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Treatment of Backwashed Water to remove Heavy Metals and Radionuclides by Ceramic Filter

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ABSTRACT. The aim of this study is to assess the usefulness of ceramic filter for treating sand filter backwash water to remove heavy metals and radionuclides under controlled flux. The treated water is recycled inside water treatment plant to reduce the wastage of water sources and enhance the effectiveness of water resources management. Daily, typical backwash water produced from sand filter represents about 7% of raw water and it usually is disposed of because of its contamination due to heavy metals like iron (Fe), manganese (Mn) and radionuclides like radium (Ra). This amount of water is very critical in arid region which already are suffering from scarcity of water resources. The main advantages of using ceramic filter as compared to conventional sand filter is using such an amount of backwash water which consume only 0.7% of raw water which is 10 times less than backwash water produced from sand filter. The proposed treatment process was operated without any chemical addition with continuous filtration using ceramic filter. Under 300-430 L/m^{2}h flux, the pilot plant was operated 24 h for 60 days, with 1 min backwash every day. The process was achieved about 98.5%, 91.2% and 99.2% removal efficiency for Fe, Mn and Ra, respectively. Such technology can decrease backwash water from the conventional water treatment plants and would enhance effectiveness of sustainable water resources management.

Keywords: Ceramic filter, Backwash water, Flux, Iron, Manganese, and Radionuclides

1. Introduction

Sustainable water resources management is an essential solution to conserve natural resources especially in arid region like Saudi Arabia. Exploitation of any water resource and diminishing any wastage is substantial [1]. Disposal of sand filter backwash water produced from conventional water treatment is an example. The amount of backwash water can be reached up to 10% of treated water. In addition, its media has a high affinity to accumulate radionuclides due to chelating agents like iron and manganese oxides lead frequently media replacement complicated. There are different filtration processes including conventional slow or rapid sand filtration, manganese greensand filtration, anthra/sand or ironman sand filtration, electro-media filtration, membrane filtration (micro-, ultra-, nano- filtration) and ceramic filtration [2, 3, 4]. Among of these processes, ceramic filter is easily for clean by backwash, has a low quantity of backwash water comparing to sand filter, and has a low affinity to adsorb heavy metals and radioactive materials comparing to sand filter media.

Groundwater in Qassim region, Saudi Arabia, contains heavy metals like iron and manganese and radioactive materials like radium and radon as a gas. The reduced forms of ferrous (Fe^{2+}) and manganous (Mn^{2+}) divalent ions are soluble in groundwater and are removed in conventional water treatment by oxidation process followed by sand filtration. Typical iron concentrations in groundwater are 1.0 to 10 mg/L. On the other hand, manganese exists less frequently than iron and in smaller amounts. Typical manganese values in groundwater range from 0.1 to 1.0 mg/L [5].
Generally, iron and manganese in water are not considered to be health risks but when they exceed the maximum contaminant levels (MCL), they will be discolored water and cause taste and odor issues followed by consumer complaints and a general dissatisfaction with the water utility. United State Environmental Protection agency (USEPA) [6] has established secondary drinking water standards for iron and manganese. The MCLs for iron and manganese are 0.3 milligrams per liter (mg/l) and 0.05 mg/l, respectively. The processes for removing iron and manganese from water are based on the oxidation of relatively soluble Fe(II) and Mn(II) to insoluble Fe(III) and Mn(III, IV). The most common chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate, and ozone in addition to use of oxygen in air as the oxidizing agent [7]. In contrast, radium concentrates in the bone when ingested biochemically similar to barium and calcium. The USEPA, under the Safe Drinking Water Act, has set the Maximum Contaminant Level Goal (MCLG) for combined (^{226}Ra, ^{228}Ra) at zero pCi/L (pico-Curie per Liter) at which no

known effects on human health occur and has an adequate margin of safety. This level of protection based on the best available science can prevent potential health problems [8]. Radium can be formed when uranium and thorium undergo radioactive decay and can constantly be produced by the radioactive decay of uranium and thorium. They are found in small amount in few soil and rocks. The main radium isotopes found in the environment are ^{226}Ra and ^{228}Ra with an atomic weight of 226 and 228, respectively. Occurrence of Ra in groundwater in a variety of geologic sittings were found in USA [9], Spain [10], Brazil [11], Egypt [12] and Saudi Arabia [13, 14].

The aim of this study is to assess ceramic filter (CF) for treating rich heavy metals and radionuclides - specifically, Fe, Mn and Ra – from sand filter backwash water under controlled flux. The other aim of this paper is to recycle the treated water inside the water treatment plant to reduce the consumption of water sources and enhance water resources by appropriate management.

2. Materials and Methods

2.1. Materials

To determine radium concentrations, four liters of backwash water pass 7 mL of cation exchange resin namely C100 using manostat cassette pump operated at 60-70 RPM. Then drying the resin in tissue culture dish and store the samples inside a lead container at least for two days before analysis.

2.2. Methods

All samples were analyzed in General Directorate of Water Services (GDWS) laboratory in Qassim, Saudi Arabia. Fe and Mn concentrations were analyzed using an inductively coupled plasma mass spectrometer (PerkinElmer, NexION™ 300 ICP-MS) with Limit of Quantification (LOQ) = 0.7 μg/L for both Fe and Mn. Hyper pure germanium detector system model (GC3023) connected with crystal model (7500SL) and lead shields model (A360) were used for analyzing ^{226}Ra, ^{228}Ra radioactivity. The system is equipped with multi-channel analyzer (DSA1000) connected with PC using (GENNIE 2000) software. Liquid nitrogen has been used for cooling (to

–200˚C). For every sample, GENNIE 2000 was operated for 21600 seconds and programed to detect ^{226}Ra using its transition energy 186 kev and ^{228}Ra using its transition energy 911kev [13].

2.3. Pilot Plant

The pilot plant with a maximum capacity 125 m^3/d and filter area 12 m^2 was operated continuously for 60 days, 24 hrs with 1 min a day backwash using 0.2-0.3% of permeate water without chemical addition with using 0.1 µm CF from ItN, Germany. Max feed Fe and Mn concentrations are 300, 100 mg/L and maximum filtration temperature is 60˚C. The pilot plant was operated under 300-430 L/m^2h flux and 30-43 mbar transmembrane pressure (TMP).

2.4 Fouling Mechanism

Decline in flux can be used to determine fouling mechanism and confirmed the changes in TMP. Different models were developed to identify the mechanism of fouling such as cake-layer formation, standard pore blocking, intermediate pore blocking and complete pore blocking [15, 16, 17]. In this regards, Hermia [15] model was used in this study which is based on the following equation (1):

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (1)$$

Where V is filtrate volume (m^3), t filtration time (h), k constant pressure filtration and n = 0.5, 1, 1.5 and 2 for cake-layer formation, standard pore blocking, intermediate pore blocking and complete pore blocking, respectively. A cake layer forms on the membrane surface through the accumulation of the particle sizes larger than the size of the membrane pore. The cake layer grows with time and does not penetrate inside the pore. As a result, the cake may increase the efficacy of particle removal. However, the cake causes the decline of the flux as the membrane resistance increases due to the cake-layer formation. The permeation flux variation for the cake-layer formation can be expressed by the following linear equation (2):

$$\frac{1}{J^2} = \frac{1}{J_0^2} + k_{cl}t \quad (2)$$

In the same manner, the standard pore blocking can be expressed by the following linear equation (3):

$$\frac{1}{J^{1/2}} = \frac{1}{J_0^{1/2}} + k_{sb}t \tag{3}$$

Also, the intermediate pore blocking can be expressed by the following linear equation (4):

$$\frac{1}{J} = \frac{1}{J_0} + k_{ib}t \tag{4}$$

Final, the complete pore blocking can be expressed by the following linear equation (5):

$$\ln J = \ln J_0 + k_{cb}t \tag{5}$$

Where J is flux in (L/m^{2}h), J_0 initial flux, and constants k_{cl}, k_{sb}, k_{ib} and k_{cb} are the system parameters related to cake-layer formation model, standard pore blocking, intermediate pore blocking and complete pore blocking, respectively. A plot of $1/J^2$, $1/J^{1/2}$, $1/J$ and lnJ versus time (t) gives a straight line with a slope of k_{cb}, k_{ib}, k_{sb} as well as k_{cl}, and y-intercept of $1/J_0^2$, $1/J_0^{1/2}$, $1/J_0$ and lnJ_0. Also, Membrane productivity can be described by the temperature water mass transfer coefficient (MTC). The procedure of estimating MTC values is explained elsewhere [18].

3. Results and Discussion

3.1. Sand Filter Backwash Water Sampling

Table (1) shows the quality of sand filter backwash water analyzed every 15th day before treatment by CF. Although the water was very turbid and had high level of heavy metals and radium, the pH were normal and within 7.62±10. The maximum concentrations of Fe, Mn and Ra were 6.3 ppm, 5.12 ppm and 6000 pCi/L, respectively.

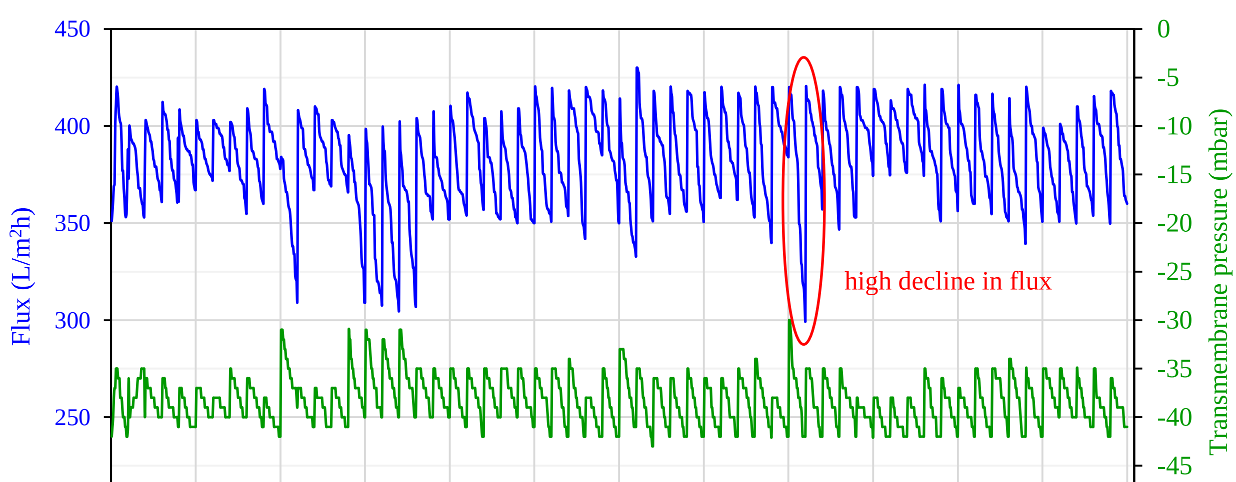
Table (1): Quality of sand filter backwash water before treatment of CF.

Parameters	1st day	15th day	30th day	45th day	Average
pH	7.51	7.7	7.72	7.67	7.65
Turbidity (NTU)	17.6	39	52.4	43.6	38.15
Fe (ppm)	6.1	5.5	6.3	5.7	5.9
Mn (ppm)	5.12	1.14	1.39	1.38	2.26
Total Ra (pCi/L)	4000-6000*				5000
Conductivity (µs/cm)	9360	9155	9538	9634	9422

* based on the GDWS experience

3.2. Operating the Pilot Plant

The pilot plant connected to the tank containing sand filter backwash water was equipped with mechanical mixer. The water was filtered directly without using chemical addition for 60 days. Pilot plant was operated under normal water temperature (38-42˚C) and there were no clear effects in filtration process and this finding was in line with another study results [19]. Flux and transmembrane pressure were investigated, recorded hourly and plotted as shown in Fig. (**1**). The maximum and minimum fluxs were 430 and 300 L/m^{2}h, respectively, which reasonable for such water that has 38 NTU turbidity. Sprinkle enhanced high-pressure backwash for 1 min and was enough to regenerate the CF performance. In only seven out of sixty days, the flux was dropped down 330 L/m^{2}h and the normal minimum flux during one day period filtration is 350 L/m^{2}h. Changes in flux and TMP for two days period filtration is illustrated in Fig. (**2**). As shown in the figure, flux and TMP had same pattern with time until backwash process was repeated to recover the CF performance.



Journal of Engineering and Computer Sciences, Qassim University
Vol. 13, No. 2, pp. 1-15 (July 2020 /Dhu-Al-Qi'dah 1441H)

Fig. (1). CF flux and transmembrane pressure during operation of pilot plant for 60 days without showing backwash effects

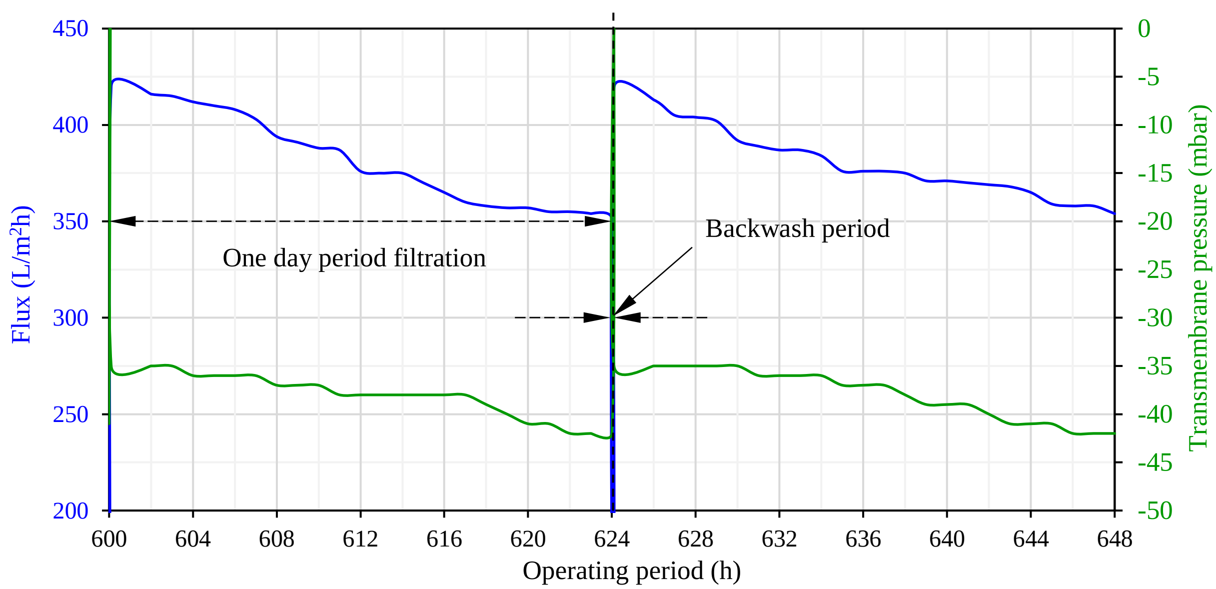


Fig. (2). CF flux and transmembrane pressure for two days of operation showing backwash effects

3.3 Treated Water

Table (2) summaries the treated water characteristics and shows high removal efficiencies achievement for turbidity, Fe, Mn and Ra. Removal efficiencies were calculated between average values shown in Table (**1** comparing to average values in Table (2). Turbidity was measured in the feed and filtrate water during pilot experiments to assess the solids rejection of CF. Results of turbidity analyses indicated that CF achieved high rejection of particulate contaminants. Specifically, 99.6 % of the water quality data showed filtrate turbidity less than 0.17 NTU. It is important to note that the treated water samples were generally collected after backwashing event for two to three hours to eliminate any effects of backwash process on water samples. Also, Fe and Mn removal by CF was assessed by measuring their concentrations in the feed and treated water during pilot experiments. As shown in Table (2), the measured Fe and Mn values indicated that the CF was more effective for removing Fe than Mn. Maximum removal were 98.5% and 91.2%, respectively. Regarding Ra removal, CF was very effective and achieved 99.2% removal for total Ra to reach around 31 pCi/L which is very reasonable if water be recycled and mixed with influent water for treatment plant used reverse osmosis (RO) for removing high total dissolved solids (TDS).

However, CF has no effects on conductivity as shown in Table (2) as compared to Table (1). In contrast, treated water has SDI less than 1 that means no fouling effects on RO process may occur. However, last period of experiment was concentrated on operational conditions of pilot plant rather than water characteristics.

Table (2): Treated water after treatment of CF.

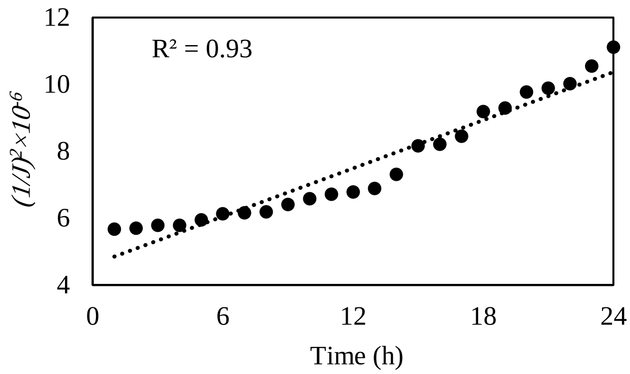
Parameters	**1st day**	**15th day**	**30th day**	**45th day**	**Average**	**%Removal**
pH	7.85	7.79	7.77	7.71	7.78	--
Turbidity (NTU)	0.15	0.16	0.13	0.17	0.15	99.6
Fe (ppm)	0.1	0.08	0.08	0.08	0.09	98.5
Mn (ppm)	0.23	0.23	0.16	0.18	0.2	91.2
^{226}Ra (pCi/L)	9.8	10.1	10.2	10.3	10.1	
^{228}Ra (pCi/L)	17.7	18.1	18.1	18.2	18.0	
Ra (pCi/L)	28.1 ± 2.9					99.2
Conductivity (us/cm)	9385	9146	8547	9625	9176	
SDI	0.6	0.3	0.3	0.6	0.45	

3.4 Fouling characteristic

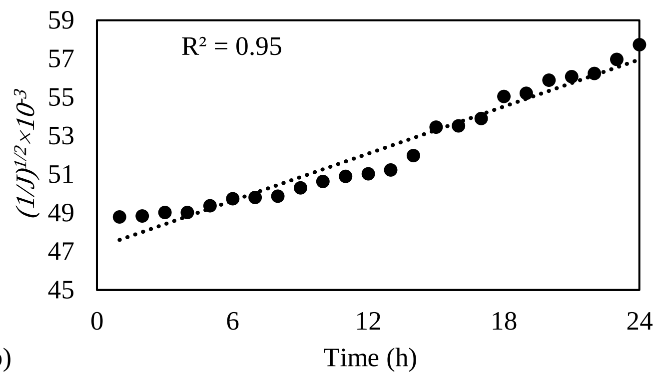
Selected CF is unique microfilter coated by nano-polymer layer to control fouling and optimize Fe, Mn, and Ra removal. To determine the type of fouling eq (2)-eq(5) were applied using worst case of filtration that showed high decline in flux as illustrated in Fig. (**1**). Fig. (***3***) shows high correlation for the four fouling models. However, complete pore-blocking model was higher than others ($R^2 = 0.96$) indicating that chemical cleaning was required. Note that, the trend of Figure (3d) comparing to Figure (3a, b, c) is due to natural logarithm used in eq (5). However, CF supplier recommend that chemical cleaning shall be applied every two months by using citric acid and HCl (pH = 2 – 2.5).

The MTC value was determined through linear regression of flux on TMP with time as illustrated in Fig. **(*4*.** The trend lines were developed by using Microsoft EXCEL and show that negative slope of MTC with time, indicating that MTC decreased with time under a given time period and experimental conditions and can be used as an indicator for the long term of CF fouling.

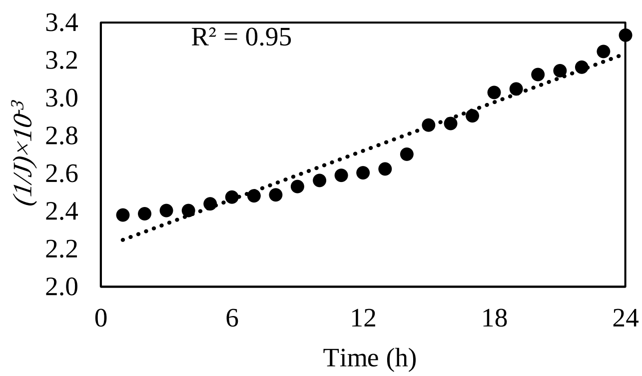
Journal of Engineering and Computer Sciences, Qassim University
Vol. 13, No. 2, pp. 1-15 (July 2020 /Dhu-Al-Qi'dah 1441H)



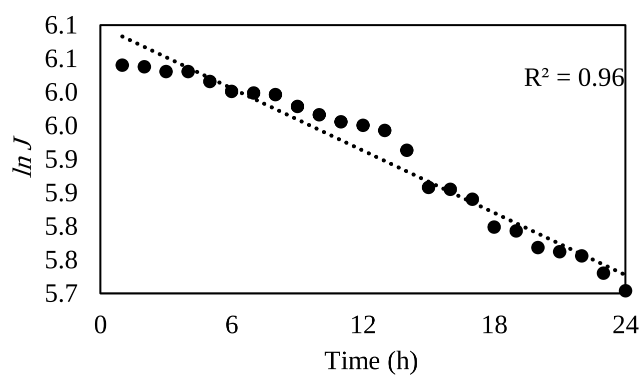
(a)



(b)



(c)



(d)

Fig. (3). Correlation between flux and time: (a) cake-layer formation model, (b) standard pore-blocking model, (c) intermediate pore-blocking model, and (d) complete pore-blocking model

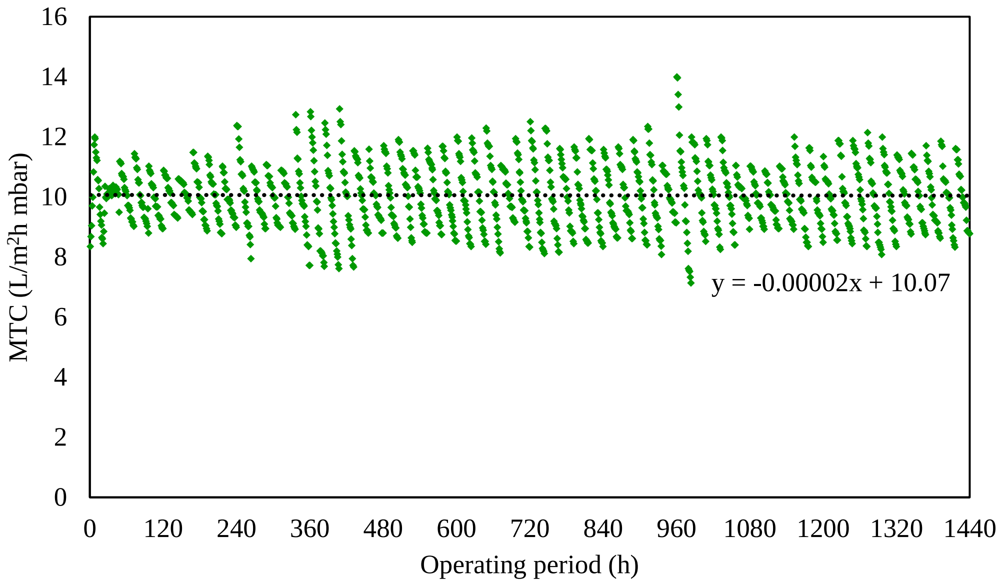


Fig. (4). MTC vs. operating time illustrate slightly negative liner trend line

4. Conclusions and Recommendations

Selected CF treated sand filter backwash water and produced water with a reasonable quality to be recycled within water treatment plant. CF can reduce the operational cost, the energy consumption and also the amount of wastewater which may represent around 70-80% of disposed water. It lead to conserve water resources and reduce the waste of land which otherwise is used as evaporation pond. The evaporation pond used for collecting backwash water, discharged form Buraidah water treatment plant, Saudi Arabia, is located approximately 10 kilometers south of the plant. As a result, of decreasing the amount of discharged water, the cost of operating water pumps for transfer of backwash water to the pond will reduce significantly. The recovery for water treatment is enhanced and can be reached to more than 97%. Ceramic filter in this regards can be developed to enhance its recovery and reduce fouling and scaling. During this study, CF was robust and has a high resistance for fouling and scaling although the sand filter backwash water has a high concentration of TDS and suspended solids. Oxidation of Fe & Mn and appropriate use of oxidants for Ra before sand filtration may change the characteristic of sand filter backwash water is recommended to be investigated for determining its effects on the performance of ceramic filtration process.

5. Acknowledgements

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معالجة رجيع المياه لإزالة المعادن الثقيلة و المركبات المشعة باستخدام الفلاتر السيراميكية

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(قدم للنشر في 2020/03/07 وقبل للنشر في 2020/04/01)

ملخص البحث. تهدف هذه الدراسة إلى تقييم امكانية استخدام الفلاتر السيراميكية لمعالجة مياه الرجيع الناتجة من الفلاتر الرملية لإزالة المعادن الثقيلة والمركبات المشعة مع التحكم بترشيح المياه عبر الفلاتر السيراميكية. المياه المعالجة ستعاد إلى نفس محطة التنقية مرة أخرى لتقليل الفاقد من المياه حفاظاً ورفعاً لكفاءة إدارة مصادر المياه. يومياً، يفقد حوالي 7% من مصادر المياه في محطات تنقية المياه التقليدية ويتخلص منها دون فائدة بسبب تلوثها بالمعادن الثقيلة مثل الحديد والمنجنيز و المركبات المشعة كالراديوم. وتعد تلك الكمية كبيرة وحرجة في المناطق الصحراوية التي تفتقد إلى مصادر المياه المتجددة. وتتميز الفلاتر السيراميكية بقلة حجم الفاقد من المياه جراء عملية الغسيل العكسي والذي يمثل 0.7% من المياه الخام أي مايعادل عشر مياه الرجيع الناتجة من الفلاتر الرملية. العملية المقترحة في البحث عملت دون اضافة أي كيماويات وتحت تشغيل مستمر للفلاتر السيراميكية. قيمة الترشيح كانت تتفاوت بين 300-430 لتر/م2 بالساعة، مع تشغيل بمعدل 24 ساعة ولمدة 60 يوماً مع غسيل عكسي لمدة دقية واحدة باليوم. حققت العملية ازالة بمعدل 98.5% و 91.2% و 99.2% لكل من الحديد والمنجنيز والراديوم على التوالي. مثل هذه التقنية ستقلل الفاقد من المياه في المحطات التقليدية وستحقق الحصول على إدارة مستدامة لمصادر المياه.