

Ranges and Fitting Ratios of Natural Aggregates for a Sustainable and Effective Fe⁰/Sand/Pozzolan Ternary Device Using Orange Methyl

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Abstract: The remediation effectiveness of a Fe⁰/Sand/Pozzolan (Fe⁰/S/Pz) ternary device using an azo-dye for characterization is demonstrated herein. Optimal operating conditions, which specify the proportions of solid materials, such as iron (Fe⁰), sand (S), and pozzolan (Pz), in the reactive zone (RZ), are essential factors for the performance of such heterogeneous devices. Thus, the operative indicator orange methyl (OM) of 2 mg/L was used. Performance parameters such as pH, released iron of the collected water, flow rate, and fading power were measured using filter devices containing (1) 100% Fe⁰, (2) 25%/75% Fe⁰/S, (3) 25%/75% Fe⁰/Pz, (4) 25%/0%/75% Fe⁰/S/Pz, (5) 25%/25%/50% Fe⁰/S/Pz and (6) 25%/50%/25% Fe⁰/S/Pz for a correlation of proportions, reactivity, and performance. The experiments lasted thirty (30) days per device. It turns out that ranges of 25% ≤ % Fe⁰ ≤ 60%, 25% ≤ %S ≤ 50%, and 25% ≤ %Pz ≤ 50% are quite enough. The ternary device, in ratios of 25%/50%/25% Fe⁰/S/Pz, is an excellent decontaminant of orange methyl OM, with regulation of pH and residual iron levels, for acceptable flows. There are therefore beneficial effects of the association of a non-expansive porous material with Fe⁰-based filters to delay clogging by collecting corrosion products (CPs). 25%/50%/25% Fe⁰/S/Pz device allow to reduce greatly the proportion of iron in the reactive zone (RZ) since pure iron devices are not recommended due to clogging. 25% ≤ % Fe⁰ ≤ 60%, 25% ≤ %S ≤ 50%, and 25% ≤ %Pz ≤ 50% could provide a necessary framework for all Fe⁰-bed filters.

Keywords: Aqueous Corrosion, Fe⁰-bed Filters, Orange Methyl, Pozzolan, Ratio, Sand, Zero-valent Iron

1. Introduction

The exploitation of local materials consists of their valorization in order to develop inexpensive technologies. This is the case for filtering devices intended to facilitate access to drinking water for the most deprived populations and those distant from the distribution networks of drinking water [1]. The Fe⁰/Sand/Pozzolan filter (Fe⁰/S/Pz) is a ternary device with a heterogeneous reactive zone (RZ) embedded between two layers of sand [2]. The full value of this device is within the limits and the cost of other existing filtration methods. Indeed, the 3-Kolshi generation filter has a 100% Fe⁰ layer surmounted by a layer of sand. However, although presented

as being very effective for the decontamination of arsenic, it has been shown to be limited in terms of the loss of porosity and rapid clogging [3-4]. The Sono filter, made of a layer of porous materials, has a long lifespan, but is not very effective in decontaminating micropollutants, microorganisms, and viruses, and cannot reach the expected distribution [5-6]; it will therefore be replaced by the KAF filter developed and distributed in Nepal [3]. The latter, effective for arsenic and pathogens, has also been found to have limitations for certain classes of contaminants [7]. Some systems have even been abandoned [8-9].

The Fe⁰/S/Pz filter is a possible solution to the above-mentioned limitations, as the heterogeneous nature of the RZ

makes Fe⁰ filters universal filtering devices [10-11]. The decontamination process, elucidated herein [1], involves the concomitant decontamination of materials from the RZ. Actually, the Fe⁰-based filters removal process seems to be clarified despite the confusion and flaws that have long marred the understanding and interpretation of its remediation mechanisms [12-14]. Fe⁰ filters are an efficient technology for environmental sanitation [15-21], the production of drinking water [3, 5-6, 8, 22-25], and the treatment of wastewater [16, 26-28]. Fe⁰ cannot coexist with water; it undergoes oxidation, corrosion of Fe⁰ [11, 30] into Fe²⁺ ions, thus implying the couple Fe²⁺/Fe⁰ (a). The hydroxide ions (OH⁻) can come either from the reduction reaction of water (b) or from that of dissolved dioxygen (c). The reaction (c) is predominant as soon as the quantity of oxygen is sufficient. In anoxic conditions, in the presence of acidic waters (in the case of natural waters), the following process takes place [29] as shown in figure 1 below detailing the corrosion process. Furthermore, experience shows that on the surface of metal are formed iron oxides and hydroxides; even if the hydroxides are formed more quickly, they are generally less stable than the corresponding oxides. Thus, Fe₂O₃ appears in place of Fe(OH)₃, formed more quickly, they are generally less stable than the corresponding oxides. Thus, Fe₂O₃ appears in place of Fe(OH)₃. FeO is not stable at room temperature and is not taken into account [31-36]. These equations show that Fe⁰ is a source of Fe²⁺ and H⁺. Fe⁰ thereby generates reducing agents [37-41], and the consumption of H⁺ ions induce an increase in pH. The

contribution of Fe⁰ and, therefore, of Fe⁰ filters to the process of removing contaminants is related to the expansive nature (the increase in volume) of iron corrosion products (CPs) [42], the precipitation of iron hydroxides [43-44], and their adsorbent properties for a wide range of soluble species [23, 45-46]. As a result of volumetric expansion, Fe⁰-filters are subject to loss of porosity and, therefore, loss of permeability [35, 47-48]. The solid CPs are iron hydroxides and iron oxides such as Fe₃O₄, Fe₂O₃, FeOOH, Fe(OH)₂, and Fe(OH)₃ [26-27, 48-50]. These minerals have little or no positive permanent surface charge generated by the adsorption of protons on the surface of the corroded material [51-52]. The reactivity of Fe⁰ towards the contaminant is related to the affinity of the oxide layer for the species present and not for passivated iron [53-55]. The suitability of Fe⁰ (Fe⁰-filters) for environmental sanitation therefore results from its ability to generate iron minerals which act as collectors of contaminants (adsorption) [5, 11, 20, 56-61]. Precipitated minerals gradually fill the interstitial space inside the filter, resulting in a loss of permeability and clogging, but the elimination of contaminants due to their size is increased [30, 62-63]. Fe⁰ filters allow the removal of contaminants in natural waters from the aqueous phase by adsorption, co-precipitation, and size exclusion [64-68]. The main groups of biological and chemical contaminants that have been efficiently treated by Fe⁰ systems by batch and column processes are RCl (halogenated hydrocarbons), dyes, anions, heavy metals, pathogens, and pharmaceutical compounds [13].

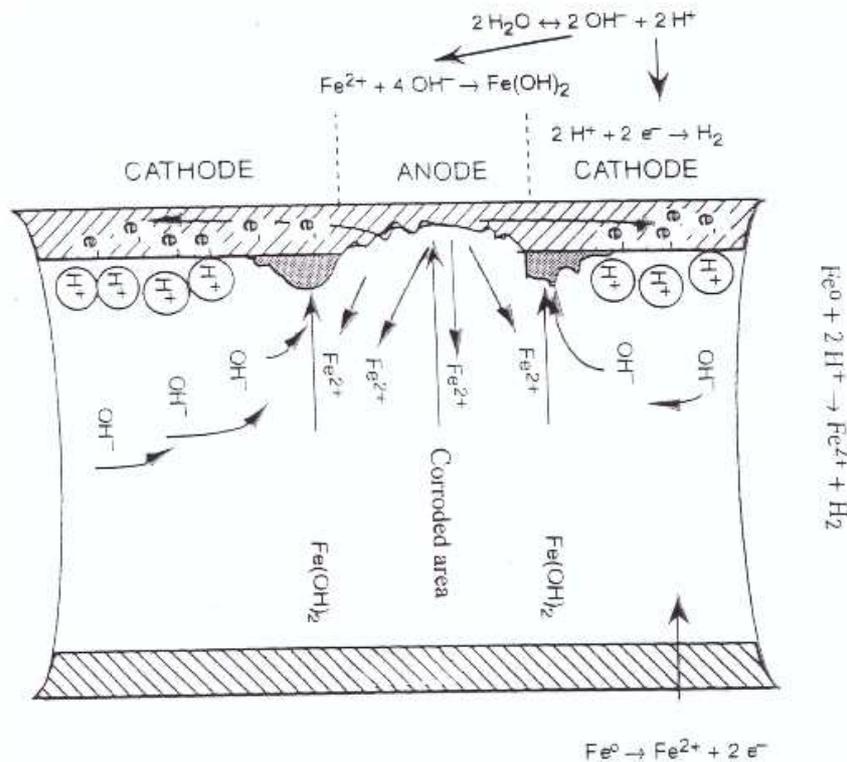
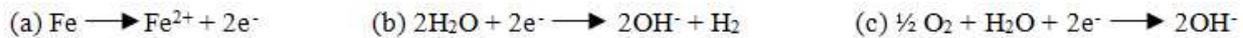


Figure 1. Corrosion process in anoxic conditions.

Even if the filtering power of Fe⁰-filters no longer needs to be proven, and even if corrosion products CPs act as contaminant collectors, it is advisable to avoid pure Fe⁰-filters, such as columns with a zone containing 100% Fe⁰ like in the Harza method [14, 69]. The universal equation of the Fe⁰-filter, based on the filling of the initial porosity of a granular bed by the iron corrosion expansion process, indicates that the volumetric proportion in a filter bed should hardly exceed 60%, and that the most durable filters contain only 25% iron [13, 70].

Besides Fe⁰, the Fe⁰/S/Pz filter contains sand (S) and pozzolan (Pz).

The sand (S) is made up of 85% to 95% silica, an inorganic polymer SiO₂ or SiO₂·xH₂O, consisting of an assembly of silicic acid Si(OH)₄ molecules condensed in tetrahedral geometry. At pH > 2, silica has a negative charge on the surface, favoring the fixation of positively charged species. The reactivity of silica strongly depends on its surface properties, i.e., the place of physicochemical interaction processes with the medium. It is governed by the nature of the groups present on its surface, including (Si-OH) and (Si-O-Si) groups. The reactivity of silica in an aqueous medium depends on the availability of the Si-OH groups; these are acid-base and adsorption sites, also involved in the reaction processes of silica. (Si-O-Si) are hydrophobic groups with low reactivity and therefore are hardly involved in surface chemistry in aqueous solutions [71]. Silica is very often added to Fe⁰ to remedy the problem of chemical compaction of the iron bed which causes the clogging of the pores [26, 72-74], generally caused by the CPs of iron which are responsible for decontamination, among other things.

Pozzolan (Pz) is a material with various physicochemical characteristics. With a neutral pH, its average chemical composition is 45% SiO₂, 15% Al₂O₃, 15% Fe₂O₃, and other minor oxides [75]. It also contains lime, sodium, potassium, and many trace elements. The study of its physical characteristics reveals a high porosity, a low density, a capacity for absorbing water and odors, an aptitude for water retention, a large specific surface area, and a filtering and draining action, thus it has wide applications in the filtration and purification of water [76-78]. Its honeycomb structure and porosity give it a water absorption capacity of 20% to 30% of its dry weight [79]. Because of its SiO₂ content, in addition to its high porosity, pozzolan (Pz) has surface phenomena similar to those of sand (S) due to the silanol groups [71].

The proportions of the Fe⁰/S/Pz device are studied using orange methyl (OM) to create a micropollutant model [80]. Orange methyl (OM) is generally used in acid-base assays as a color indicator. Its turning zone is [3.1, 4.4], which makes it possible to note the presence of an acid medium (it turns red) or a basic medium (it turns yellow) [81]. Given its physicochemical properties, OM naturally exhibits a great affinity for solid surfaces of

opposite charge such as certain iron CPs [82]. Since certain iron CPs have a positive surface in natural waters, we could therefore expect decontamination facilitated by strong electrostatic attractions and vice versa, like the surface of silica in an aqueous medium. The choice of OM is not trivial, since it is found in industrial and domestic waste.

The present work aims to establish the optimal operating conditions by quantifying the proportions of solid materials such as iron Fe⁰, S, and Pz in the RZ. Thus, the operative indicator OM was used. Performance parameters such as fading power, pH, released iron of the collected water, and flow rate were measured using the following filter devices: (1) 100% Fe⁰, (2) 25%/75% Fe⁰/S, (3) 25%/75% Fe⁰/Pz, (4) 25%/0%/75% Fe⁰/S/Pz (5) 25%/25%/50% Fe⁰/S/Pz, (6) 25%/50%/25% Fe⁰/S/Pz, for ratio, reactivity, and performance correlations.

2. Materials and Methods

2.1. Chemicals

OM is used in acid-base dosages as a colored indicator. Its cornering zone is between [3.1-4.4] and allows to mark the presence of an acid medium, it turns red, or a basic medium, it turns yellow. It naturally has a great affinity for solid surfaces of opposite loads such as certain Fe⁰-CPs [52, 81]. The OM comes from KEM LIGHT PVT Laboratories. LTD, Mumbai, India. The solution used has a concentration of 2.0 mg/L; the pH value is 5.2, this concentration is chosen to be close to natural pollution conditions [55]. A standard iron solution, 990 µg/mL from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA) was used to calibrate the spectrophotometer. The L (+) -ascorbic acid from E. MERCK, Darmstadt. 90% ethanol; sodium acetate from ANALAR; 1.10 o-phenanthroline from NORMAPUR used as a reagent for Fe²⁺ complexation require for spectrophotometric reading, 0.2 g/L concentration [2, 81, 86-88].

2.2. Solid Materials

Three materials were used to carry out this work with six (6) devices, (1) 100% Fe⁰, (2) 25%/75% Fe⁰/S, (3) 25%/75% Fe⁰/Pz, (4) 25%/0%/75% Fe⁰/S/Pz (5) 25%/25%/50% Fe⁰/S/Pz, (6) 25%/50%/25% Fe⁰/S/Pz, with RZs containing varying proportions of materials. All samples are from Cameroon.

2.2.1. Metal Iron

The iron used in this work is iron wool made by the steel mills of Cameroon (Douala, Cameroon) and marketed in the various local markets; its granulometry is less than 1 mm. This material has shown its effectiveness in discoloring methylene blue [89]. It is used without treatment. The X-ray fluorescence analysis reveals: 0.62% Mn, 0.52% Si, 0.23% Cu, 0.2% Cr, and 0.09% Ni.

2.2.2. Sand

Sand (S) is a conductive natural aggregate used to modify the hydraulic conductivity of geotechnical systems. The sand used herein is a natural material taken in the Vina River (Cameroon), washed and rinsed with water boiled at 100°C for 3 hours and then dried at 110°C for 4 hours, it constitutes the different layers L₁ (upper), L₂ (intermediate or RZ) and finally L₃ (lower). For its availability and mixing agent, sand was used in Fe^o/H₂O systems [90-91]. The average chemical composition per X-ray diffraction reveals: 81.5% SiO₂, 5.60% Al₂O₃, 4.71% Fe₂O₃, 3.86% CaO, 1.75% TiO₂, 0.91% K₂O, 0.48% P₂O₅, 0.26% SO₃, 0.32% MnO, 0.08% SrO, 0.03% V₂O₅.

2.2.3. Pozzolan

The pozzolan (Pz) used comes from Idenau (Southwest, Cameroon) and has undergone the same pre-treatment as sand. It is L₂ layer (RZ). Pozzolan has a porosity of 60% which serves as a reservoir for Fe^oCPs [2, 75-76]. And has adsorption and absorption properties. The average chemical composition per X-ray diffraction is: 81.18% SiO₂, 10.00% Al₂O₃, 2.19% Fe₂O₃, 0.59% CaO, 0.46% TiO₂, 3.60% K₂O, 0.05% MnO, 0.02% SrO, 0.02% ZrO₂.

The chemical compositions were determined with the involvement of the Mission for the Promotion of Local Materials (MIPROMALO) in Yaoundé, Cameroon.

The table 1 below is a rundown of the materials in the top layer of the filter (L₁), in the reactive zone (RZ) or (L₂), and in the filter output (L₃), for a six column. A porous membrane separated the two layers of materials.

Table 1. Symbol, Granulometry, source, and nature of the materials used - ¹Communal Market, ²North Region, ³South West Region.

N°	Materials	Symbol	Granulometry	Source	Nature
1	Iron	Fe ^o	≤ 1 mm	Collected (CM ¹)	Adsorbent Generator
2	Sand	S	1 mm	Collected (NR ²)	Adsorbent
3	Pozzolan	Pz	2 mm	Collected (SWR ³)	Porous Absorbent / Adsorbent

Table 2. Names, Mass (g), and Proportions (%) of Fe^o, S, Pz in different filter processes.

	Column 1	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Filtering		Fe ^o	Fe ^o /S	Fe ^o /Pz	Fe ^o /S/Pz	Fe ^o /S/Pz	Fe ^o /S/Pz
Process		100%	25%/75%	25%/75%	25%/0%/75%	25%/25%/50%	25%/50%/25%
Mass (g)		(g)	(g)	(g)	(g)	(g)	(g)
1	L ₁	60	60	60	60	60	60
2	Fe ^o (RZ)	40	10	10	10	10	10
3	S (RZ)	00	30	0	00	10	20
4	Pz (RZ)	00	00	30	30	20	10
5	L ₃	120	120	120	120	120	120

2.3. Methods

2.3.1. Analytical Settings

For each specific RZ filter, we measured the filtering power of each device according to the proportions of the materials, pH, residual iron, and flow rate, for the most efficient device. The pH was measured using a Hanna model HI991301 pH-meter multifunction (temperature, conductivity). The OM content in the filter was determined using a UV-Vis spectrophotometer at 461 nm (Ling type 9100-9400) with a spectral range of 320–1100 nm. The effectiveness of fading the filter in the initial MO (C_o) was dependent on the residual OM content; the efficiency (E) to discoloration is given by the following relationship:

$$E(\%) = \left(1 - \frac{C_e}{C_o}\right) \times 100.$$

Residual iron was determined according to the 1.10 o-phenanthroline protocol. [86]. The UV-Vis spectrophotometer was read at 510 nm.

2.3.2. Filter Devices and Proportions

The six filter devices listed below were used to determine ratios. The reactive zone (ZR) contained 40 g of material for each filter, which corresponds to 100%. This percentage was distributed in filters according to filter devices; see Table 2. The RZ or L₂ (Fe^o/S/Pz) was sandwiched between two layers of sand (S) L₁ and L₃. Each day, 0.5 liters of orange methyl solution were filtered through each filtering device. The following different proportions were studied: 100% Fe^o; 25%/75% Fe^o/S; 25%/75% Fe^o/Pz; 25%/25%/50% Fe^o/S/Pz; and 25%/50%/25% Fe^o/S/Pz, as shown in figures 2 and 3.

2.3.3. Diagrams of the Experimental Processes

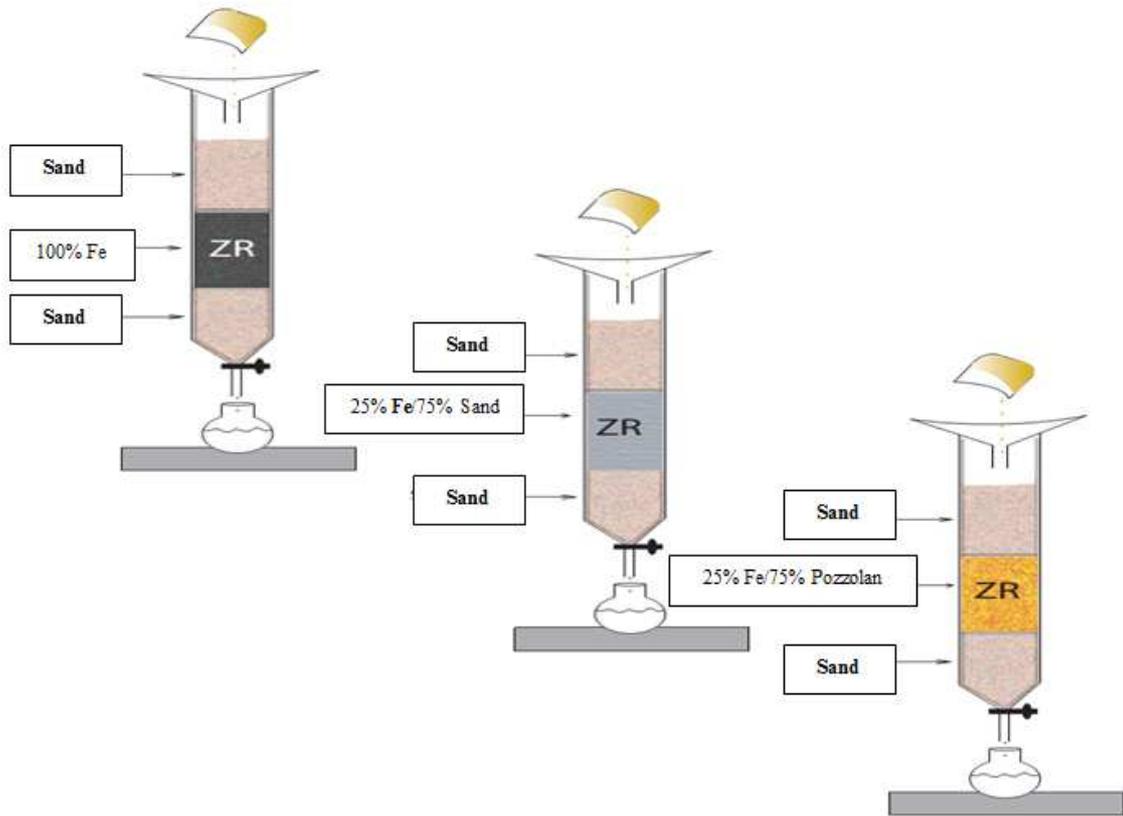


Figure 2. Binary Filtering Devices.

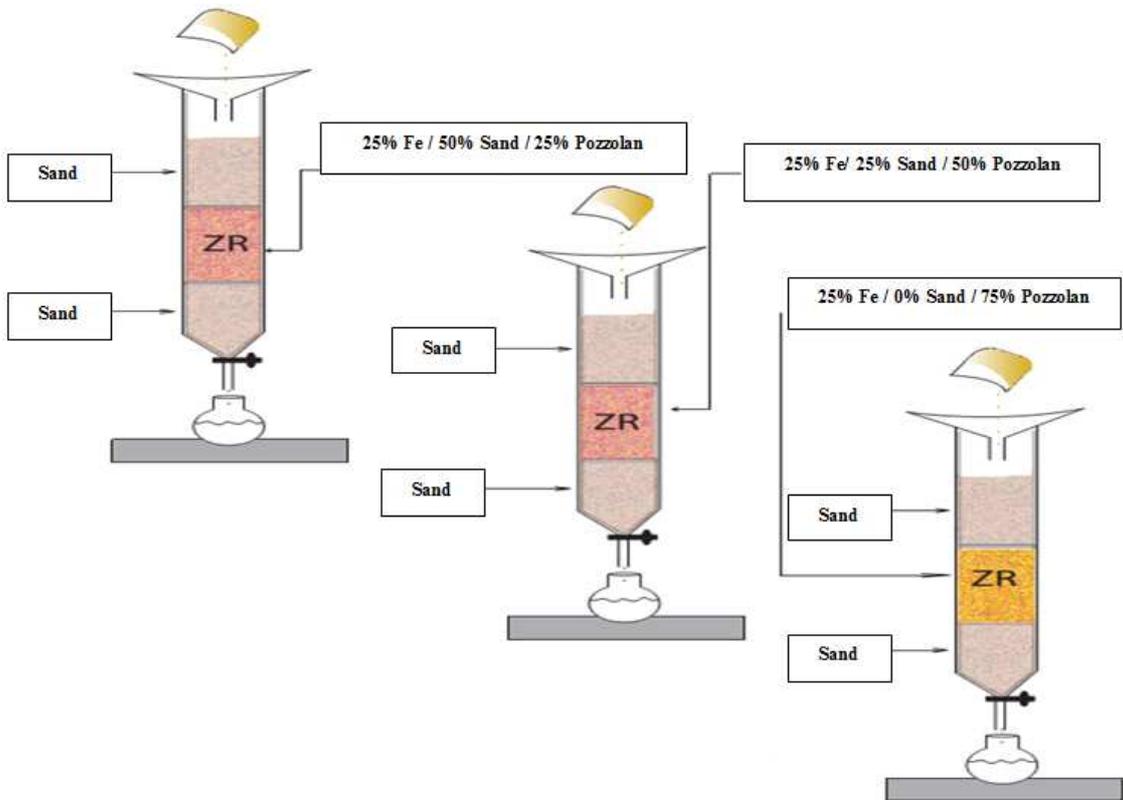


Figure 3. Ternary Filtering Devices.

3. Results and Discussions

3.1. OM Discoloration

3.1.1. Proportions of Fe⁰, S, and Pz in Binary Fe⁰-bed Filters

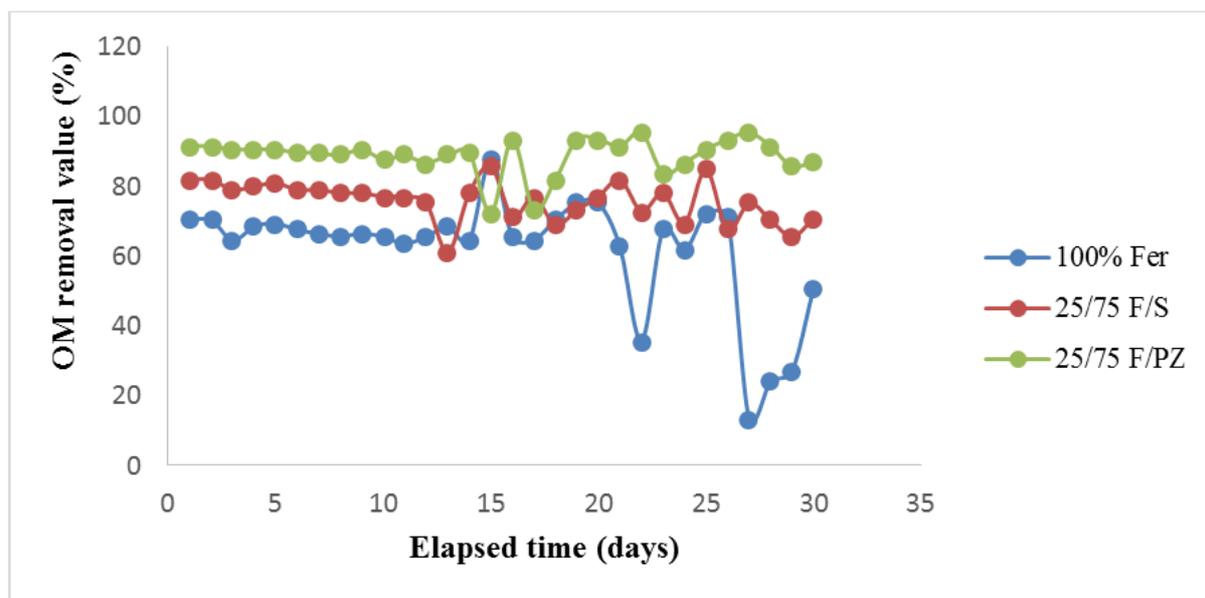


Figure 4. Orange methyl (OM) discoloration with mono and binary filter devices. $[OM]_0 = 2 \text{ mg/L}$.

Figure 4 depicts the effectiveness of the fading filters containing 100% Fe⁰; 25%/75% Fe⁰/S; and 25%/75% Fe⁰/Pz. The experimental device is that described in Subsection 2.3.2 and 2.3.3 in which the reactivity of the 100% Fe⁰-filter was compared to the filters containing 25%/75% Fe⁰/S and 25%/75% Fe⁰/Pz, in the presence of an OM solution at 2 mg/L and at pH = 5.2. These three devices differed only in terms of the RZ embedded between the two layers of sand. In binary devices, the proportion of Fe⁰ decreases from 100% to 25%, a decrease of 75%.

As a result, we found that the decrease in the proportion of Fe⁰ in filters did not result in a loss of responsiveness, but rather there was a resurgence when the Fe⁰ was combined with the S, and this was again more likely with Pz. We therefore went from a 70% average discoloration rate to 80% for an RZ Fe⁰/S, and 90% for an RZ Fe⁰/Pz. With a 25% Fe⁰ filter, the efficiency of discoloration improved, which corroborates the fact that it is necessary to avoid pure Fe⁰ filters, and that the most durable filters contain no more than 25% Fe⁰ [2, 69, 70, 83-85]. The binary filtering device 25%/75% Fe⁰/Pz was the most effective. Actually, such a result is an excellent report on the contribution of the RZ nature over the lifetime of the filtering system. These results are consistent with the disposal process of Fe⁰-based filters. Pure, they are prone to rapid clogging [29, 35, 48]; associated with S [82] and Pz [2, 71, 75-78], they are improved [12-14, 70]. The reactivity of the Fe⁰, and largely that of Fe⁰-based filters, involves electrochemical reactions of the wet corrosion of iron, and generates adsorbents that collect contaminants responsible for the discoloration. So, 100% Fe⁰ ≤ 25%/75% Fe⁰/S ≤

25%/75% Fe⁰/Pz.

3.1.2. Proportions of Fe⁰, S, and Pz in Ternary Fe⁰-bed Filters

Figure 5 depicts 25%/0%/75% Fe⁰/S/Pz, 25%/25%/50% Fe⁰/S/Pz, and 25%/50%/25% Fe⁰/S/Pz devices. The experimental process is that described in Subsection 2.3.2 and 2.3.3 in which the 100% Fe⁰ filter was transformed into a ternary device with three materials in the RZ. The filters with 25%/0%/75% Fe⁰/S/Pz, 25%/25%/50% Fe⁰/S/Pz, and 25%/50%/25% Fe⁰/S/Pz were tested with OM solution (2 mg/l) and a pH = 5.2. These three devices differed only in terms of the RZ sandwiched between the two layers of sand. Since the initial proportion of Fe⁰ in the scheme was now divided by four (4), we varied the rate of S (0%, 25%, and 50%) and Pz (25%, 50%, and 75%) in the RZ of the various ternary filtering devices.

The concomitant presence of the three materials in the RZ and the combined effect of their responsiveness reduced the rate of materials in the device while maintaining the efficiency at discoloration. Because of the great absorbent power of the Pz [71, 76-79], 25% seems to suffice in the presence of S and Fe⁰. Furthermore, 25% S also seems to be sufficient within a ternary device with 25%/25%/50% Fe⁰/S/Pz. Some studies were found that the presence of different functional groups in the dyes such as OM, can be an important factor for selective interaction with iron oxide nanoparticles [2, 26-27, 94]. The properties to serve the system as receptacles for Fe⁰CPs, makes Fe⁰/S/Pz stable device, which allow to reduce the proportion of Fe⁰ in the RZ, Figure 5.

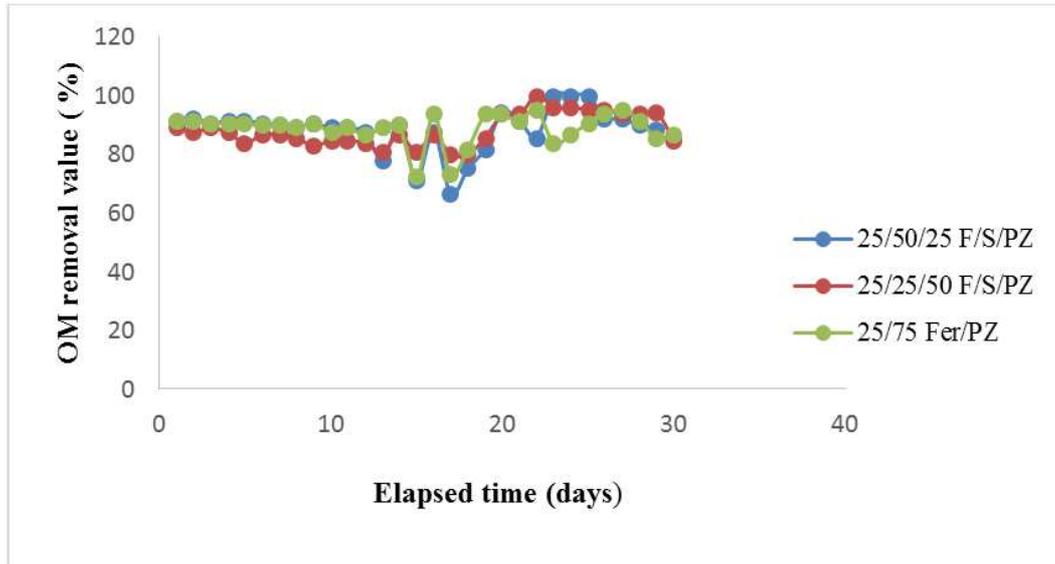


Figure 5. OM discoloration with ternary filter devices. $[OM]_o = 2 \text{ mg/L}$.

However, silica is very often added to Fe^0 to remedy the problem of chemical compaction of the iron bed that causes clogging of the pores [26, 72-74], which is usually caused by iron CPs that are responsible for decontamination, among other things; therefore, it is important to retain a sufficient proportion of sand to ensure this does not occur early. The

$Fe^0/S/Pz$ ternary device in proportions of 25%/50%/25% is a good compromise, since $25\%/0\%/75\% \text{ } Fe^0/S/Pz \approx 25\%/25\%/50\% \text{ } Fe^0/S/Pz \approx 25\%/50\%/25\% \text{ } Fe^0/S/Pz$. nevertheless, it would be more accurate to suggest that for discoloration ranges of $25\% \leq \% Fe^0 \leq 60\%$, $25\% \leq \% S \leq 50\%$, $25\% \leq \% Pz \leq 50\%$ are quite enough [2, 70].

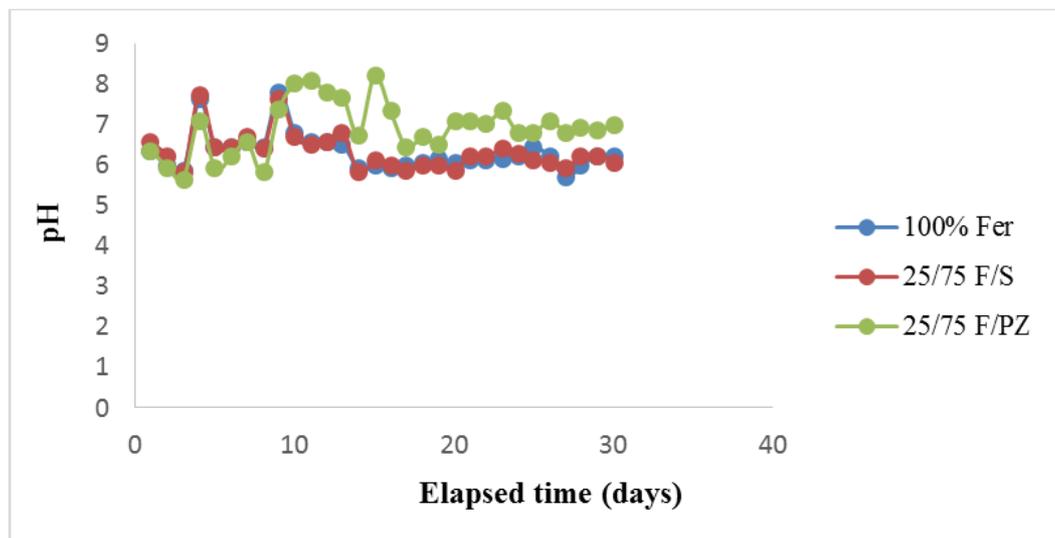


Figure 6. pH value with mono and binary filter devices. $[OM]_o = 2 \text{ mg/L}$, initial pH = 5.2.

3.2. pH Value

3.2.1. Proportions of Fe^0 , S, and Pz in Binary Fe^0 -bed Filters

Figure 6 depicts the pH with 100% Fe^0 ; 25%/75% Fe^0/S ; and 25%/75% Fe^0/Pz . These curves were therefore obtained from a 75% reduction in Fe^0 in the RZ. The measured pH values for the three devices have mean values between 6.5 and 7.5, which are acceptable according to the WHO guidelines (6.5 to 9.5). We did not see a change in pH due to

the association of sand in the binary filters for these proportions in the RZ; this was true even if the reactivity processes were different, since Fe^0 CPs are responsible for decontamination [2, 11, 29-68]. Sand reacts through surface phenomena: silanol clusters thus attract opposite-charged species and vice versa through repulsion of OM [26, 71-79]. Thus, the supply of Pz to the 100% Fe^0 filter slightly changed the pH because the Pz, due to its porous structure, could adsorb the OM and the iron CPs, resulting in an increase in pH [29, 76-78].

3.2.2. Proportions of Fe⁰, S, and Pz Materials in Ternary Fe⁰-bed Filters

Figure 7 depicts 25%/0%/75% Fe⁰/S/Pz, 25%/25%/50% Fe⁰/S/Pz, and 25%/50%/25% Fe⁰/S/Pz devices, and shows that for a proportion of 25% Fe⁰, the variation in the proportions of S at 25%, 50%, 75%, and Pz at 25%, 50%, 75% in the ternary devices always had a pH of between 6.5

and 7.5. The curves are even identical for the first fortnight, and the difference is not significant for the rest of the filter's life. From a 50% rate of Pz in the filtering device, the addition of this material seems to have no effect on the pH. The ternary device of 25%/50%/25% Fe⁰/S/Pz still represents a good compromise for pH correction. The 25%/25%/50% Fe⁰/S/Pz device provides a pH > 7.

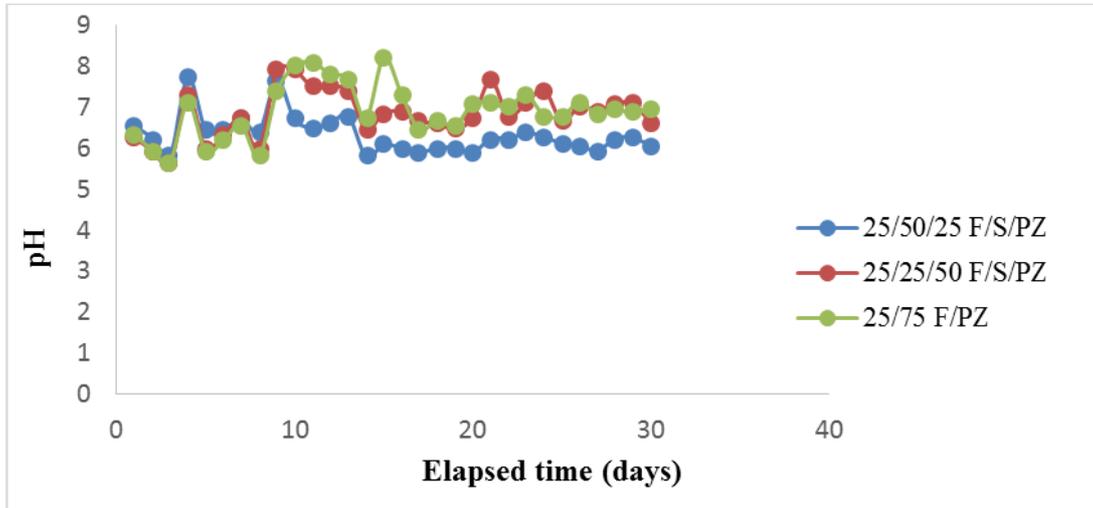


Figure 7. pH value with ternary filter devices [MO]₀ = 2 mg/L, initial pH = 5.2.

3.3. Iron Release

3.3.1. Proportions of Fe⁰, S, and Pz in Binary Fe⁰-bed Filters

Figure 8 depicts Fe⁰-CPs with 100% Fe⁰; 25%/75% Fe⁰/S; and 25%/75% Fe⁰/Pz, and the presence of iron in the collected water of 100% Fe⁰ and 25%/75% Fe⁰/S devices. The lack of iron for the 25%/75% Fe⁰/Pz filter shows the need to combine Fe⁰ with Pz as to retain the Fe⁰-CPs.

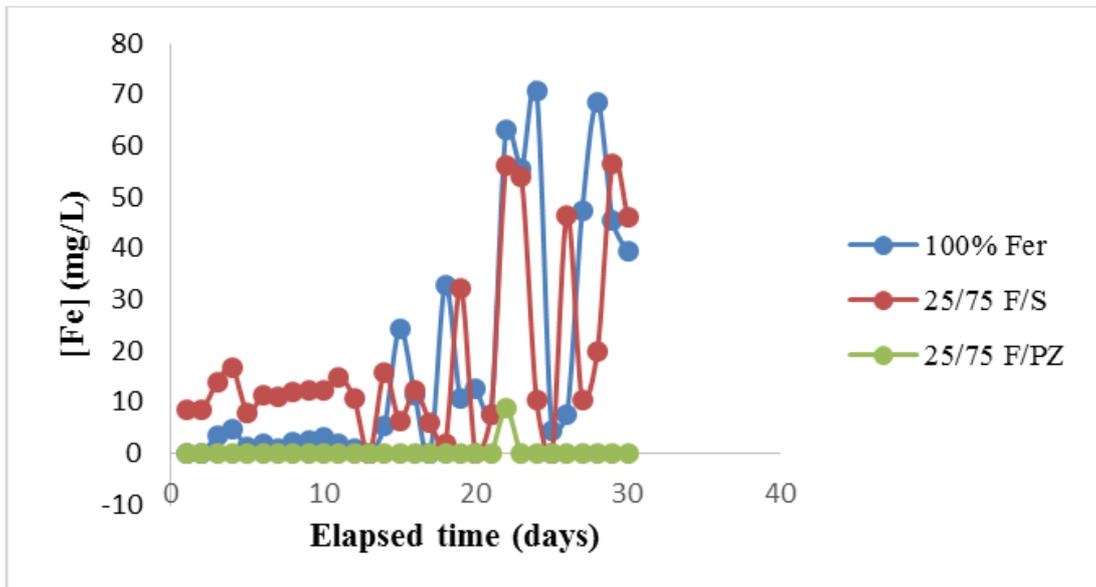


Figure 8. [Fe] (mg/L), OM filtrate, with mono and binary filter devices.

3.3.2. Proportions of Fe⁰, S, and Pz in Ternary Fe⁰-bed Filters

Figure 9 confirms the value of associating Fe⁰ with other

materials. Indeed, the passage of Fe²⁺ in solution during the oxidation of the Fe⁰ seemed to depend on the proportion of Pz in the RZ. The residual iron content was almost zero at 75% Pz in the RZ of a ternary device.

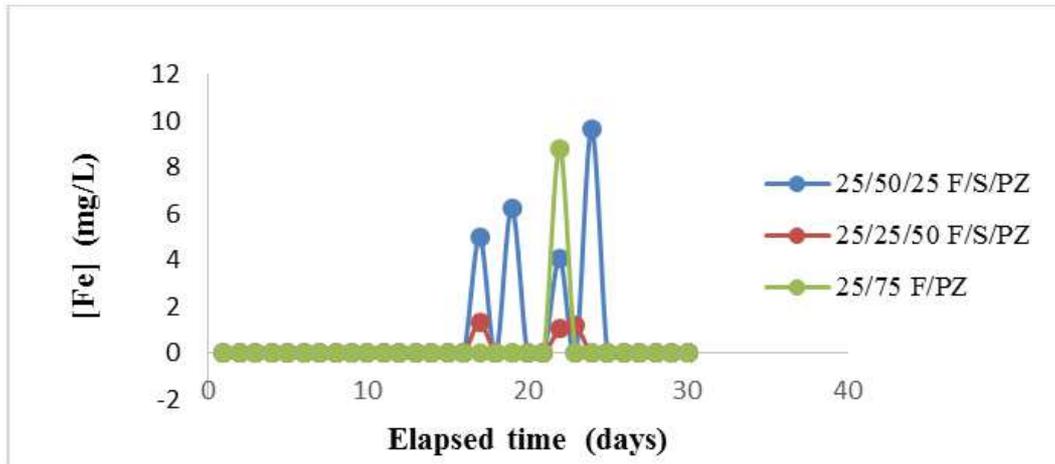


Figure 9. [Fe] (mg/L), OM filtrate, with ternary filter devices.

At 50% Pz in the RZ, the released iron content was negligible. At 25% Pz, this rate was slightly more effective, and even reached about 10 mg/l; however, this value remained well within the range of the WHO recommended values. A judicious ratio of $25\% \leq Pz \leq 50\%$ in a ternary device is effective. Even though the pH value significantly impacts the extent of Fe^0 dissolution, it

has been demonstrated elsewhere and refs cited therein that in this pH range, the solubility of iron is minimal [95]. So, S and Pz are not only admixing agent in Fe^0/H_2O systems, but they actually contribute to the elimination process as explained above. Therefore, Pz absorption/adsorption capacity makes $Fe^0/S/Pz$ an excellent device.

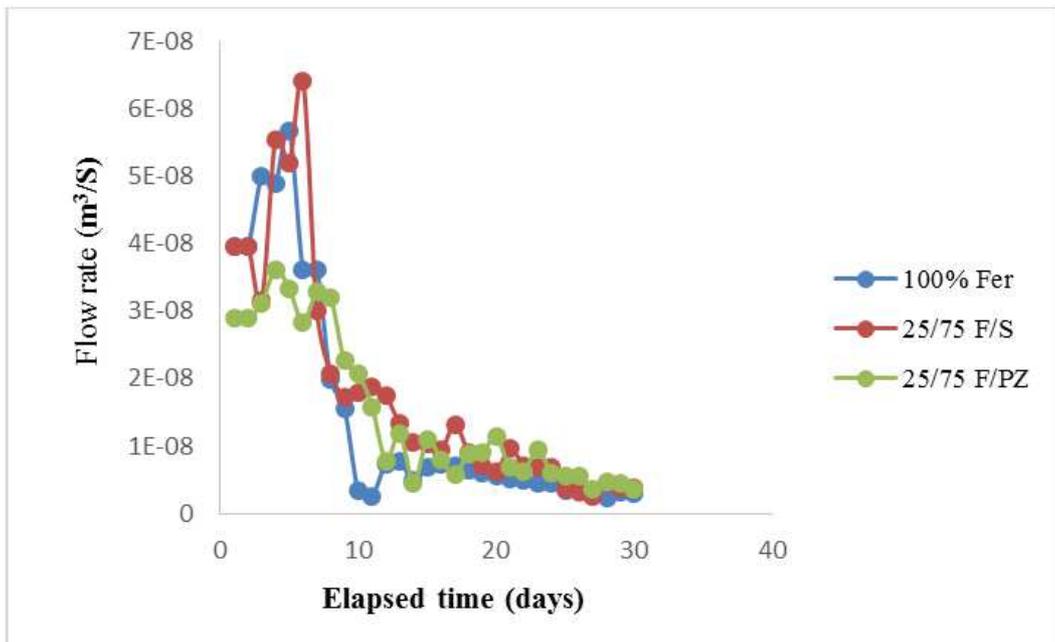


Figure 10. Flow rate (m^3/s) with binary filter devices.

3.4. Flow Rate

3.4.1. Proportions of Fe^0 , S, and Pz in Binary Fe^0 -bed Filters

Figure 10 corroborates what is said above. Indeed, the filter loses its porosity over time; however, it was the 25%/75% Fe^0/Pz filter that had the lowest throughput. This could be explained by the clogging of the pores of the Pz which would precipitate the clogging. The Pz effectively

contributes to the elimination of released iron in the medium and discoloration of the OM, but at the expense of flow rate.

The decrease of flow is attributed to the progressive clogging due to accumulation of OM in the initial pores and interstices systems. It is now agreed that pure Fe^0 systems are efficient but not sustainable. The replacement of a fraction of Fe^0 by a non-expansive porous material was therefore found as alternative approach [2, 5, 97-98].

3.4.2. Proportions of Fe⁰, S, and Pz in Ternary Fe⁰-bed Filters

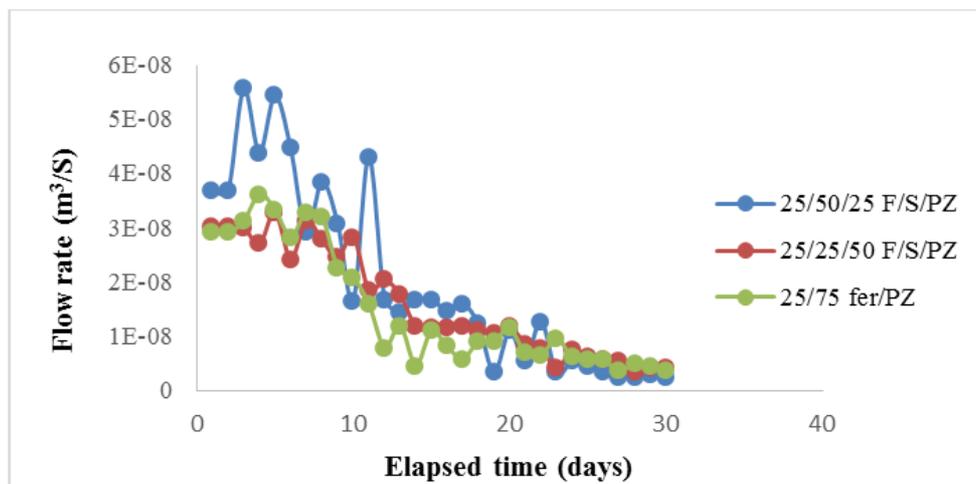


Figure 11. Flow rate (m^3/s) with ternary filter devices.

Figure 11 shows the evolution of the flow based on the content of Pz and S in the ternary filtering devices. It appears, therefore, that a high proportion of Pz hinders the flow, while a high proportion of S (sand) improves it. The filter containing 25%/50%/25% Fe⁰/S/Pz still seems to be the best compromise since it had the highest flow during the first 15 days and seems almost identical to the others in the second half of the filter's life. Such a device shows the need to introduce sand as to increase the porosity of the filter, and therefore, to improve its effectiveness in the fluidity of the filtering process. The Pz remains necessary for its contribution to the collection of micropollutants and in situ-generated Fe⁰-CPs.

4. Conclusion

This work aimed to establish the optimal operating conditions of a Fe⁰/S/Pz device through an OM colored indicator. For this, filtering devices containing 100% Fe⁰, 25%/75% Fe⁰/S, 25%/75% Fe⁰/Pz, 25%/0%/50% Fe⁰/S/Pz, 25%/25%/50% Fe⁰/S/Pz, and 25%/50%/25% Fe⁰/S/Pz material ratios in the RZ were used. The results obtained show that a 100% Fe⁰-filter is effective for discoloration of OM but allows residual Fe²⁺ to pass through the filter and is thus prone to early clogging. The combination of another material with the Fe⁰-bed filter is necessary. This was shown by the binary filter containing 25%/75% Fe⁰/Pz for which we obtained excellent discoloration of OM and elimination of the released iron in the filter at the expense of flow. The addition of sand was indispensable in terms of avoiding compaction. A ternary filter containing 25%/50%/25% Fe⁰/S/Pz constitutes the most effective device in terms of decontamination of OM and the flow rate. Ratios may vary within the ranges $25\% \leq \% \text{Fe}^0 \leq 60\%$, $25\% \leq \% \text{S} \leq 50\%$, and $25\% \leq \% \text{Pz} \leq 50\%$ for good pH correction and concrete mitigation of residual iron according to the WHO recommendations. These frames leave room for the

introduction of other materials into the RZ for the implementation of quaternary systems Fe⁰/S/Pz/X. They also provide a framework for any experimenter, for reproducibility and accuracy of results.

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