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Reactivity and Permeability Dynamics of a Fe^0/ Sand/ Pozzolan/ Charcoal Filter Bed for Water Treatment

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Abstract

This experimental study focuses on optimizing the proportions of constituent materials in a quaternary reactive zone (RZ) based on zero-valent iron (Fe°) for water decontamination. The system investigated combines Fe° (25%), pozzolan (Pz, 25%), sand (S), and natural charcoal (C) in varying proportions. Three (03) filtration systems were tested: (1) 25%Fe°/45%S/25%Pz/05%C; (2) 25%Fe°/35%S/25%Pz/15%C; (3) 25%Fe°/25%S/25%Pz/25%C. Methyl orange (OM) at 2 mg/L and pH 5.2 served as the tracer micropollutant. The parameters monitored over forty (40) days included residual iron, decontamination rate, conductivity, flow rate, redox potential, and pH. The results indicate that all three systems initially release Fe^{2+} (3.4 to 5.1 mg/L) through anodic corrosion of Fe°. The system containing 25% C maintains lower and more stable concentrations (maximum 3.4 mg/L), indicating better-distributed corrosion. The highest decontamination efficiency is observed in the 25%Fe°/25%S/25%Pz/25%C system, which is more performant and durable, with a decontamination rate between 98–100% and low, stable conductivity. This system also exhibits a low flow rate and high reactivity based on its potential values. All three systems raise pH values due to the buffering effect of charcoal.

Keywords: Zero-valent iron; filtration; methyl orange; pozzolan; charcoal; decontamination

1. Introduction

Population health remains a priority for the development of third-world countries. Water security is a prerequisite for existence. Water is becoming increasingly scarce, and the available quantity is threatened by unprecedented demographic growth. Accelerating universal access to safe drinking water (and sanitation) is the goal of the United Nations Sustainable Development Objectives [1, 2]. Decentralized solutions, such as small-scale water treatment units, are therefore necessary [3–5]. Peri-urban and urban areas have found themselves in difficulty; access to good-quality water has become difficult, and populations have opted to return to former natural supply sources. Water filtration through Fe° beds has proven to be one such affordable technology [2, 6–9]. Metallic iron is a suitable material for water treatment by filtration. It has been used successfully in various regions of the world to eliminate arsenic pollution [10, 11], as well as a variety of pollutants including fungicides, nitrates, and pesticides [11, 12]. Studies have established the universal filter equation for iron filters [13–15]. This dimensionless equation, based on the filling of the initial porosity of a granular bed by the expansive process (volume increase) of iron corrosion, indicates that the volumetric proportion in a filter bed should hardly exceed 60%. Moreover, the most durable filters will contain only about 25% iron. During the filtration process, pollutants are removed by adsorption, co-precipitation, and filtration.

Metallic iron (Fe°) is an example of a reactive material that can be used for water treatment and environmental sanitation. The removal of halogenated aliphatic compounds, aromatic compounds, nitro-aromatics, bacteria, heavy metals, and viruses has been achieved [16, 17]. Initially, the short lifespan of 100% Fe° filters was their main drawback. Loss of permeability is linked to the volumetric expansion that characterizes metal corrosion. Studies have shown that the volumetric proportion of Fe° in the filter bed should be reduced to a maximum [18]. Thus, a fraction of the particles in the filtration system must be a non-expansive material (gravel, pumice, sand) [19, 20]. The sizing of each filtration system is a function of the availability of materials (Fe° and other aggregates), the reactivity of the materials used, the kinetics of water flow, and the extent of contamination [21]. Fe° filtration has been developed for groundwater treatment in trenches known as "permeable reactive barriers." This technology has demonstrated its capacity to treat groundwater polluted by several classes of biological and chemical contamination.

In fact, the removal mechanism by Fe°-based filters appears to be clarified despite the confusions and gaps that have long tainted the understanding and interpretation of its remediation mechanisms [22–24]. Fe° cannot coexist with water; it undergoes oxidation, corrosion of Fe° [25, 26], into Fe^{2+} ions, thus involving the Fe°/Fe^{2+} couple (a). Hydroxide ions (OH^-) can originate either from the water reduction reaction (b) or from that of dissolved dioxygen (c). Reaction (c) is predominant as soon as the quantity of oxygen is sufficient [27]. In anoxic environments, in the presence of acidic waters (in the case of natural waters), the following process occurs [28] as illustrated in Figure 1 below (Is appear in the introduction, following the third paragraph) [27], thus detailing the corrosion process.

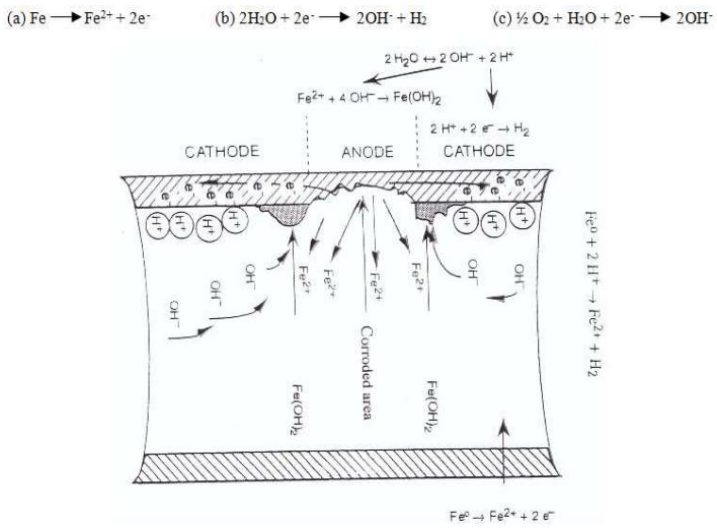

Figure 1: Corrosion in an anoxic environment [27].

Moreover, experience shows that iron oxides and hydroxides form on the metal surface; even though hydroxides form more rapidly, they are generally less stable than the corresponding oxides. Thus, Fe_2O_3 appears in place of $Fe(OH)_3$. Fe° is not stable at room temperature and is not taken into account [29–32]. These equations show that Fe° is a source of Fe^{2+} and H^+ ions. Fe° thus generates reducing agents [33, 34], and the consumption of H^+ ions induces an increase in pH. The contribution of Fe° and, consequently, of Fe°-based filters to the contaminant removal process is linked to the expansive nature (volume increase) of iron corrosion products [35], to the precipitation of iron hydroxides, and to their adsorbing properties for a wide range of soluble species [36]. Due to volumetric expansion, Fe°-based filters are subject to a loss of porosity and, consequently, a loss of permeability [31]. The solid corrosion products are iron hydroxides and oxides such as Fe_3O_4, Fe_2O_3, FeOOH, $Fe(OH)_2$, and $Fe(OH)_3$. These minerals have a permanent positive surface charge, little or not at all generated by proton adsorption on the surface of the corroded material [37, 38]. The reactivity of Fe° toward the contaminant is related to the affinity of the oxide layer for the species present and not for the passivated iron. The suitability of Fe° (Fe filters) for environmental sanitation thus results from its capacity to generate iron minerals that act as contaminant collectors (adsorption) [10, 25]. The precipitated minerals progressively fill the interstitial space within the filter, leading to a loss of permeability and clogging, but the removal of contaminants due to their size is increased [39, 40]. Fe°-based filters allow the removal of contaminants present in natural waters from the aqueous phase by adsorption, co-precipitation, and size exclusion. The uncertainty about the long-term permeability of Fe° filters stems from the evidence that aqueous iron corrosion is a volume-expansive process.

Even though the filtering power of Fe°-based filters no longer needs to be proven, and even though corrosion products act as contaminant collectors, it is advisable to avoid pure Fe° filters. The universal equation of the Fe°-based filter, based on the filling of the initial porosity of a granular bed by the

expansion process of iron corrosion, indicates that the volumetric proportion in a filter bed should hardly exceed 60%, and that the most durable filters contain only 25% iron [23, 41].

In Fe° metallic bed filtration systems, besides Fe°, the Fe°/S/Pz filter contains sand (S) and pozzolan (Pz). Sand (S) is composed of 85% to 95% silica, an inorganic polymer SiO_2 or $SiO_2 \cdot xH_2O$ consisting of an assembly of silicic acid molecules $Si(OH)_4$ condensed in a tetrahedral geometry. At pH > 2, silica has a negative surface charge, favoring the fixation of positively charged species. The reactivity of silica depends strongly on its surface properties, that is, on the site of physicochemical interaction processes with the medium. Silica is very often added to Fe° to remedy the problem of chemical compaction of the iron bed that causes pore clogging [19, 42, 43], generally caused by iron corrosion products (CPs) which are responsible, among other things, for decontamination. Pozzolan (Pz) is a material with varied physicochemical characteristics. With a neutral pH, its average chemical composition is 45% SiO_2, 15% Al_2O_3, 15% Fe_2O_3, and other minor oxides [44]. Its alveolar structure and porosity give it a water absorption capacity of 20% to 30% of its dry weight [45]. Due to its SiO_2 content, in addition to its high porosity, pozzolan (Pz) exhibits surface phenomena similar to those of sand (S) due to silanol groups [46].

Some studies have presented the different ranges: $25\% \leq Fe° \leq 60\%$, $25\% \leq S \leq 50\%$, and $25\% \leq Pz \leq 50\%$ are quite sufficient. The ternary device, in the proportions 25%/50%/25% Fe°/S/Pz, constitutes an excellent decontaminant for methyl orange (OM) [27]. The proportions of the Fe°/S/Pz/C device are studied using methyl orange (OM) to create a micropollutant model [47]. Given its physicochemical properties, OM naturally exhibits a high affinity for solid surfaces of opposite charge, such as certain iron corrosion products [48].

The main objective of this work is to establish the optimal operating conditions by quantifying the proportions of solid materials such as S and C in the quaternary RZ Fe°/S/Pz/C while maintaining the proportions of Fe° at 25% and Pz at 25%. Thus, the operational indicator OM will be used. Performance parameters such as decolorizing power, pH, iron released into the collected water, flow rate, potential, and conductivity will be measured using the filtrates of the following filtration devices: (1) 25%Fe°/45%S/25%Pz/05%C; (2) 25%Fe°/35%S/25%Pz/15%C; (3) 25%Fe°/25%S/25%Pz/25%C for correlations between proportions, reactivity, and performance.

2. Materials and Methods

2.1. Materials

2.1.1. Iron (Fe°)

Fine-quality "Grand Ménage" brand iron wool purchased in Douala (Cameroon) was used. Its average elemental composition was not determined because it has been proven not to be a determining reactivity parameter in itself for Fe° in general. Recent work [49] presented the first systematic study comparing the intrinsic reactivity of Fe°. The elemental composition (%) of the material they tested was: Fe: 99.08; Co: 0.05; Cu: 0.27; Ni: 0.11; and Cr: 0.49. The Fe° wool was cut into 0.5 mm sections to be used as a generator of iron hydroxides for contaminant trapping [8, 50]. Metallic iron is a suitable material for water treatment by filtration. It has been used successfully in various regions of the world to eliminate arsenic pollution, as well as a variety of pollutants including fungicides, nitrates, etc. During the filtration process, pollutants are removed by adsorption, co-precipitation, and filtration.

2.1.2. Sand (S)

Sand (S) is a natural conductive aggregate used to modify the hydraulic conductivity of geotechnical systems. It is an easily accessible material for populations. It has been used for water sanitation in slow filters. Slow sand filtration has been identified as an appropriate technology for water treatment in rural areas, so much so that it is recognized as an adequate technology for eliminating pathogenic microorganisms contained in water. It comes from the Vina River, one of the tributaries of the Logone River (in Cameroon). Chemical composition: SiO_2: 81.50%; Al_2O_3: 5.60%; Fe_2O_3: 4.71%; CaO: 3.86%; TiO_2: 1.75%; K_2O: 0.91%; P_2O_5: 0.48%; SO_3: 0.26%; MnO: 0.32%; SrO: 0.08%; V_2O_5: 0.03%; ZrO_2: 0.03%; Cr_2O_3: 0.03%; ZnO: 0.01%; CuO: 0.01%; NiO: 0.01%; Nb_2O_5: 0.01%; Rb_2O: 0.005%.

2.1.3. Pozzolan

Pozzolan has a porosity of 60%, which serves as a reservoir for Fe° corrosion products [44, 51]. It possesses adsorption and absorption properties. Unlike other natural rocks, pozzolan has a high water content, which can vary from 8 to 13% depending on the ambient hygrometric state. Closed pores are those that cannot be penetrated by a fluid, and open pores are those that communicate with the atmosphere. A good-quality natural pozzolan contains few non-reactive mineral phases such as clays or quartz. They mainly contain silica and alumina. This composition changes from one geographical area to

another. This pozzolan comes from the town of Idénau in Cameroon, in the South-West region. Chemical composition of Pz: SiO_2: 68.88%; Al_2O_3: 13.30%; Fe_2O_3: 11.19%; CaO: 0.59%; TiO_2: 0.46%; K_2O: 3.60%; MnO: 0.05%; SrO: 0.02%; ZrO_2: 0.02%; ZnO: 0.005%; Rb_2O: 0.01%.

2.1.4. Natural Charcoal

The natural charcoal used here comes from the carbonization of a species found in Central Africa, particularly in Cameroon in the Littoral region.

• Ayous (C)

Ayous, scientifically known as Triplochiton scleroxylon, belongs to the Sterculiaceae family and is a large deciduous tree reaching 50 meters in height. Ayous is widely distributed in the forest zone of West and Central Africa, from Cameroon and Guinea to the Central African Republic, and from South Gabon to the Democratic Republic of Congo. Fresh wood has an unpleasant odor that disappears upon drying. Ayous wood is light, with an average density of 0.38 kg/m³ at 12% moisture content. The wood dries easily and quickly in air, with a risk of deformation; mechanical properties are low. It is easily worked. The wood is widely used for interior joinery, panelling, moldings, furniture, rotary-cut and sliced veneers for inner and outer plywood layers, as firewood, and for charcoal. Recent work has demonstrated its adsorption capacity by removing OM [52]. The ayous species used in this work comes from Yassoukou (Cameroon).

Traditional Carbonization Procedure

We obtained these species in the Littoral regions of Cameroon. Previously dried in the form of wood pieces of 50 to 60 cm, which we further cut into small pieces varying in size between 15 and 20 cm. These wood pieces underwent another drying period of 10 days, sheltered from certain weather conditions, in a traditional kitchen to prepare them for carbonization. We set up a traditional kiln and introduced 10 kg of the species, applied a flame, and covered it. This phase lasted 2 hours; this first step allowed reducing the moisture content. The mass obtained as charcoal was 3.37 kg for Ayous. Having noted that this mass was still high, one day later we carried out another carbonization that lasted 1 hour, then proceeded to sieving and finally weighing: 2.32 kg for Ayous.

2.2. Material Treatment

Our various materials underwent treatments before their use:

✓ The iron sample used in our study is pre-treated, as it is commercial iron wool; consequently, pre-treatment was not necessary.

Sand, pozzolan, and natural charcoal are treated according to the following process:

✓ Sieving of samples:

We sieve our different samples of sand, pozzolan, and natural charcoal using inert polyethylene sieves to obtain particles with a granulometry ≤ 0.5 mm for sand and iron wool, and ≤ 1 mm for pozzolan and natural charcoal.

✓ Washing:

Using abundant potable water, we wash our samples to eliminate organic matter and certain odors, if present.

✓ Boiling:

Our materials are then brought to ebullition at 100°C for 3 hours in a water bath to eliminate microorganisms.

✓ Drying in an oven for 4 hours at 110°C and storage in sterilized jars.

Table 1 below presents the different materials used, specifying the particle size, source, symbol and chemical nature. It is the first table in the materials and methods section, in section 2.2.

Table 1: Source, Symbol, Granulometry, and Nature of the Materials Used.

Materials	Source	Symbol	granulometry	Nature
Iron	Local markets	Fe°	≤ 0,5 mm	Adsorbent generator
Sand	Ngaoundéré Vina	S	≤ 0,5 mm	Adsorbent
Pozzolan	Idénau	Pz	≤1 mm	Porous adsorbent/absorbent
Ayous charcoal	Yassoukou	C	≤1 mm	Poreuse adsorbant/ absorbant

Table 2 below, located in section 2.2. of the materials and methods section, is the second table presenting the composition of the reactive zones of the three filtration devices assembled during the experiment.

Table 2: Compositions of the Reactive Zones (RZ) of Each Filtration Device. Material masses in grams (g) and proportions in percentage (%).

Reactive zone (RZ)	Fe°(g)	Fe°(%)	S(g)	S(%)	Pz (g)	Pz(%)	C(g)	C(%)
Fe°/S/Pz/C	10	25	18	45	10	25	2	5
Fe°/S/Pz/C	10	25	14	35	10	25	6	15
Fe°/S/Pz/C	10	25	10	25	10	25	10	25

Figure 2 below presents a prototype of the variant reactive zone filtering device (Is located in the Materials and Methods section, just above the last paragraph of section 2.2).

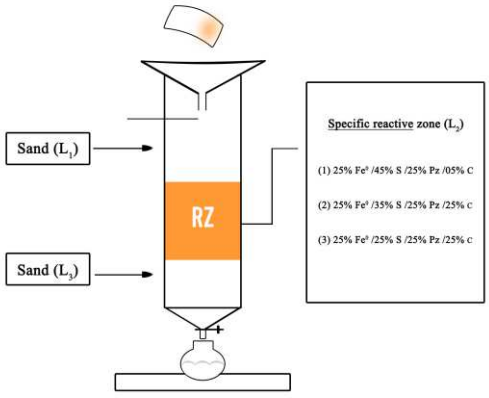

Figure 2: Three (03) experimental filtration devices with their specific reactive zone.

Each filtration device has a total material mass of 220 g, comprising layer L1 (m = 60 g sand), layer L2 (m = 40 g reactive zone), and layer C3 (m = 120 g sand); therefore, all our devices are equal in total

material mass. The first step consisted of introducing the materials into the different columns in the following order: L_3 bottom layer, L_2 RZ intermediate layer, and L_1 top layer.

2.3. Chemical Products

2.3.1. Fe^8 Dosage Solution

· Demineralized water, the solvent used for preparing all solutions;

· L(+)-ascorbic acid $C_6H_8O_6$ from E. Merck, Darmstadt, with a molar mass of 176.13 g/mol, prepared at a concentration of 7.1 g/L. The ascorbic acid solution was used to reduce Fe(III) in solution to Fe(II). Ascorbic acid also degrades dyes and eliminates interferences during iron determination.

· Ethanol CH_3CH_2OH at 90%;

· A standard iron solution for the calibration curve from Aldrich Chemical Company Inc (Milwaukee, Wisconsin, USA) with a concentration of 990 µg/mL and density 1.010, used to calibrate the spectrophotometer used for analyses.

· A saturated solution of sodium acetate trihydrate ($NaCH_3COOH \cdot 3H_2O$) from Analar, with a molar mass of 136.08, purity 99.0%, at a concentration of 1300 g/L.

· 1,10-phenanthroline $C_{12}H_8N_2$ from NORMAPUR for complexing Fe^{2+} ions necessary for spectrophotometer reading. The solution prepared at a concentration of 0.2 g/L was used for residual iron determination by spectrophotometry. The solution was prepared by dissolving 0.5 g of white crystals of 1,10-phenanthroline monohydrate in 25 mL of absolute ethanol (99.7% purity). The orthophenanthroline used came from ACROS Organics (Geel, Antwerp, Belgium) and was used to complex Fe(II) in solution.

To adjust our pH values, we used:

· NaOH for stabilizing MO; the solution prepared at a concentration of 40 g/L at pH 13.1;

· Hydrochloric acid HCl from NORMAPUR: density 1.16, molar mass 36.5 g/mol, purity 32%, with the solution prepared at a concentration of 1 M.

2.3.2. Methyl Orange (OM) Solution Dosage

OM is used in acid-base titrations as a colored indicator. Its color change range is between [3.1–4.4], allowing it to mark the presence of an acidic medium (turns red) or a basic medium (turns yellow). It naturally has a high affinity for solid surfaces of opposite charge, such as certain Fe° corrosion products [38, 53]. OM comes from KEM LIGHT PVT. LTD laboratories, Mumbai, India. This micropollutant was used to demonstrate the degree of reactivity of the materials for comparative study. Thus, the solution used as a tracer in this work was prepared. The solution used has a concentration of 2.0 mg/L to approach natural pollution conditions [54]; it was prepared by diluting in 1000 mL of distilled water. The pH value is 5.2; this concentration was chosen to approach natural pollution conditions. Then, a quantity of the polluted solution was introduced into our devices to immerse the materials therein to reach an identical limit height for all, followed by 500 mL of the polluted OM solution at 2.0 mg/L with an initial pH of 5.2 ± 0.1 progressively into each filtration device. Then the various parameters such as pH, residual iron quantity, flow rate, conductivity, decontamination capacity, and potential of the filtrates from these devices were measured. Sampling was done daily for 40 days. The concentrations of MO and residual iron were determined by spectrophotometer, Spectroquant Pharo 300 UV-Vis from Sigma-Aldrich Inc (St. Louis, MO, USA). The wavelength λ for OM is 461 nm, and that for the iron solution is 510 nm; the cuvettes used are 1.0 cm. The experiùental protocol followed during this work is summarized in figure 3 below (Is located at the end of section 2.3.2. of the Materials and Methods section).

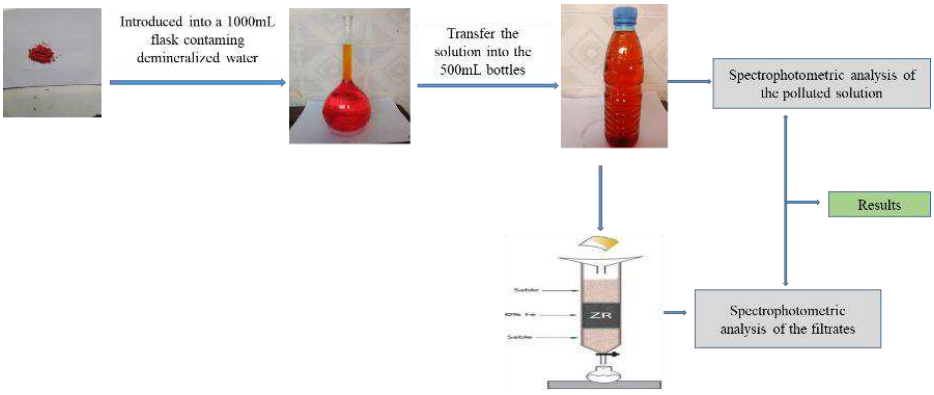

Figure 3: Experimental protocol for evaluating filtration devices with methyl orange (OM) as tracer.

3. Results and Discussion

3.1. Evaluation of Residual Iron Values of the Filtration Systems

Figure 4 below illustrates the changes in residual iron concentration of the filter media used in these filtering systems (Is the first figure in the Results and Discussion section, section 3.1.).

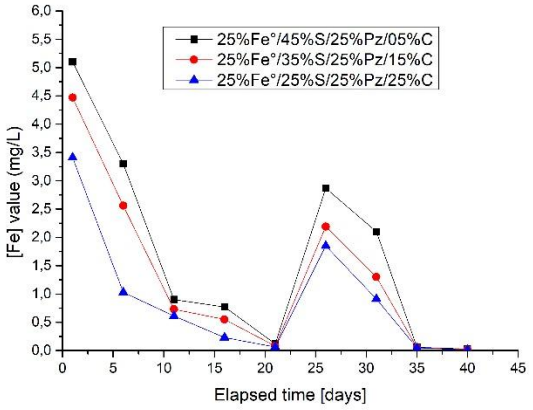

Figure 4: Curves showing dissolved iron variation of filtrates from 25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C filtering devices; [OM] = 2 mg/L; pH = 5.2; m_{RZ} = 40 g.

Analysis of the residual iron concentration monitoring graph for the filtrates of the three Fe(0) metallic bed filtration systems reveals an electrochemical behavior. This monitoring allows tracing the corrosion kinetics of Fe°. In the first days of the experiment, the values are high (from 3.4 to 5.1 mg/L), indicating rapid and intense oxidation of the iron surface. This phenomenon is explained by the anodic oxidation reaction of iron in aqueous medium:

$Fe° \rightarrow Fe^{2+} + 2e^-$ (E1).

This initial dissolution would be favored by the presence of dissolved oxygen. The rapid decrease in [Fe] between days 1 and 12 is explained by the precipitation and adsorption of these ferrous ions in the form of hydroxides or oxides ($Fe(OH)_2$, Fe_3O_4) on the surface of the filter bed [55]. The transient rise observed between days 14 and 26, with a notable peak (up to 2.9 mg/L for the low-C system), would reveal the dynamics of the oxide layer. This increase would suggest a local rupture of passivation: the oxide layer becomes porous or detaches under the effect of mechanical stresses, exposing the underlying metallic iron to corrosion again. This process is essential in electrochemistry because it shows that the metallic bed is

not simply consumed linearly but undergoes cycles of passivation/activation. In view of the foregoing, we believe that the 25%Fe°/45%S/25%Pz/05%C filtration system would be the most reactive in terms of iron release. The maximum concentrations observed (5.1 and 2.9 mg/L) indicate that C, as a conductive material, would favor the formation of galvanic micro-cells. The 25%Fe°/25%S/25%Pz/25%C system, with an increased proportion of charcoal (25%), maintains lower and more stable iron concentrations (maximum 3.4 mg/L). Increasing the charcoal fraction improves the overall conductivity of the bed, but the release kinetics would be slower and more controlled. The absence of an abrupt rise after day 20 would suggest a better distribution of corrosion over the entire available surface, avoiding the formation of preferential corrosion zones [56]. Concerning the 25%Fe°/35%S/25%Pz/15%C system, with an intermediate position, it would have a moderate rise on day 26 (2.2 mg/L), illustrating a balance between the accelerating effect of corrosion and the buffering effect of inert aggregates that dilute reactivity [57]. The presence of charcoal in these mixtures is not neutral; it would modify the local electrochemical potential and accelerate iron corrosion, resulting in more marked iron concentration peaks. However, the low values after day 35 for all systems (close to 0 mg/L) would indicate that almost all the released iron has been trapped in the form of precipitates, confirming that Fe°-based filtration acts as an effective geochemical sink for dissolved iron.

3.2. Evaluation of Methyl Orange Decontamination Rate Values of the Filtration Systems

The removal capacity of methyl orange by these three filtering systems is illustrated in figure 5 below (Is the sixth figure in the Results and Discussion section, section 3.2.)

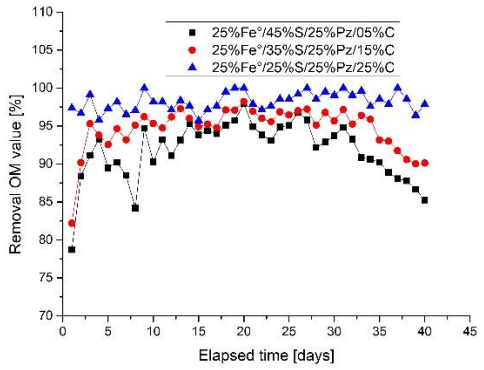

Figure 5: Curves showing the variation of decontamination efficiency for OM in filtrates from 25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C filtering devices; [OM] = 2 mg/L; pH = 5.2; m_{RZ} = 40 g.

These methyl orange (OM) removal curves by zero-valent iron (Fe°)-based filter beds reveal distinct performance dynamics depending on the reactive mixture composition.

The 25%Fe°/25%S/25%Pz/25%C filtration system stands out for its highest and most stable performance throughout the experimental period. From the first days, it reaches removal rates approaching 98–100%, and it is the only one to maintain these quasi-optimal levels for more than 30 days before showing a slight decrease, remaining above 97% at the end of the experiment (40 days). This remarkable stability is explained by the combined effect of the three adjuvants present in equal proportions. Pozzolan and charcoal, as porous non-expansive materials, act as support agents that trap iron corrosion products and delay clogging of the reactive zone. This would allow Fe° to conserve a large part of its active surface for the electrochemical degradation of the dye, explaining the persistence of its effectiveness [58]. The 25%Fe°/35%S/25%Pz/15%C system shows intermediate performance with an initial phase of power increase followed by a more marked degradation. It reaches its maximum on day 20 (around 98%), then declines progressively to stabilize around 90% at the end of 40 days. The reduction in the charcoal proportion (from 25% to 15%) seems to be the limiting factor. Charcoal plays a crucial role in adsorbing corrosion products and regulating electrochemical processes at the Fe° interface. A lower quantity of this carbonaceous material leads to a more rapid accumulation of corrosion products on the iron surface, thus reducing the system's reactivity in the long term [27]. Then, the 25%Fe°/45%S/25%Pz/05%C system is the least performant of the three. Although it also reaches a peak efficiency of around 97% midway, it exhibits the lowest removal rates at the beginning (around 78% on day 1) and experiences a much more pronounced decline from day 25, dropping to around 85% at the end of the experiment. This configuration is characterized by the highest sand proportion (45%) and the lowest charcoal proportion (5%). Sand is an inert material that offers few adsorption sites for corrosion products compared to pozzolan and charcoal. Its relative dominance reduces the bed's capacity to manage iron precipitates, accelerating the passivation phenomenon of the reactive surface [27, 58].

These observations fall directly within the principles of electrochemistry applied to Fe° beds, where zero-valent iron acts as an electron donor ($E° = -0.44$ V), capable of reducing azo dyes such as methyl orange. This process is intrinsically linked to iron corrosion, which generates Fe^{2+} ions and corrosion products. The addition of natural porous materials such as sand, pozzolan, and charcoal fundamentally modifies the dynamics of this process by diluting Fe°; these materials ensure better contact between the contaminated water and the reactive iron surface. Pozzolan and charcoal, through their porosity and high specific surface area, adsorb iron precipitates that would otherwise accumulate on Fe° and block active sites. This "cleaning" effect is essential for maintaining the system's reactivity over the long term. The carbon contained in charcoal plays a crucial role in promoting galvanic micro-cells with iron, thus accelerating electron transfer to the pollutant. It also helps buffer pH and adsorb part of the dye [52]. The progressive degradation observed in filtration systems with low charcoal content (5% and 15%) is therefore mainly due to the accumulation of these corrosion products that eventually passivate the iron surface, reducing its electrochemical efficiency. In contrast, the system with 25% charcoal (and 25% pozzolan) would benefit from a synergy that considerably delays this passivation phenomenon [27, 58].

The study demonstrates that the long-term performance of a Fe°-based filter bed for methyl orange removal depends less on the total amount of iron than on the balance between the different components of

the reactive zone. The balanced quaternary system (25%Fe°/25%S/25%Pz/25%C) is clearly superior because it combines the reducing action of iron, the retention capacity of pozzolan, and the activating and adsorbing effect of charcoal. This configuration allows not only achieving quasi-total removal rates but above all maintaining them over time, which is an essential criterion for any wastewater treatment application. Conversely, systems where charcoal is in a minority proportion see their efficiency drop rapidly, confirming that carbon is the key element for ensuring the durability and clogging resistance of these electrochemical treatment devices.

3.3. Evaluation of Conductivity Values of the Filtering Systems

These curves in figure 6 present the evolution of conductivity values for the three filtering devices (Is the third figure in the Results and Discussion section, section 3.3.).

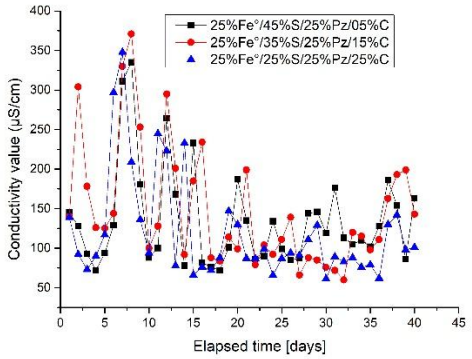

Figure 6: Curves showing the conductivity variation of filtrates from 25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C filtering devices; [OM] = 2 mg/L; pH = 5.2; m_{RZ} = 40 g.

Conductivity serves as an indirect indicator of the ionic concentration in solution, which evolves over time under the effect of electrochemical reactions and sorption processes. The conductivity values measured for the three Fe(0) metallic bed filtration systems (25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C) reflect the complex dynamics of the reductive degradation of methyl orange (OM).

The three curves show significant fluctuations with very pronounced peaks (maxima), notably between the 3rd and 8th day. These peaks suggest a rapid release of Fe^{2+} ions and ionic species from the rupture of the azo bond, before these ions are consumed again by precipitation or adsorption reactions. The system with 15% C shows the highest conductivity values, which could indicate greater Fe^{2+} production at this stage of the reaction [59]. Fe° is the heart of the electrochemical reaction; its corrosion in aqueous medium releases electrons that directly reduce the -N=N- bond of methyl orange, forming less toxic

aromatic amines [60, 61]. Sand (S) and Pozzolan (Pz) play a support and filtration role. Pozzolan, due to its porous nature, could retain certain species and promote dye adsorption on active sites. Regarding natural charcoal (C), it acts mainly as an adsorbent material; its presence influences conductivity by adsorbing OM molecules and intermediate ions, which explains the notable differences between the curves, particularly the decrease in conductivity observed after the initial peaks. After the initial peaks (between 10 and 25 days), conductivities stabilize at lower values (between 50 and 150 µS/cm). This ionic depletion is consistent with the precipitation of iron hydroxides (surface passivation) and lower ion production as the OM degradation reaction continues and becomes exhausted.

The degradation kinetics of methyl orange by Fe° generally follows a zero-order kinetic model under certain conditions, meaning the degradation rate is constant as long as the Fe° surface is active. The fluctuations observed in your data could reflect this complex kinetics, where the iron surface is constantly evolving (corrosion, passivation by reaction products) [60]. The fact that the system with 25% charcoal shows globally lower and more stable conductivity values could be a sign of a buffering effect or more efficient adsorption of ionic species by the charcoal, thus limiting the measured conductivity. Conversely, the system with 15% charcoal appears less effective at containing ion release, resulting in higher conductivity peaks.

3.4. Evaluation of Flow Rate Values of the Filtering Systems

The analysis of the flow rate curves (figure 7) reveals significantly different adsorption kinetics among the three filter materials for the methyl orange pollutant (Is the third figure in the Results and Discussion section, section 3.4.).

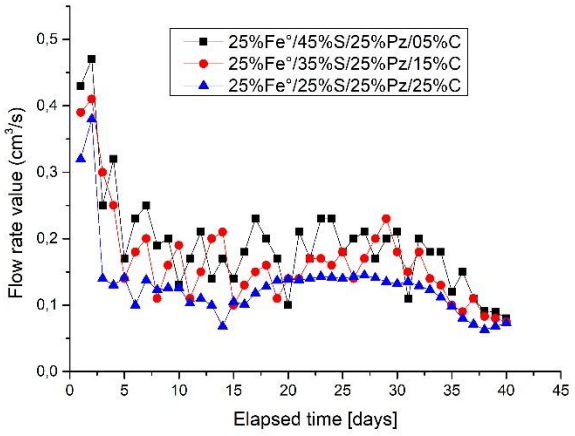

Figure 7: Curves showing the flow rate variation of filtrates from 25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C filtering devices; [OM] = 2 mg/L; pH = 5.2; m_{RZ} = 40 g.

Analysis of the hydraulic performance of these three metallic iron (Fe°)-based filtration systems reveals a complex competition between treatment efficiency and physical durability of the filter bed. The behavior observed in these experimental columns is typical of Fe°/sand/pozzolan systems, where the drop in flow rate is the direct result of the internal geochemical evolution of the medium.

For all three systems, the abrupt drop in flow rate (from ~0.45 to ~0.2 cm^3/s) is mainly due to an initial "rinsing" effect. The finest particles present in the sand (S) and pozzolan (Pz) are mobilized and come to clog the pores, thus reducing hydraulic conductivity. This phase is inevitable and constitutes a period of physical stabilization of the medium [62, 63]. From day 5 to 25, the nature of the additives (S, Pz, C) plays a crucial role. The 25%Fe°/35%S/25%Pz/15%C system maintains a significantly higher flow rate than the 25%Fe°/45%S/25%Pz/05%C system. Although charcoal (C) is often porous, a higher percentage (15%) seems to improve the overall permeability of the mixture, probably by creating a more aerated structure or limiting bed compaction. Conversely, the 25%Fe°/25%S/25%Pz/25%C system has the lowest flow rate, suggesting that too high a proportion of pozzolan or a specific granulometry creates a stronger hydraulic resistance, despite its intrinsic porosity [55, 57]. After 30 days, the flow rates converge and stabilize around 0.1 cm^3/s. This convergence indicates that the system has reached a new hydrodynamic equilibrium. The smallest pores are now clogged, but a network of "preferential channels" has developed, allowing water to circulate in a reduced but sufficient volume to maintain flow [63].

The progressive decrease in flow rate is the visible symptom of two major processes occurring simultaneously within the Fe° bed [62]. Mineral precipitation is the dominant mechanism; Fe° corrosion releases Fe^{2+} ions that react with carbonates, silicates, and dissolved oxygen in the water to form iron oxides (magnetite, maghemite) and other minerals. These precipitates accumulate in the pore spaces, drastically reducing porosity and hydraulic conductivity. Under accelerated conditions, this porosity reduction can reach 45% in only 72 days [64]. Anaerobic iron corrosion and methyl orange degradation can generate gases (hydrogen, nitrogen). These gas bubbles can obstruct pores, contributing secondarily but significantly to permeability loss [62, 63]. The literature shows that Fe°/pozzolan mixtures are effective and durable because pozzolan can improve long-term permeability compared to sand alone. It probably acts as an inert and porous support which, unlike sand, can maintain a certain structure even when iron precipitates form [57, 63]. The system with 15% charcoal maintains the best flow rate and is consistent with the idea that charcoal, as a porous material, can provide alternative flow paths and a better retention capacity for precipitates, delaying complete clogging [55]. The convergence of flow rates to a low level (~0.1 cm^3/s) suggests that the system reaches a state of "partial clogging." Although this state protects the medium from total collapse, the reduced volume considerably decreases the contact time between water and Fe°. In a real system, this means the pollutant might no longer be treated efficiently because water flows through too rapidly [63]. The 25%Fe°/35%S/25%Pz/15%C system seems the most promising in terms of maintaining flow rate over the first 25 days; however, the general trend shows that all systems are subject to inevitable mineral clogging.

3.5. Evaluation of Potential Values of the Filtering Systems

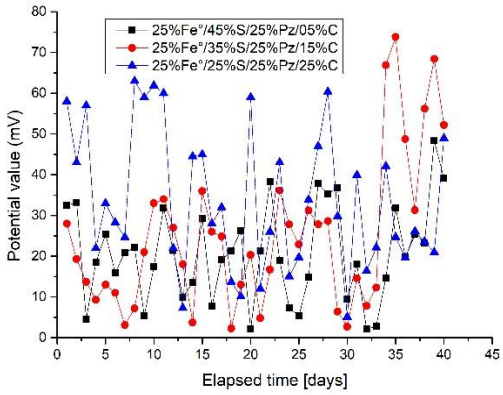

Figure 8: Curves showing the potential variation of filtrates from 25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C filtering devices; [OM] = 2 mg/L; pH = 5.2; m_{RZ} = 40 g.

Analysis of the electrode potential data (in mV) over time for methyl orange adsorption by different filter materials reveals distinct behaviors (figure 8 above, is the fifth figure in the Results and Discussion section, section 3.5.). The fluctuations in the oxidation-reduction potential illustrated in your graph constitute a valuable indicator of the reactive dynamics within each system. Low values (< 30 mV) mark reducing conditions, favorable for methyl orange (OM) degradation. They signal strong Fe° activity (corrosion) and production of Fe^{2+}/H_2 ions, indicating that the system is in full action. High values (> 40 mV) reflect oxidizing (less reducing) conditions, often linked to local Fe° depletion or water renewal that "consumes" the reducing power [66]. The 25%Fe°/45%S/25%Pz/05%C system is the most stable; values remain mostly between 20 and 40 mV, suggesting optimal synergy. Pozzolan (Pz) and sand (S) ensure good permeability, preventing clogging, while charcoal (C) adsorbs OM, which maintains iron activity [67]. For the 25%Fe°/35%S/25%Pz/15%C system, it shows the most erratic behavior. The very high peaks (up to ~73 mV) at the beginning, followed by sharp drops, would indicate an unstable system, probably due to rapid clogging by iron oxides (passivation) because of the high carbon content [66]. The 25%Fe°/25%S/25%Pz/25%C system is the most reactive (lowest potentials); however, the very low sand content (25%) would suggest a high risk of long-term clogging. The strongly oscillating values would indicate an alternation between phases of high activity and obstruction [68]. The composition of the system (5% C) offers the most stable and durable electrochemical signature, essential for continuous treatment. Conversely, the system (15% C) shows marked instability, and the system (25% C) a risk of long-term clogging. These observations underscore the importance of the balance between iron reactivity and granular structure (sand/pozzolan) to avoid passivation and preserve filter efficiency.

3.6. Evaluation of pH Values of the Filtering Systems

pH a key parameter in water treatment, and figure 9 illustrates the changes in the pH values of the filtrates from these filtration systems during the experiment (Is the sixth figure in the Results and Discussion section, section 3.6.).

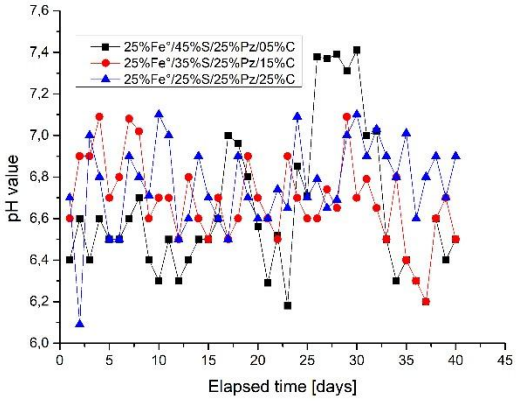

Figure 9: Curves showing the pH variation of filtrates from 25%Fe°/45%S/25%Pz/05%C, 25%Fe°/35%S/25%Pz/15%C, and 25%Fe°/25%S/25%Pz/25%C filtering devices; [OM] = 2 mg/L; pH = 5.2; m_{RZ} = 40 g.

pH is a key indicator in zero-valent iron (Fe°)-based systems. The pH fluctuations observed in the graph are directly linked to two major processes: iron corrosion and methyl orange (OM) dye reduction. The three curves show significant variations, with values approximately between 6.1 and 7.4 over 40 days. No system falls below neutrality (pH 7), indicating that the medium is buffered by the presence of materials (sand, pozzolan, charcoal) or reaction products.

The upward trend in pH at the beginning of the experiment (up to ~7.4) is a direct consequence of Fe° corrosion in aqueous medium. The iron oxidation reaction releases hydroxide ions (OH^-), which increases the alkalinity of the medium [69].

$$Fe° + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (E2)$$

In parallel, methyl orange (MO) degradation would consume protons (H^+) for the reduction of the azo bond, which could also contribute to this pH increase [60]. The 25%Fe°/45%S/25%Pz/05%C system shows the most marked fluctuations; pH rises rapidly to ~7.4 on day 30, then drops abruptly. This instability suggests rapid corrosion due to the high proportion of Fe° (25%), causing a massive release of Fe^{2+} ions. These ions can then precipitate in the form of hydroxides ($Fe(OH)_2$) or carbonates, causing the pH to drop by consuming OH^- [57]. For the 25%Fe°/35%S/25%Pz/15%C system, pH values are more stable, often above 6.5. The increase in charcoal proportion (C) from 5% to 15% would probably play a buffering role limiting excessive pH drops, contrary to the 05% C system [70]. The

25%Fe°/25%S/25%Pz/25%C system, for its part, shows a lower initial pH (~6.1) followed by a progressive rise. The high charcoal proportion (25%) and low sand proportion (25%) modify hydraulic conductivity and Fe° accessibility. The overall higher pH than the other systems would suggest that the corrosion reaction is less intense initially, possibly due to initial passivation of the iron grains by carbon, or better aeration (via pozzolan) favoring the formation of stable oxides.

Pozzolan (Pz), being an alumino-silicate material, has a high specific surface area and can adsorb Fe^{2+} ions. This can limit the accumulation of ferrous ions in solution, slowing OH^- production and explaining why the blue system (relatively richer in pozzolan) has a lower pH [57]. Charcoal (C), as a carbonaceous material, can catalyze oxidation-reduction reactions and interact with dissolved oxygen, creating local micro-environments where pH may be more acidic or more basic depending on the dominant reaction (iron oxidation vs. dye reduction). pH values above 6.0 confirm that methyl orange reduction by Fe° is chemically favorable, even at near-neutral pH. The variations observed over 40 days demonstrate that the systems are not at equilibrium and that the competition between iron corrosion (which alkalinizes) and iron oxide precipitation (which acidifies) governs pH dynamics. The system with 15% charcoal seems to offer the best operational stability.

4. Conclusion

This study demonstrates that the long-term performance of a Fe°-based filter for OM removal depends less on the total amount of iron than on the balance between the components of the reactive zone. The balanced quaternary system 25%Fe°/25%S/25%Pz/25%C proves clearly superior: it combines the reducing action of iron, the retention and adsorption capacity of pozzolan, and the activating, buffering, and adsorbing effect of charcoal. This system allows achieving quasi-total removal rates (> 97%) and maintaining them over time, an essential criterion for any water treatment application. Conversely, systems where natural charcoal is in the minority see their efficiency drop rapidly due to the accumulation of corrosion products that passivate the iron surface. Charcoal thus appears as a key element for the durability and clogging resistance of these electrochemical devices. However, the 25% C system has a low flow rate and a risk of long-term clogging. This work confirms the interest of Fe°-based filters associated with natural porous materials (sand, pozzolan, charcoal) as a decentralized, affordable, and effective technology for access to drinking water in peri-urban areas.

Data availability statement

All data generated or analysed during this study are included in this published article and supplementary information files.

Ethical approval and accordance

Not applicable

Consent to Publish

Not applicable.

Consent to Participate

Not applicable

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Competing interests

The authors have no relevant financial or non-financial interests to disclose.

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Dipita Kolye, E. Y. H.: *Conceptualization, methodology, investigation, resources, writing original manuscript*

Suzanne Makota S. N.: *Resources, validation, format analysis, writing review and editing*

Djokam Dongue, S. A.: *Conceptualization, methodology*

Mintang Fongang, U. A.: *Conceptualization, methodology*

Watat, V. A.: *Conceptualization, methodology*

Dika Manga, J. M.: *Resources, supervision*

All authors read and approved the final manuscript.

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