

Iron and Manganese Removal through Adsorptive Filtration based on Zeolites, at bank scale

Remoção de Ferro e Manganês da água bruta de abastecimento empregando Filtração Adsorativa em Zeólitas, em escala de bancada

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ABSTRACT: The aim of the current study is to assess iron and manganese removal from water used for public supply through adsorptive filtration based on natural zeolites that were chemically prepared for metal removal purposes. The research was conducted at bench scale by using water samples from two water sources in Parana State. Full cycle studies were carried out; according to them, filtration was conducted, in separate, under four filter bed conditions, namely: sand, anthracite coal, zeolite without previous chlorine application and zeolite with previous chlorine application. The zeolite filtration test without previous chlorine application recorded high mean iron and manganese removal values, - 100% and 87.96%, respectively. Based on the filtration results, the zeolite filter without previous chlorine application was the best filter media among the tested beds, under the herein proposed conditions.

Keywords: coagulation diagrams, jar test, water treatment, adsorptive filtration.

RESUMO: Esta pesquisa avaliou a remoção de ferro e manganês da água com vistas ao abastecimento público, por filtração adsorativa em zeólitas naturais, preparadas quimicamente para a remoção desses metais. A pesquisa foi feita em escala de bancada de laboratório e para as amostras de água foi realizada a mistura de dois mananciais superficiais do Estado do Paraná. Foram realizados ensaios em ciclo completo, com a filtração ocorrendo em quatro leitos filtrantes: areia, carvão antracito, zeólita sem adição prévia de cloro e zeólita com adição prévia de cloro. No ensaio de filtração em zeólita sem adição prévia de cloro, foram obtidas remoções médias elevadas de ambos os metais, de 100% e 87,96% para ferro e manganês, respectivamente. Diante dos resultados de filtração, foi possível concluir que, nas condições propostas, o filtro de zeólita sem adição prévia de cloro apresentou-se como melhor meio filtrante dentre os leitos testados.

Palavras-chave: diagramas de coagulação, jartest, tratamento de água, filtração adsorativa.

INTRODUCTION

Iron is one of the most abundant elements found on Earth's surface. It can be found in water deriving from both soils and minerals, so that the dissolution of these, such as organic matter decomposition in or around the water source, can contribute to the presence of this metal in water bodies (Castañeda, 2010; Ramos, 2010; Moruzzi; Reali, 2012). Industrial, mining, steel-industry and metal corrosion wastes are other iron sources found in water. Several industrial procedures require removing iron from water used in operations, as well as from water supply, since this metal can lead to different issues, such as changes in water color and turbidity levels, ferruginous bacteria growth in water supply, precipitates' incidence in washing machines and boilers, scale formation in water pipes (which generates significant load losses), as well as stain formation on sanitary appliances, clothes and fabrics, among others (Moruzzi; Reali, 2012; Chatuverdi; Dave, 2012; Rocha *et al.*, 2006 *apud* Souza Silva *et al.*, 2023).

Manganese is an element often found dissolved in groundwater; its organoleptic properties turn it into a pollutant (Taffarel; Rubio, 2010). Its harmful effects on water are like those generated by iron, although they are more severe. Its presence in water is almost always simultaneous to that of iron, although at significantly lower concentration (Azevedo Netto; Richter, 1991; El Araby, Hawash; El Diwani, 2009).

The oxidation of these metals based on using chlorine, potassium permanganate (KMnO₄), chlorine dioxide (ClO₂), ozone (O₃) or even oxygen (through aeration) is the technology most often used to remove iron and manganese from water, since it forms precipitates that can be removed through sedimentation and/or filtration processes in water treatment plants (WTP) by taking into consideration the medium pH.

However, according to Vistuba (2010), oxidation followed by sedimentation and/or filtration has the disadvantage of requiring a larger number of operational steps in WTPs, and it results in additional costs with reagents and energy, besides the risk of forming by-products capable of harming human health, such as trihalomethanes, haloacetic acids, among others (Dantas *et al.*, 2011).

Dantas *et al.* (2011) and Hameed, Awad and Al-Uqaily (2019) introduced options for removing these metals based on using pre-oxidative steps. These steps comprise several chemical agents, such as hypochlorites, ozone and chlorine gas, for iron and manganese compounds' precipitation and removal purposes.

Adsorption is a process capable of binding chemical species to the surface of suspended particles called adsorbents. It is a mass transfer operation, since it transfers a given constituent from the liquid phase to the solid one. This process takes place on the adsorbent's external surface in macropores, mesopores, micropores and submicropores, although the adsorbed material prevails in micropores and submicropores (Metcalf; Eddy, 2016). Sometimes, adsorbent materials require the deposition of iron or manganese oxide layers for adsorption purposes (Tarasevich *et al.*, 2012; USA, 2013).

According to Katsoyiannis and Zoubolis (2002), adsorptive filtration is a technology capable of removing contaminants from the liquid phase by applying a thin layer of iron oxides on the filter medium grains. This procedure enables the bed to remove soluble heavy metals through sorption and, simultaneously, to particulate precipitated metals through filtration.

Zeolite is one of the filter beds used to achieve adsorptive filtration. It was defined by Dal Bosco, Jimenez and Carvalho (2004) as mineral comprising a tetrahedral, three-

dimensional structure of SiO_4 and AlO_4^- , with molecular-sized cavities where water molecules can pass through and where ion exchange takes place due to charge imbalance, which involves trivalent aluminum. The high specific surface area resulting from particles' porosity enhances the ion exchange capacity of zeolites.

According to the US Environmental Protection Agency (USEPA, 1993), the adsorption action on the particles due to the deposition of a iron oxide layer over a wide pH range, allows reducing metals to much lower final concentrations than those observed for precipitation processes. Adsorptive filtration can be much more effective in situations whose precipitation caused by oxidation is not viable (Chatuverdi; Dave, 2012).

Tarasevich et al. (2012) highlighted the use of adsorptive filtration technology, which was modified by impregnating manganese dioxide (MnO_2) on Clinoptilolite-type zeolites' surface to remove iron and manganese from artesian aquifer water. It was done based on using 0.1% potassium permanganate solution (KMnO_4) to impregnate the manganese dioxide on the zeolite surface. Iron and manganese removal value close to 100% was recorded for the herein collected samples. Affluent iron concentrations ranged from 4.9 mg/dm^3 to 5.2 mg/dm^3 , whereas manganese concentrations ranged from 1.1 mg/dm^3 to 1.4 mg/dm^3 .

The aim of the current study was to investigate the adsorptive filtration technique based on using clinoptilolite zeolite impregnated with manganese oxide to remove dissolved Fe and Mn from spring water used for public supply purposes.

MATERIALS AND METHODS

The present research used raw water collected at the inlet of a WTP that accounts for supplying a medium-sized municipality in Paraná State. Different volumes of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and manganous sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) solutions were added to the samples until they reached the iron and manganese concentrations previously set for filtration tests.

The following parameters were analyzed in both raw and study water: pH (HANNA HI2221 pH meter), turbidity (HACH 2100Q turbidimeter), apparent and true color (HACH DR 6000 UV-Vis spectrophotometer), total iron (Thiocyanate method, MERCK, 19--) and total manganese (Formaldoxin method, MERCK, 1977). These last two analyses were carried out with commercial kits and readings were performed in HACH DR 6000 UV-Vis spectrophotometer.

All physicochemical analyses were carried out in compliance with methodologies recommended by APHA (1998).

Study water treatability tests required plotting coagulation diagrams to get the optimum coagulation pH x coagulant dosage pair. Tests simulating full cycle water treatment, as well as adsorptive filtration tests conducted in different filter media, such as sand, anthracite coal and zeolites, were carried out in static reactor equipment of the 6-test jar test type, PoliControl FlocControl III model (10 to 600 rpm); transparent acrylic filters were attached to the aforementioned equipment and filled, in separate, with 15 cm of the aforementioned filter materials.

Coagulation diagrams

Polyaluminum Chloride (PAC) was herein used as coagulant.

Coagulation diagrams were plotted to help determining the optimum pair of coagulation pH x coagulant dosage values. It was done to optimize the rapid mixing stage and to find the best removal efficiencies for the parameters assessed in the subsequent stages.

Accordingly, pH values x PAC dosage were established at the following values in order to plot the diagrams: pH - 3.0, 4.5, 6.0, 7.5, 9.0 and 10; PAC dosages – 10, 15, 20, 25 and 30 mg.L⁻¹.

Jar tests were carried out by setting the PAC dosages for each jug and by varying the coagulation pH (triplicate tests for each PAC dosage), in order to plot the coagulation diagrams. PAC solution was used at the concentration of 20 g.L⁻¹; 0.1 N hydrochloric acid or 0.1 N sodium hydroxide was used to correct water pH values.

Turbidity removal efficiency was assessed at sedimentation time of 14 minutes (referring to sedimentation speed of 0.5 cm.min⁻¹) in order to select the optimum operating pair.

Two study water types, herein called water type 1 and water type 2, were used in the experiment. They were collected in different days; therefore, they presented different pH, turbidity and color features. The optimum operating pair was set for the full-cycle treatability tests.

Full-cycle water treatability tests

Three filter media were selected for bench filtration tests, namely: sand, anthracite coal and clinoptilolite zeolite impregnated with manganese oxide.

The methodology proposed by Di Bernardo, Dantas and Voltan (2011) was used in the full-cycle treatability tests. Metal concentrations in the raw study water subjected to filtration tests were 1.6 mg.L⁻¹ iron and 1.0 mg.L⁻¹ manganese (Censaio). These concentrations were obtained by adding ferrous sulfate and manganese sulfate solutions to these metals' pre-existing concentrations in raw water.

It was necessary dosing chlorine into the decanted water before filtration, at residual free chlorine concentration ranging from 1 to 2 mg.L⁻¹, in order to activate zeolites' adsorptive and selective capacity, in compliance with recommendations by the manufacturer. Therefore, the chlorine oxidation-based zeolite filtration test used 12% sodium hypochlorite (NaClO) solution to get residual concentration of 2.5 mg.L⁻¹ and chlorine in the decanted water. CHEMetrics Vacu-vials CLORO K-2513 kit was used to measure residual chlorine.

Filtration tests were carried out (in triplicate) on sand, anthracite coal, zeolites pre-oxidized with chlorine, as well as on chlorine-free zeolites, to assess the need of conducting pre-oxidation procedures.

The remaining iron and manganese concentrations in the study water were analyzed at the end of both sedimentation and filtration processes conducted with all herein adopted filter media.

All filter materials were washed before the filtration tests.

The adopted filtration rate was based on the methodology by Di Bernardo, Dantas and Voltan (2011). It was set between 71 and 91 m³.m⁻². day⁻¹, which corresponded to filtration flow rates of 14 and 16 mL.min⁻¹. The flow rate was manually controlled based on using the overflow control rods in the Jar test equipment. The adopted filtration time was twenty minutes.

RESULTS AND DISCUSSIONS

Coagulation diagrams

Mean values recorded for water quality featuring parameters, such as pH, turbidity and color of raw water samples collected at the WTP, and added with iron and manganese, are shown in Table 1.

Table 1. Featuring samples collected to plot the coagulation diagrams, after iron and manganese addition

Parameters	Unit	Water type 1	Water type 2
		Average	Average
pH	-	7.1	7.2
Turbidity	NTU	59.9	24.9
Apparent colour	uH	393.7	219.0
True colour	uH	89.7	24.9

Figure 1 shows the coagulation diagrams plotted in triplicate at sedimentation time of 14 minutes ($V_s = 0.5 \text{ cm}\cdot\text{min}^{-1}$), based on using two collected raw water samples (water types 1 and 2). Each point in Figure 1 indicates the turbidity removal rate.

The highest turbidity removal rates were observed for coagulation pH values close to neutral (between 6.5 and 7.5). Some higher removal rates were observed at coagulation pH close to 8.0.

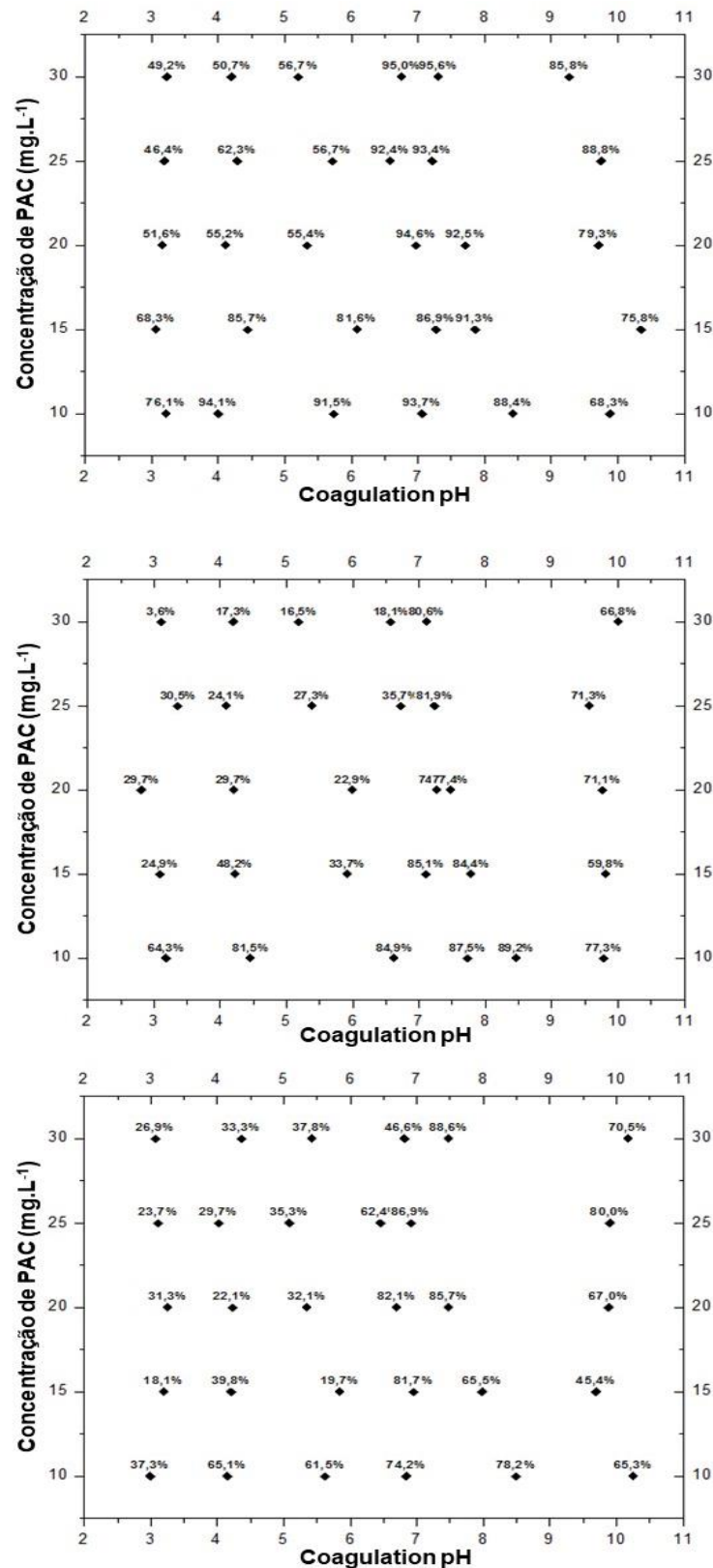
Turbidity removal efficiency rates ranged from 85% to 95%. Lower coagulant doses, mainly the lowest dose of $10 \text{ mg}\cdot\text{L}^{-1}$, resulted in high removal efficiency values close to those observed for the highest doses of the applied coagulant, at the observed best pH range. Thus, it was not necessarily increasing PAC application to get significant improvement in turbidity removal rates, under the herein tested conditions.

Raw water pH values ranging from 7.1 to 7.2, as well as the observation that the best turbidity removal took place at coagulation pH range close to neutral, were considered at the time to select the optimum pH, which was based on the context requiring little or no acid or base addition to the samples.

The use of the lowest PAC dose possible was taken into consideration at the time to select the coagulant dose, since this factor leads to lower costs with chemical products at WTP. Based on the plotted graphs, higher coagulant doses did not lead to turbidity removal rates significantly higher than those recorded for lower doses of it. Therefore, PAC dose of $10 \text{ mg}\cdot\text{L}^{-1}$ was adopted for the subsequent filtration tests.

Thus, coagulation pH equal to 7.0 and PAC dosage equal to $10 \text{ mg}\cdot\text{L}^{-1}$ was the optimum coagulation pH x coagulant dosage pair set for the filtration trials.

Figure 1. Coagulation diagrams (coagulation pH versus coagulant dosage) plotted for aluminum polychloride, based on gross turbidity removal rate, at sedimentation time of 14'00".



Adsorptive filtration tests

Three samples were used to feature the study water before the filtration tests. Mean values observed for the assessed physicochemical parameters are shown in Table 2.

Table 2. Featuring raw water samples collected for bench filtration tests.

Parameters	Unit	Water type 1	Water type 2	Water type 3
		Average	Average	Average
pH	-	6.8	7.2	6.9
Turbidity	NTU	30.4	17.3	38.9
Apparent colour	uH	231.7	98.5	292.3
True colour	uH	50.0	21.0	50.7
Iron	mg.L ⁻¹	0.6	0.6	1.3
Manganese	mg.L ⁻¹	0.3	0.1	0.2

Iron and manganese concentrations in water samples were close to each other in two water samples. The third sample recorded iron concentration higher than that of manganese. The addition of ferrous sulfate and manganese sulfate solutions to reach the pre-set concentrations of 1.6 mg.L⁻¹ iron and 1.0 mg.L⁻¹ manganese took into account the pre-existing concentrations of these metals in the assessed water.

Bench-Scale Filtration Tests - Test Condition = 1.6 mg.L⁻¹ iron and 1.0 mg.L⁻¹ manganese

Results of tests simulating the full cycle configuration with filtration in the tested filter media are shown in Table 3. It shows values observed for remaining metals after 14'00" sedimentation (value at the filter inlet) and in the filtered water (value at the filter outlet), as well as the mean removal efficiency value observed after filtration (based on metals' concentration at the filter inlet) and its corresponding standard deviation.

Iron was removed from the water during sedimentation in all cases. Affluent concentration of 1.6 mg.L⁻¹ has decreased after 14'00" sedimentation, and it resulted in lower concentrations of this metal when it reaches the filters.

Metal removal through sedimentation is explained by the presence of the Fe³⁺ ionic species, which is insoluble (precipitated), found in surface water in the presence of oxygen, as well as in water with pH ranging from 7 to 8. This range encompasses the coagulation pH value set for the current study (pH = 7.0). These aspects were also observed in studies conducted by Baes and Mesmer (1976) cited by Chatuverdi and Dave (2012), and Moruzzi and Reali (2012).

The rapid mixing stage in Jar test allows oxygen molecules to have access to the system - i.e., to promote aeration – and it contributes to both medium oxidation and iron precipitation. This factor turns sedimentation followed by filtration into an alternative iron removal process (English SD, 1985 cited by Nakayama; Bucks, 1991). According to Chatuverdi and Dave (2012), the iron precipitate generated after the oxidation process, and removed through sedimentation, is in its ferric hydroxide Fe(OH)₃ form.

Table 3. Iron and manganese removal data (remaining values, mean removal efficiency value and standard deviation), after 14'00" sedimentation and after filtration, observed for the tested filter beds (sand, anthracite coal, zeolites without previous chlorine addition and zeolites previously added with chlorine).

Samples		Iron (mg.L ⁻¹)	Manganese (mg.L ⁻¹)	Average Removal Efficiency		Standard Deviation	
				Ir	Mn	Ir	Mn
Sand Filter							
1st repetition	14'00''	0.25	0.80	65%	4.17%	8.66	7.22
	Filter	0.10	0.80				
2nd repetition	14'00''	0.25	0.80				
	Filter	0.10	0.80				
3rd repetition	14'00''	0.80	0.80				
	Filter	0.20	0.70				
Anthracite Coal Filter							
1st repetition	14'00''	0.25	0.80	81.11%	-154%	20.09	2.62
	Filter	0.10	2.00				
2nd repetition	14'00''	0.25	0.80				
	Filter	0.00	2.20				
3rd repetition	14'00''	0.60	0.80				
	Filter	0.10	1.90				
Zeolite filter without prior addition of chlorine							
1st repetition	14'00''	0.50	0.80	100%	87.96%	0.00	0.80
	Filter	0.00	0.10				
2nd repetition	14'00''	0.50	0.90				
	Filter	0.00	0.10				
3rd repetition	14'00''	0.70	0.80				
	Filter	0.00	0.10				
Zeolite filter with prior addition of chlorine							
1st repetition	14'00''	0.30	0.80	100%	75%	0.00	0.00
	Filter	0.00	0.20				
2nd repetition	14'00''	0.30	0.80				
	Filter	0.00	0.20				
3rd repetition	14'00''	0.40	0.80				
	Filter	0.00	0.20				

Iron removal rate observed for the sand filter medium reached 65.0% due to Fe³⁺ precipitates' formation in solid agglomerates that can be removed through filtration. This finding was also observed in studies conducted by Lemos Filho et al. (2011) and Castañeda, Passos and Benetti (2012).

Affluent manganese concentration of 1.0 mg.L⁻¹ has also decreased metal concentrations in the water after sedimentation, although it was less efficient than iron. Mean manganese removal rate through filtration reached 4.17%.

These findings are explained by the extremely slow manganese oxidation, from soluble Mn²⁺ to insoluble Mn⁴⁺, in the presence of dissolved oxygen, at water pH lower than 9.5 (Moruzzi; Reali, 2012). The manganese precipitate generated after the oxidation process was in its manganese hydroxide Mn(OH)₄ form (Ferreira, 2009).

Iron removal process based on anthracite coal recorded mean efficiency of 81.11%, also due to likely formation of ferric hydroxide $\text{Fe}(\text{OH})_3$ precipitates that can be removed through sedimentation

Vistuba *et al.* (2013) worked with raw water presenting mean iron concentration of 0.453 mg.L^{-1} and recorded mean removal efficiency of $79\% \pm 3$ for adsorbent charcoal - it was close to values observed in the current study.

Mean iron removal efficiency herein observed for anthracite coal reached 81.11%, also due to likely formation of ferric hydroxide precipitates $\text{Fe}(\text{OH})_3$, which could be removed through sedimentation.

Manganese recorded increased concentration from 0.80 mg.L^{-1} to around 2.00 mg.L^{-1} , after filtration, in the current study. This behavior suggests likely solubilization of this metal in the filter bed particles, which led to increased concentrations of it in the filtered water, even after the material had been previously washed.

The filtration test conducted with Clinoptilolite-type zeolite free from pre-oxidation stage has shown quite positive results, since it recorded mean iron removal efficiency equal to 100%.

Thus, it is possible stating that part of the iron was removed in insoluble state, in the form of precipitated $\text{Fe}(\text{OH})_3$ (Chatuverdi; Dave, 2012). In addition, when it comes to materials presenting adsorptive filtration capacity, as well as to changes in the filtration matrix on their surface, this removal happens simultaneously through soluble metals' sorption and particulate materials' filtration. Thus, the total iron removal herein observed at the filter inlet involved the retention of both the particulate and soluble fractions of the remaining unoxidized iron (Katsoyiannis; Zoubolis, 2002).

Manganese, which was not removed through sand or anthracite coal using, was removed through zeolite using at efficiency rate higher than 85% in all repetitions. Deviations from the mean were considerably smaller than those observed for sand and anthracite coal, which recorded removal values close to zero for both metals. Slow manganese oxidation due to unfavorable pH points towards a situation, according to which, most of the soluble manganese fraction was removed through adsorptive filtration on the Clinoptilolite zeolite surface. Similar behavior was observed by Vistuba *et al.* (2014), who used zeolites to remove manganese without previous oxidation and reached mean removal rate of 66%.

Soluble manganese removal has indicated that chlorine addition to decanted water (pre-oxidation) was not necessary and that it could be dismissed under the herein adopted conditions. This finding points towards the removal of this metal via adsorption and/or ion exchange, which is also observed in zeolites, as explained by Dal Bosco, Jimenez and Carvalho (2004).

Once the adsorptive filtration test had been carried out with zeolite free from chlorine addition, the test was carried out with the addition of this oxidizer to check whether, or not, there was increased removal of the investigated metals. It is so, because chlorine addition should lead to the precipitation of iron and manganese compounds.

The iron concentration entering the filter in the zeolite filtration process associated with pre-oxidation stage for iron removal purposes was lower than the one observed in the other test conducted with zeolites, on average. Total iron removal was observed in all test repetitions. Mean manganese removal efficiency rate was significantly lower than the one observed in the previous test conducted with zeolites. Standard deviation reached zero for both metals.

The comparison between zeolite tests, with and without chlorine addition, has evidenced that pre-oxidation based on chlorine did not have significant influence on the removal of the investigated metals, mainly of manganese, which even recorded lower values for all repetitions and for the mean.

Statistical analysis

Analysis of Variance (ANOVA) was applied to collected data in order to check whether there was significant difference among all four treatments - namely: sand, anthracite coal, zeolite without previous chlorine addition and zeolite previously added with chlorine - for iron and manganese (variables) removal purposes.

To do so, iron and manganese removal-efficiency data normality was checked through Shapiro-Wilk test, which showed normal data distribution, at 5% confidence level.

Tukey's test was applied to efficiency data, at 5% significance level ($\alpha = 5\%$), in order to check whether there was significant difference between mean efficiency values observed for the adopted iron and manganese removal treatments.

Table 4 shows results of Tukey test applied to the samples.

Table 4. Results observed for mean iron and manganese removal efficiencies of all four tested treatments (sand, anthracite coal, zeolite with previous chlorine addition and zeolite without previous chlorine addition), based on Tukey test, at 5% significance level.

Analysis of variance	Iron	Manganese
DF residue	8	8
F treatments	7.15*	355.66**
Overall mean	86.53	3.24
Standard deviation	10.94	10.21
MSD (5%)	28.60	26.71
CV (%)	12.64	315.17
Tukey test at 5%		
Sand	65.00 b	4.17 b
Anthracite coal	81.11 ab	-154.17 c
Zeolite without chlorine	100.00 a	87.96 a
Zeolite with chlorine	100.00 a	75.00 a

Significance level: **1%; *5%

DF: degrees of freedom; MSD: minimum significant difference; CV: coefficient of variation.

Based on iron removal results, there was significant difference between removal rates achieved by sand and zeolite treatments, at 95% confidence level. This finding proved that zeolites were significantly more efficient in removing this contaminant from the analyzed samples under the tested conditions. Results observed for anthracite coal did not significantly differ from those recorded for sand or zeolites, and its removal efficiency was on a par with that of the other three treatments. Chlorine addition to the two zeolite-based treatments did not lead to significant difference in iron removal rates, and it means that its addition to the medium was not necessary under the tested conditions.

On the other hand, manganese removal rates observed for zeolite-based treatments were significantly different from those observed for sand and coal treatments, at 95% confidence level. Thus, zeolite-based treatments performed better in removing this

contaminant from the analyzed samples. There was no significant difference in manganese removal rates between the two zeolites media, and it means that chlorine addition did not lead to better manganese removal performance under the tested conditions.

CONCLUSIONS

Fe and Mn incidence in water used for public supply purposes is a issue that must be solved by sanitation companies for different reasons, such as compliance with the legislation providing on water quality control and monitoring processes for human consumption purposes.

By considering adsorptive filtration as alternative technology to conventional filtration, one can get to the conclusion that:

- a) adsorptive filtration based on using zeolites was effective in removing iron and manganese from water;
- b) water pre-oxidation with chlorine before adsorptive filtration was not significantly efficient in removing iron and manganese from it, as confirmed in the Tukey test results;
- c) adsorptive filtration based on zeolite was efficient, since manganese in soluble state was removed from water at pH level unfavorable to its precipitation and without oxidant addition;
- d) iron removal from water through all tested filter media was associated with its precipitation, due to favorable pH's influence resulting from air insertion in the Jar test procedures, which led to the oxidation of metal ions.

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