in Table 1.

Determination of zeolite exchange capacity

First, put the zeolite sample 0.5 g into a 250 ml conical beaker; then put 100 ml phosphide-containing water (which is prepared from Sodium Phosphate diluted in distilled water with the concentration of PO_4^{3-} 250 mg/L) into the beaker; and then shake this mixture at 220 rpm for 60 minutes at ambient temperature; finally, the remaining concentration of phosphide in the prepared water was determined by stannous chloride reducing method after 15 minutes quiet setting (SEPA 1989). The exchange capacity of zeolite can be calculated from the variety of phosphate concentration (determination with PO_4^{3-}) in the prepared water.

RESULTS AND DISCUSSION

Zeolite activation

The selection of activate chemicals

Some natural zeolite with the size of 10 ~ 30 mesh was put into a beaker, which is full of $MgCl_2$ and $CaCl_2$ mixing solution. After 48 hours immersed in this solution, zeolite was taken out and rinsed 3 times with distilled water; and then the sample was heated at a temperature of 150°C for 1.5 hours. Different exchange capacities of zeolite treated with different concentrations of $MgCl_2$ and $CaCl_2$ are listed in Table 2.

It can be seen from the data in Table 2 that $MgCl_2$ could strongly improve exchange capacity of activated zeolite,

Table 2 | Effect of concentration of $MgCl_2$ and $CaCl_2$ on the exchange capacity of zeolite

$MgCl_2$(%): $CaCl_2$(%)	0: 10	0: 20	10: 0	20: 0	20: 10	30: 0
Exchange capacity (mg/g)	2.31	2.67	3.01	4.02	4.08	4.48

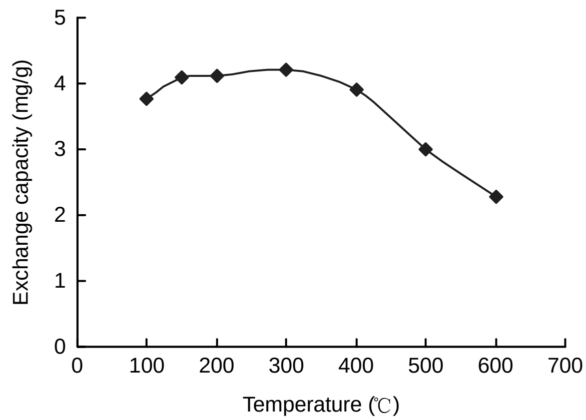

Figure 1 | Exchange capacity of zeolite as a function of activation temperature at 1.5 hours heating time.

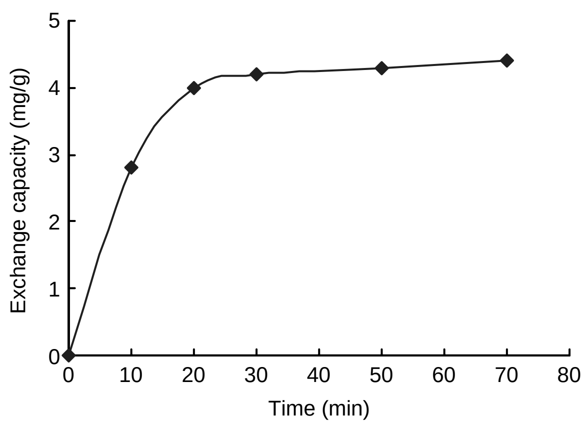

Figure 2 | Exchange capacity of zeolite as a function of contact time.

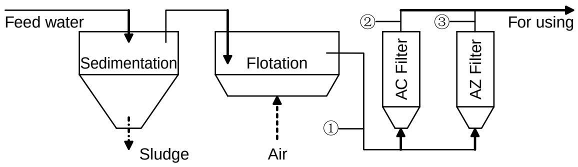

Figure 3 | Flow diagram of water treatment for potable water in the waterworks (①,② and ③ represent the three points of sample collection for Flotation tank overflow, Activated carbon filter overflow and Activated zeolite filter, respectively).

while $CaCl_2$ could only weakly. So only $MgCl_2$ solution was selected as an activate chemical with optimal concentration of 20%, according to the experimental results and considering the cost of activation.

Effect of heating temperature on zeolite activation

After immersed in 20% $MgCl_2$ solution for 48 hours, zeolite was taken out and rinsed 3 times with distilled water; and then was heated at different temperatures for 1.5 hours in muffle. The results are illustrated in Figure 1 in the form of exchange capacity vs. heat temperature.

It can be seen from the graph that the exchange capacity of activated zeolite increased with increasing temperature before 300°C (from 3.76 mg/g of 100°C, 4.09 mg/g of 150°C, 4.11 mg/g of 200°C, to 4.20 mg/g of 300°C), but decreased with increasing temperature after 300°C (from 3.90 mg/g of 400°C, 3.01 mg/g of 500°C, to 2.27 mg/g of 600°C), so 300°C was chosen as the optimal activation temperature.

Effect of contact time on exchange capacity of zeolite

Exchange capacity of activated zeolite changed with the changing of contact time, and this change trend is illustrated in Figure 2.

The exchange capacity of activated zeolite increased with increasing contact time. These increases were strong in the range of 0 to 20 minutes, and then became mild, and 90% of the total exchange capacity can be reached at 20 minutes, as shown in Figure 2. Hence, 20 min was considered to be a reasonable contact time.

Application of activated zeolite in a waterworks

The activated zeolite prepared from Baiyin clinoptilolite, by the optimal activation method mentioned above, was applied in Lanzhou Railway Waterworks for advanced treatment of potable water. In this waterworks, two parallel filter units (one is activated carbon filter, and another is activated zeolite filter) were used and investigated at the same time, in order to compare the effects of water purification by activated carbon and activated zeolite.

General situation of the waterworks

Lanzhou Railway waterworks can produce potable water from the Yellow River, with the throughput of $3 \times 10^4 m^3$ per day. Figure 3 shows the flow diagram of water treatment of the waterworks: feed water from the Yellow River was

Table 3 | Comparison of water quality between China National Water Quality Standard and the overflow of waterworks' flotation tank (partly)

mg/L	Hardness	Soluble solid	Iron	Manganese	Arsenic	Sulfate	Chloride	Anion detergents
Standard	450	1,000	0.3	0.1	0.05	250	250	0.3
Overflow	223 ~ 176	355 ~ 184	0.05 ~ 0.03	0.09 ~ 0.02	0.5 ~ 0.01	61 ~ 41	49 ~ 30	0.1 ~ 0.01

Table 4 | Operation parameters of the activated zeolite and activated carbon towers

Parameters					
Tower	Particle size (mm)	Filter velocity (m/h)	Contact time (min)	Expansivity (%)	Wash intensity ($L/m^2 \cdot h$)
Activated zeolite	0.5 ~ 2	8.9	20	5.25	16.0
Activated carbon	0.5 ~ 2	8.7	20	3.46	12.2

Table 5 | Advanced treatment for potable water with activated zeolite or activated carbon (mg/L)

		Time							
Items	Overflow	October	November	December	January	February	March	April	May
Hardness	Flotation	223	254	217	244	213	215	178	176
	AZ	201	203	180	228	208	201	178	173
	AC	203	203	212	215	208	201	176	172
Soluble solid	Flotation	184	270	274	304	342	355	264	256
	AZ	170	261	255	268	319	328	240	231
	AC	163	254	265	286	334	338	232	230
Iron	Flotation	0.05	0.05	0.04	0.05	0.04	0.04	0.04	0.03
	AZ	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.00
	AC	0.04	0.04	0.02	0.02	0.02	0.03	0.04	0.03
Manganese	Flotation	0.05	0.02	0.05	0.05	0.05	0.05	0.09	0.07
	AZ	0.01	0.01	0.03	0.03	0.03	0.03	0.05	0.04
	AC	0.01	0.01	0.03	0.03	0.03	0.04	0.05	0.04
Arsenic	Flotation	<0.01	<0.01	0.05	0.01	0.03	0.5	0.014	0.013
	AZ	0.00	<0.01	0.046	0.013	0.022	0.031	0.010	0.009
	AC	<0.01	<0.01	0.020	0.026	<0.01	0.17	0.009	0.008
Sulfate	Flotation	59	60	61	60	60	59	42	41
	AZ	58	58	58	56	56	56	40	40
	AC	59	60	61	58	60	59	42	41
Chloride	Flotation	32	33	49	42	43	46	30	32
	AZ	32	33	49	44	47	54	30	32
	AC	34	33	48	44	45	59	31	31
Anion detergents	Flotation	0.03	0.1	0.03	0.06	0.05	0.06	0.03	0.01
	AZ	0.02	0.00	0.24	0.04	0.02	0.04	0.01	0.00
	AC	0.03	0.00	0.28	0.04	0.03	0.04	0.01	0.00

Note: AZ is the abbreviation for activated zeolite, and AC is the abbreviation for activated carbon.

Table 6 | Average value of water quality of the overflow from activated zeolite tower in 1999 (mg/L)

Items	Iron	Manganese	Arsenic	Chloride	Fluoride	Ammonia-N	Nitrate-N	Nitrite-N
Overflow	0.025	0.02	0.01	40	0.25	0.226	2.49	0.02

firstly treated by sedimentation process; and then the overflow was treated by flotation process; lastly, the water was passed through an activated carbon filter or an activated zeolite filter, before being used as potable water. The National Water Quality Standard of China and the water quality of overflow from the waterworks' flotation tank are listed partly in Table 3.

Advanced treatment for the potable water

In the filter unit, one part of the overflow from the flotation tank passed through the activated zeolite tower, and the other part passed through the activated carbon tower, as shown in Figure 3. Both the two towers have the same size with 1.2 m in diameter and 2.89 m in height. Operation parameters of the two towers are listed in Table 4.

If turbidity of the filter tower overflow exceeding 3.0 mg/L, the filter process would be paused, while the filter materials (activated carbon or activated zeolite) were washed from obverse 15 minutes and reverse 15 minutes, respectively. If the water quality cannot be improved by the filter process when activated carbon or activated zeolite was adsorption saturation, activated carbon would be exchanged, and activated zeolite would be regenerated. With the condition of NaCl concentration 5% ~ 8%, filter velocity 8 m/hour and regeneration time 5 hours, exchange capacity of the zeolite could be recovered 94% ~ 97%.

Since October 1997, an activated zeolite tower has been applied for the advanced treatment of potable water, paralleled with an activated carbon tower, in Lanzhou Railway Waterworks. Water quality of overflows from the flotation tank, activated zeolite tower and activated carbon tower were always investigated, and some investigation data are listed in Table 5 and Table 6. All of the water quality analysis was done by the methods described in *Examination and Analysis Methods for Water and Wastewater* (SEPA 1989)

The observed date, as shown in Tables 5 and 6, indicated that the activated zeolite could remove hardness, iron, manganese, arsenic, anion detergent, sulfate and soluble solid effectively. As a filter material, the activated zeolite is similar to the activated carbon, but much cheaper for preparation and much easier for regeneration, so it is possible to substitute activated zeolite for activated carbon in the advanced treatment of potable water.

CONCLUSIONS

Natural zeolite is widespread in China, and its price is only 10% ~ 20% of activated carbon, even considering the cost of zeolite activation. So it is possible to decrease greatly the treatment cost for waterworks in China, if activated carbon can be substituted by activated zeolite.

The optimal activation parameters for the clinoptilolite originating from Baiyin are 20% $MgCl_2$ solution, 300°C heating temperature and 20 minutes contact time.

The real application of the activated zeolite in Lanzhou Railway Waterworks indicated that the zeolite could remove hardness, iron, manganese, arsenic, anion detergent, sulfate and soluble solid effectively. Moreover, it can be seen from the long time operation that the filter unit of activated zeolite was stable for contaminant removing and water purifying. So it is possible to substitute activated zeolite for activated carbon in the advanced treatment of potable water.

REFERENCES

Farkas, A., Rozic, M. & Mikocevic, Z. B. 2005 Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials* **117**(1), 25–33.

Ji, M., Yang, J. & Sun, L. N. 2005 Study on removal micro-organic matter of water by activated carbon. *China J. Public Health* **21**(3), 291–292.

Liang, X. 2005 Application of activated carbon pretreatment in softening water station. *China Water and Wastewater* **21**(2), 74–75.

Meng, H., Peng, C. & Xiao, J. 2001 Study on removal phosphide from wastewater by activated zeolite. *Multipurpose Utilization of Mineral Resources* **22**(4), 10–14.

SEPA 1989 *Examination and Analysis Methods for Water and Wastewater*. China Environmental Science Press, Beijing, China.

Trgo, M. & Peric, J. 2003 Interaction of the zeolite tuff with Zn-containing simulated pollutant solutions. *Journal of Colloid and Interface Science* **260**(1), 166–175.

Xiao, J. 2002 Research on removing ammonia - nitrogen from wastewater by actived zeolite. *J. Lanzhou Railway University (Natural Sciences)* **21**(1), 87–89.

Zhang, S., Guo, Y. & Zhu, X. 2005 Study on advanced purification of discharge water of Baiguishan Water Plant by IBAC. *Techniques and Equipment for Environmental Pollution Control* **6**(8), 72–74.

First received 15 June 2006; accepted in revised form 25 December 2006