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Application of Iranian natural zeolite and blast furnace slag as slow sand filters media for water softening

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ABSTRACT

Aims: The aim of this study was to determine water softening behavior of Iranian natural zeolite and blast furnace slag (BFS) as materials of slow sand filters (SSFs) in small communities' water resources.
Materials and Methods: Three filters setups were prepared from the plexiglass tubes each by 9 cm inner diameter and 120 cm height. The used filter media were included conventional sand, BFS and Iranian natural zeolite. The filtration rate was adjusted between 0.1 and 0.24 $m^3/m^2/h$ and hence that the flow rate of each filter was 1.5 L/h. Turbidity, total hardness and EC of water samples were analyzed before and after the treatment process according to standard methods.
Results: The mean turbidity removal efficiencies in the studied filters were 98.82%, 98.98% and 98.97% for conventional SSF, slag modified filter (SMF) and zeolite modified filter (ZMF), respectively. The mean EC reduction efficiencies in SSF, SMF and ZMF also were similar and were 9.99%, 11.02% and 10.73%, respectively. The mean total hardness removal efficiencies in SSF, SMF and ZMF were 21.19%, 51.95% and 66.3%, respectively.
Conclusions: It is concluded from this study that modified filter media, SMF and ZMF, are very good options for total hardness and turbidity removals in communities that have some problem with this parameter.

Key words: Hardness, modified slow sand filter, physicochemical quality, water resources

INTRODUCTION

In the absence of access to safe drinking water resources, decentralized drinking water treatment enhance the quality of potable water resources for poor communities.[1] Slow sand filter (SSF) is one of the earliest forms of potable water resource treatment that remains as an important process for water purification throughout the world.[2] The major aims of SSF application are primarily coliforms removal and then turbidity removal.[3]

Some ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) are released into water resources as it dissolves rocks and minerals.[4] These cations as well as other ions such as iron, manganese and strontium can cause water hardness.[5] Hard water can cause scale buildup in water distribution network,

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fixtures and appliances and can in turn cause a drop in performance. The hardness of drinking water is determined mainly by its content of Ca^{2+} and Mg^{2+}. Water softening is defined as a treatment process where the Ca^{2+} and Mg^{2+} ions are removed from water.[4] Natural ion-exchangers (zeolites) such as clinoptilolite are crystallized, hydrated alumosilicate alkaline and earth alkaline cations. These exchangers possess endless 3-D crystal structures, which make them hard in water and insoluble[6] and exchanges one ion from the water with another one in the zeolite. Zeolites exchange sodium (Na^{+}) with Ca^{2+} and Mg^{2+}. These natural green sands have very good exchange capabilities and are widely used.[7] The process of ions exchange is a heterogeneous process while the zeolite structure (the changer of ion) practically does not change.[6] Natural zeolites from natural sources of SiO_4 and Al_2O_3 have good efficiency in water and wastewater treatment due to their low cost, high ion-exchange capacity and adsorption capabilities that has been reported in several works.[8-11]

Blast furnace slag (BFS) is a by-product of steel plants. When the metallurgical smelting process is completed, the lime in the flux is chemically combined with the aluminates and silicates of the ore and coke ash to form a non-metallic product called BFS. During the period of cooling and hardening from its molten state, BFS can be cooled in several ways to form any of several types of BFS products.[12] Slag, which consists of calcium oxide, aluminum oxide and other metal oxides, is an abundant by-product in steel-making process. It has been used as adsorbents to remove various heavy metals. According to a previous research, in these cases the major removal mechanisms are precipitation and adsorption on the surface of metal oxide.[13]

Ahammed *et al*., in 2010 used a two-media filter for bacteria and heavy metals removal from natural waters. It was resulted that these filters had high removal potential.[14] In another study carried out in 2007 using modified-median filter fluoride, arsenic and coliform bacteria were removed from water properly.[15] Another study in 2011 showed that 97% reduction of total and fecal coliform and also turbidity can be obtained using household sand filter. This filter has been applied for low quality water treatment. However, the biological sand filter (BSF) showed suitable option for developing countries to promote physiochemical quality of water.[16] Bleiman *et al*., in 2010 used chitosan-clay composites packed column filters to remove selenium from drinking water. The results of this study showed that selenium removal increased with the formation of selenate in water.[17] In 2011, researchers removed arsenic from drinking water using modified natural zeolite. They showed that adsorbent characterization can be affected by some parameters such as surface morphologies, chemical composition, physical properties and specific surface areas of unmodified and modified zeolites. On the other hand, the amount of arsenic adsorbed on the adsorbents not only depends upon the iron concentration in the clinoptilolite, but also depends on the initial arsenate concentrations.[18] Another study in 2011 showed the water softening behavior of sand materials such as natural zeolites in some locations of Rameswaram Island, India. It was resulted that the water softening efficiency was increased according to the increase of NaCl concentration, initial Ca^{2+} concentration and bed depth.[19] In another study in 2002, researchers used granular slag columns for lead removal. It was concluded that the apparent mechanisms of lead removal by this column are sorption (ion exchange and adsorption) on the slag surface and precipitation.[20]

As conventional SSFs only can remove coliforms and turbidity, modification techniques such as changing filter media can enhance efficiency removal of other water dissolved pollutants such as hardness agents (Ca^{2+}, Mg^{2+} and etc.). Therefore in this study, low cost materials such as zeolite and BFSs that have adsorption[21] or removal capability[19] were used as filter media. Thus, the aim of this study was to determine water softening behavior of developed SSF materials: Iranian natural zeolite and BFS in small communities' water resources. The turbidity and electrical conductivity (EC) of studied filter media also were compared.

MATERIALS AND METHODS

Filter media preparation

For filter media preparation, one of the essential stages is determination of solubility degree of filter media.[22] It was determined in acidic media by dipping 10 g of each filter media in 32 ml pure hydrochloric acid, which was mixed with 50% of distilled water and was contacted for 30 min in the lab ambient temperature. The contacted filter media was rinsed, dried at 110°C and weighted. Finally, the degree of solubility was calculated by dividing the weight lost to the initial weight and multiplying by 100. It should be noted that the dissolution rate of each filter media was not >5%.

Experimental setup

The experimental setup of this study is illustrated in Figure 1. As can be seen, pilot plant was consisting of several parts such as one water reservoir and three separated filters. Each filter had 9 cm inner diameter and 120 cm height that were prepared from plexiglass tubes. Other parts were consisted of an electro pump and hose connections. For modification of conventional SSF the zeolite and BFS were used as filter media.

The first set of SSFs [Figure 1a] similar to conventional SSFs was filled only by sand as filter media. It was maintained as control. The second set of SSFs [Figure 1b], was modified by replacing the 20 cm BFS (prepared from Isfahan steel mill company) instead of conventional sand of the bottom part. The third set of SSFs [Figure 1c], also was modified by replacing the 20 cm natural zeolite, clinoptilolite, (purchased from Miyaneh mine, North West of Iran and Semnan mine, North East of Iran) instead of conventional sand of the bottom part.

Pilot plant study

In this study, water resource for all study stages was tap water that supplied from deep well around of Zayandehroud river, Isfahan, Center of Iran. Pilot plant was included a reservoir that was filled by water and had a float sensor that was sensitive to the water surface changes. Three SSFs (one as control [Figure 1a] and two as modified types [Figure 1b and c]) were connected to the water reservoir by connection hoses and then water was pumped to each filter setup. To set a fixed height of water on the filter media (51 cm), excess water was returned to the reservoir tank through return hose. Filtration rate was adjusted between 0.1 and 0.24 $m^3/m^2/h$[23] so that the flow rate of each filter was 1.5 L/h.

Turbidity was added manually to the water reservoir by adding kaolinite clay. The water source had substantially excess total hardness and EC.

Analysis

The study parameters were included water Turbidity as nephelometric turbidity units (NTU), EC (μmhos/cm), total hardness (mg/l as $CaCO_3$) and cation exchange capacity (CEC) (meq/g) of filter media. Statistical analysis of obtained data was performed by SPSS software. PASW Statistics 18. July 30 2009 Samples turbidities were determined by a turbidimeter model TN-100 (Eutech). EC of water samples were measured by an EC meter Sension 5 (HACH LANGE). Total hardness of water samples were analyzed by Ethylene DiamineTetraacetic Acid (EDTA) titration method.[24]

To the measurement of CEC, 0.1 g of each filters media samples and 50 ml of 0.1 M HNO_3 were shaken at laboratory temperature for 15 h. Then 5 ml portion of supernatant was titrated with 0.1 M NaOH solution using methyl orange indicator. Finally, CEC was calculated as mmol H^+/g of sand materials and were reported as meq/g.[19]

RESULTS

Figures 2-7 show a turbidity removal trends and removal efficiency (%), EC removal trends and removal efficiency (%), total hardness removal trends and removal efficiency (%), respectively. Tables 1 and 2 also show the measured CEC (meq/g) values in filters media and source water quality characteristics in this study, respectively.

DISCUSSION

In this study, the studied raw water turbidity ranges were from 10 to 50 NTU, during the 41 days of filters operation. As shown in Figure 2, the turbidity removal trend was decreased by increasing the operation days. Nevertheless, due to pores plugging of filter media the removal efficiency of turbidity by modified and unmodified filters were increased. However because of high head loss obtained during filter operations, the filter cleaning was done in the day 30^{th} of

Table 1: Measured CEC values in filters media

Filter media	CEC (meq/g)
Sand	4.8
Slag	6.3
Zeolite	6.55

CEC: Cation exchange capacity

Table 2: Source water quality characteristics in this study

Parameters	Values (Mean ± SD)	Maximum permissible limit (WHO)[25]
pH	7.2 ± 0.13	6.5-8.5
Temperature (°C)	23 ± 00	16-32
Turbidity (NTU)	1 ± 0.5	1-5
Total hardness (mg/l $CaCO_3$)	750 ± 406.6	500
EC (μmhos/cm)	1030 ± 340.5	–

WHO: World health organization, SD: Standard deviation, EC: Electrical conductivity, NTU: Nephelometric turbidity units

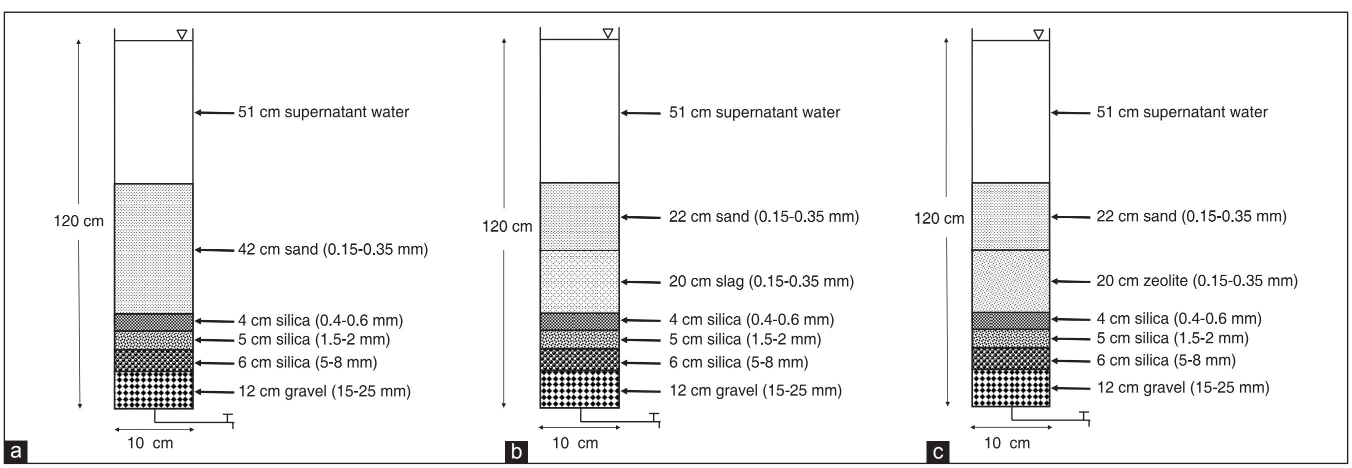

Figure 1: Pilot plant setup: (a) Conventional slow sand filter, (b) modified filter media by slag, (c) modified filter media by zeolite

operation and thus in operation days of 31-35, the turbidity amounts of treated water was increased suddenly. Results showed that three filter setups had good efficiency removal in these turbidities ranges. Because 50 NTU turbidity had high sedimentation concentration and led to clogging of the filter media, the optimum selected turbidity of the studied filters was 30 NTU. Similar study shows that the turbidity values were almost at equilibrium state for all the modified BSFs after 30 days treatment time. On the other hand, due to mechanical adsorption the head loss was increased and attachments and sedimentation of the particles clogged some of the pores. These phenomena lead to improve the BSFs efficiencies [16] that is in line with the results of the present study.

According to Figure 2, three studied filters had approximately similar performance in turbidity removal, because adsorption or precipitation was dominant processes in turbidity removal. One-way analysis of variance (ANOVA) statistical analysis also showed that there was no significant difference in measured turbidity in treated water samples between three studied filter setups ($P = 0.569$). Hence, these media had similar performance in turbidity removal and the mean and standard deviation of outlet water turbidities were 0.34 ± 0.23 NTU, 0.29 ± 0.21 NTU and 0.3 ± 0.22 NTU for sand, slag and zeolite modified media, respectively.

World Health Organization (WHO) suggested in cases where small water supplies resources are very limited and where there is limited or no treatment may not be able to achieve low levels of turbidity, producing of water that has turbidity of at least <5 NTU and if at all possible, below 1 NTU is an important requirement for water disinfection purposes.[25] One sample *t*-test showed that there were significant differences between treated water turbidities by water quality guidelines in three studied filters ($P < 0.001$). It means that all filter media could reduce raw water turbidity of 30 NTU to lower than 1 NTU and even to lower than 0.5 NTU [Table 2]. Paired samples *t*-test showed a significant difference between inlet raw and outlet treated water turbidity in three studied filters ($P < 0.001$). One-way ANOVA also indicated that there was no significant difference in turbidity removal efficiency between three studied media ($P = 0.788$). It is concluded that the slag modified filter (SMF) and zeolite modified filter (ZMF) compare to SSF had the same performance in turbidity removal [Figure 3]. Hence the turbidity removal efficiency in the filters was 98.82%, 98.98% and 98.97% for SSF, SMF and in ZMF, respectively. For turbidity removal, adsorption process is very crucial, as it takes place under physicochemical and molecular forces, which cause bridging between particles and influence the particle charge on electro kinetic forces that are responsible for the attachment between sand grains and the particles.[26] However, apparent mechanisms of pollutants removal in granular BFS column are sorption (ion exchange and adsorption) on the slag surface and precipitation.[20] Therefore, these mechanisms affect on slag ability for pollutants removal. The previous study using SSF after roughing filter modified by BFS showed that the percentage removal of turbidity was improved, where it reached up to 83% after roughing filter while reached 92% after SSF.[27]

According to Figure 4, EC reduction trend in three filter setups was equally similar. Figure 5 shows the EC reduction efficiency in conventional SSF, SMF and ZMF were 9.99%, 11.02% and 10.73%, respectively. One-way ANOVA statistical analysis also showed that there was no significant difference in measured EC in treated water samples between three studied filter setups ($P = 0.934$). Hence, these media had similar performance in EC reduction and the mean and standard deviation of outlet water EC values were 1110.8 ± 134.7 μmhos/cm, 1098.2 ± 144.2 μmhos/cm and 1101.7 ± 129.2 μmhos/cm for sand, slag and zeolite modified media, respectively. Paired samples *t*-test showed a significant difference between inlet raw and outlet treated water EC in three studied filters ($P < 0.001$) [Figure 4]. One-way ANOVA also indicated that there was no significant difference in EC reduction efficiency between three studied media ($P = 0.609$). It means that these three media were decreased slightly the inlet raw water EC. It can be concluded that the SMF and ZMF compare with SSF had the same performance in EC reduction [Figure 5].

According to Figures 6 and 7, total hardness removal trend in three studied filters was different. The removal efficiency of total hardness also was increased by increasing the operation

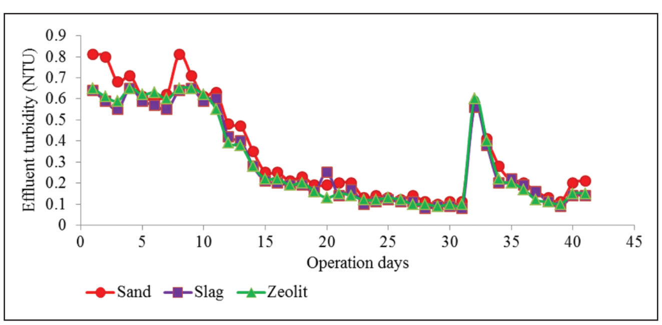

Figure 2: Turbidity removal trends (mean raw water turbidity: 30 NTU)

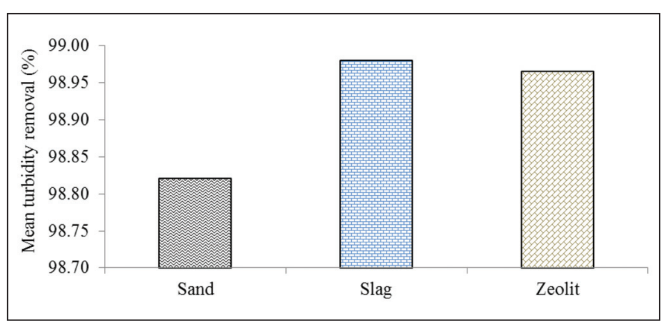

Figure 3: Turbidity removal efficiency (%) (mean raw water turbidity: 30 NTU, filtration rate: 0.1-0.24 m/h)

time. One-way ANOVA showed that there was a significant difference in effluent total hardness mean values between SSF (790.2 ± 266.2 mg/L as $CaCO_3$), SMF (436.6 ± 275.6 mg/L as $CaCO_3$) and ZMF (380.2 ± 265.6 mg/L as $CaCO_3$) ($P < 0.001$). Duncan following test also showed that there was no significant difference between ZMF and SMF in total hardness removal ($P = 0.43$). Namely zeolite and slag media comparing to sand media had greater influence in total hardness removal. Table 1 shows the measured CEC values in three filters media. As can be seen, the zeolite had higher CEC than slag and sand. So the following relation was existed:

$$CEC_{Zeolite} > CEC_{slag} > CEC_{sand}$$

One-way ANOVA also was indicated there was a significant difference in total hardness removal efficiency between three surveyed media ($P < 0.001$). It means that total hardness removal efficiency values are:

ZMF (66.3%) > SMF (51.95%) > SSF (21.19%) [Figure 7].

One sample *t*-test showed that there were significant differences between treated water total hardness by water quality guidelines in two studied filters, SMF ($P < 0.011$) and ZMF ($P < 0.001$). It means that these two filter media could reduce mean raw water total hardness of 750 ± 406.6 mg/L as $CaCO_3$ to lower than 500 mg/L as $CaCO_3$ [Table 2].

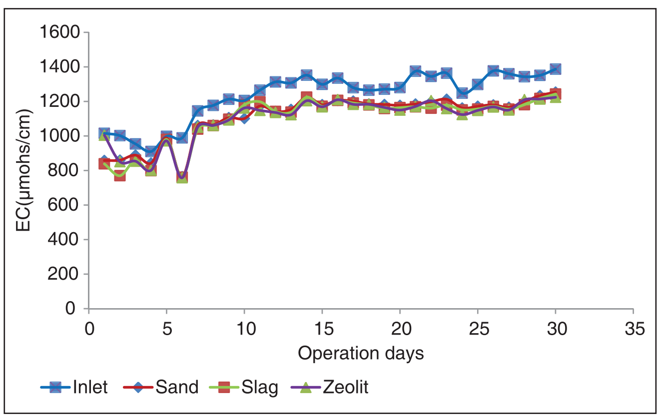

Figure 4: Electrical conductivity reduction trends, EC: Electrical conductivity

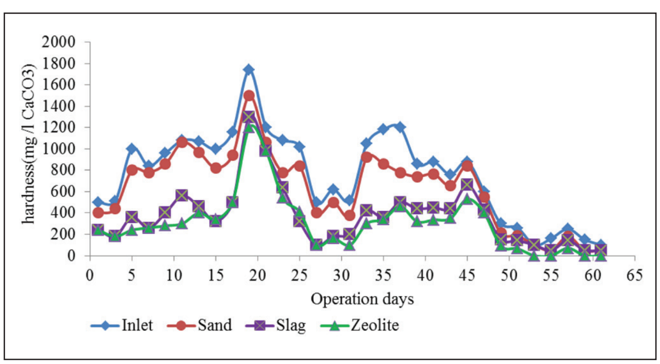

Figure 6: Total hardness removal trends

In general, the dominant mechanism of zeolites for hardness removal is ion exchange. Zeolites in total hardness removal process exchange Na^+ for Ca^{2+} and Mg^{2+}. But about slag, the mechanisms are adsorption, precipitation[28] and ion exchange.[28-31]

However, one sample *t*-test showed no significant difference between treated water total hardness by water quality guidelines in conventional SSF ($P = 0.057$). A possible cause for low water softening capacity of sand materials reported by other researchers may be attributed to the slow kinetics of the few sites responsible for Ca^{2+} removal. These sites have difficult access in the exchange of Ca^{2+} with Na^+ ions. The result is that the ionic sites associated with slow diffusion within the sand structure will be saturated with Ca^{2+}. Therefore, these sites can no longer take place in ion exchange.[19] These results were in agreement with the current study results. It is recommended further studies to determine the alternative and cheaper media with higher efficiency and appropriate methods.

CONCLUSIONS

In this study, three filters media, a conventional SSF and two cheap media: A BFS and a ZMF were operated and compared. Turbidity and total hardness removal and EC reduction in these filter setups were measured. The highest total hardness removal efficiency was related to ZMF. Although all three studied filter media had the same turbidity removal efficiency. Thus, it is concluded that the slag and zeolite are very good

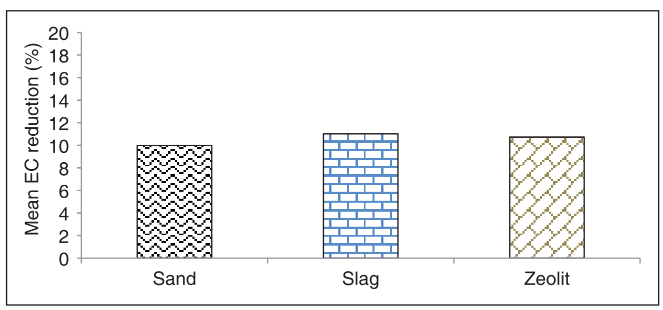

Figure 5: Electrical conductivity reduction efficiency (%), EC: Electrical conductivity

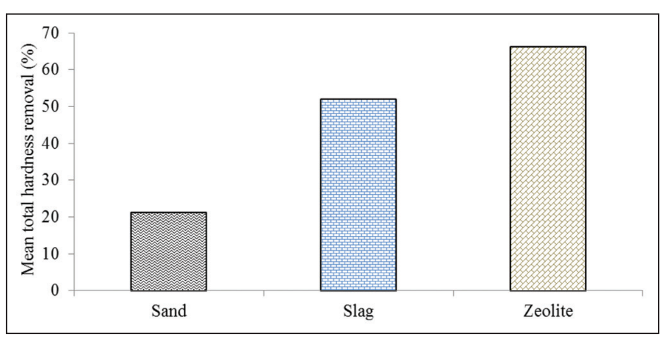

Figure 7: Total hardness removal efficiency (%)

options for total hardness removal in communities that have some problems with this parameter. As well as they show good potential for the removal of turbidity from drinking water resources. The filtered water concentrations of these parameters are under the WHO water quality guidelines.

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REFERENCES

1. Sobsey MD. Managing Water in the Home: Accelerated Health Gains from Improved Water Supply. Geneva: World Health Organization; 2002.
2. Campos LC, Su MF, Graham NJ, Smith SR. Biomass development in slow sand filters. Water Res 2002;36:4543-51.
3. Jenkins MW, Tiwari SK, Darby J. Bacterial, viral and turbidity removal by intermittent slow sand filtration for household use in developing countries: Experimental investigation and modeling. Water Res 2011;45:6227-39.
4. Yang CY. Relationship between trace metal concentrations and hardness in drinking water in Taiwan. Bull Environ Contam Toxicol 1999;63:59-64.
5. Schaep J, Van der Bruggen B, Uytterhoeven S, Croux R, Vandecasteele C, Wilms D, *et al.* Removal of hardness from groundwater by nanofiltration. Desalination 1998;119:295-301.
6. Gholikandi GB, Baneshi MM, Dehghanifard E, Salehi S, Yari AR. Natural zeolites application as sustainable adsorbent for heavy metals removal from drinking water. Iran J Toxicol 2010;4:302-10.
7. Greenleaf JE, Lin JC, Sengupta AK. Two novel applications of ion exchange fibers: Arsenic removal and chemical free softening of hard water. Environ Prog 2006;25:300-11.
8. Alvarez-Ayuso E, García-Sánchez A, Querol X. Purification of metal electroplating waste waters using zeolites. Water Res 2003;37:4855-62.
9. Breck DW. Zeolite Molecular Sieves: Structure, Chemistry, and Use. Malabar, FL: RE Krieger; 1984.
10. Costa E, De Lucas A, Uguina MA, Ruiz JC. Synthesis of 4A zeolite from calcined kaolins for use in detergents. Ind Eng Chem Res 1988;27:1291-6.
11. Lucas AD, Uguina MA, Covian L, Rodrigues L. Synthesis of 13X zeolite from calcined kaolins and sodium silicate for use in detergents. Ind Eng Chem Res 1992;31:2134-40.
12. Hedström A, Rastas L. Methodological aspects of using blast furnace slag for wastewater phosphorus removal. J Environ Eng ASCE 2006;132:1431-8.
13. Kim DH, Shin MC, Choi HD, Seo CI, Baek K. Removal mechanisms of copper using steel-making slag: Adsorption and precipitation. Desalination 2008;223:283-9.
14. Ahammed MM, Meera V. Metal oxide/hydroxide-coated dual-media filter for simultaneous removal of bacteria and heavy metals from natural waters. J Hazard Mater 2010;181:788-93.
15. Devi R, Alemayehu E, Singh V, Kumar A, Mengistie E. Removal of fluoride, arsenic and coliform bacteria by modified homemade filter media from drinking water. Bioresour Technol 2008;99:2269-74.
16. Baig SA, Mahmood Q, Nawab B, Shafqat MN, Pervez A. Improvement of drinking water quality by using plant biomass through household biosand filter - A decentralized approach. Ecol Eng 2011;37:1842-48.
17. Bleiman N, Mishael YG. Selenium removal from drinking water by adsorption to chitosan-clay composites and oxides: Batch and columns tests. J Hazard Mater 2010;183:590-5.
18. Baskan MB, Pala A. Removal of arsenic from drinking water using modified natural zeolite. Desalination 2011;281:396-403.
19. Sivasankar V, Ramachandramoorthy T. Water softening behaviour of sand materials — Mimicking natural zeolites in some locations of Rameswaram Island, India. Chem Eng J 2011;171:24-32.
20. Dimitrova SV. Use of granular slag columns for lead removal. Water Res 2002;36:4001-8.
21. Tashauoei H, Attar HM, Amin M, Kamali M, Nikaeen M, Dastjerdi MV. Removal of cadmium and humic acid from aqueous solutions using surface modified nanozeolite A. Int J Environ Sci Technol 2010;7:497-508.
22. Razeghi N. Slow sand filter for public potable water. Planning, Designing, Implementation, Operation and Maintenance. Paper No. 24 (I, R, C). Jihad Ministry of Civil Affairs and Rural Industries, 2000; 132-3. [In persian]
23. AWWA, ASCE. Water Treatment Plant Design. USA: McGraw-Hill, Inc.; 2005. p. 9.11.
24. Eaton AD, Franson MA. Standard Methods for the Examination of Water & Wastewater. USA: American Public Health Association; 2005.
25. WHO. Guidelines for Drinking-Water Quality. 4th ed. Malta, Gutenberg: World Health Organization; 2011.
26. Gerba CP, Hou K, Sobsey MD. Microbial removal and inactivation from water by filters containing magnesium peroxide. J Environ Sci Health A 1988;23:41-58.
27. El-Taweel GE, Ali GH. Evaluation of roughing and slow sand filters for water treatment. Water Air Soil Pollut 2000;120:21-8.
28. Shilton AN, Elmetri I, Drizo A, Pratt S, Haverkamp RG, Bilby SC. Phosphorus removal by an 'active' slag filter - A decade of full scale experience. Water Res 2006;40:113-8.
29. Drizo A, Forget C, Chapuis RP, Comeau Y. Phosphorus removal by electric arc furnace steel slag and serpentinite. Water Res 2006;40:1547-54.
30. Kanel SR, Choi H, Kim JY, Vigneswaran S, Shim WG. Removal of arsenic (III) from groundwater using low-cost industrial by-products-blast furnace slag. Water Qual Res J Can 2006;41:130-9.
31. Lu SG, Bai SQ, Shan HD. Mechanisms of phosphate removal from aqueous solution by blast furnace slag and steel furnace slag. J Zhejiang Univ Sci 2008;9:125-32.

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