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Article

Recycling of spent reverse osmosis membranes for the second use in clarification of wet-process phosphoric acid

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Abstract: Various techniques have been used to "clean-up" industrial phosphoric acid: precipitation, flotation, activated charcoal or clay treatment. To address membrane processes potential in phosphoric acid clarification process, this study explores the advantage of membrane techniques as new route for phosphoric acid clarification in an eco-efficient way through the use of "regenerated spent membrane". Regeneration of the spent membranes was performed on of 0.15 m^2 active area regeneration. These membrane samples were used to study the phosphoric acid clarification at a laboratory scale. They were immersed in an oxidizer for at most seven days. The samples were characterized systematically before immersion in an oxidant media. In this study, the potential to regenerate spent membranes and application of this media to clarify the 29% P_2O_5 phosphoric acid was demonstrated. This study shows, by tests that the reverse osmosis (RO) membranes achieve an abatement of 70% and 65% for solids and organic materials, respectively. These positive results will pave the way for implementing these membranes phosphoric acid treatment process. Moreover, besides being economically advantageous, the use of the spent membrane is likely an environmentally friendly route (no waste, no organic solvent and effluent to be regenerated later on).

Keywords: Membrane Chemical Regeneration; Phosphoric Acid; Clarification.

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1. Introduction

Desalination of seawater using reverse osmosis (RO) is greatly considered the most efficient and profitable not only to produce of fresh water for population but also to treat water for industrial uses [1]. The large amount of solid waste generated from RO plants in terms of spent membranes should be correctly managed. As reported by Landaburu-Aguirre et al., more than 840000 end-of-life membranes are disposed annually in the world, which is equivalent to more than 14000 tons per year [2]. In most of cases, the spent membranes are commonly disposed to landfill as classical waste management approach [3]. Nowadays, sustainable management of end-of-life membranes is a challenge of desalination industries. Coutinho de Paula et al. evaluated environmentally and economically the gains of implementing of the recycling of end-of-life RO membranes based on chemical oxidation of aromatic polyamide-based active layer using sodium hypochlorite (NaClO, 10-12%) [3]. They showed that the recycled membrane has features and performances of ultrafiltration membrane.

Fouling is generally caused by the presence of suspended materials originating from organic, inorganic; biological and colloidal [4]. These substances increase the physical or chemical degradation of the surface of the membrane, affect the quality of the feed fluid, as well as the quality of the pretreatment and the chemicals used [5]. Phosphoric acid is an important intermediate in the manufacturing of fertilizers and in the production of purified acids for the food industry, pharmaceutical products and surface treatments [6]. The wet processing corresponds to the attack of natural phosphates by sulfuric acid [7]. Various treatments have been used to clarify phosphoric acid such as coagulation flocculation, decantation, adsorption and membrane filtration [8]. Coagulation/flocculation is the most economical technique for reducing suspended solids. However, this technique does not eliminate of organic matter and produces a large amount of sludge that requires further processing. The membrane filtration, an emerging technique in this sector, is primarily used to remove particles base on their size [9]. Wet process production of industrial phosphoric acid contains diverse impurities including suspended solid, soluble compounds as well as organic matter coming from rock phosphate [10]. Clarification is an important step in the phosphoric acid purification process not only to increase the purity of produced acid but also to avoid some technical problems in industrial installations.

A study by GRAZA et al. reported the possibility of removing Pb^{2+} in an acid medium composed of phosphoric acid and perchloric acid by ultrafiltration using sodium dodecyl sulphate (SDS) as a surfactant [11].

In optimal conditions of pressure and SDS concentration, the retention rate obtained is 99% which generated a concentration of 0.24 ppm instead of 20.72 ppm. The present study aims at finding a membrane resistant to aggressive media and capable of clarifying phosphoric acid. The membranes types used are Minitan-S PTGC OMS10 (Millipore), polysulfone (propylene support) and a cut-off of 10,000 Daltons [12]. New Logic American Company has developed a filtration system for phosphorus compounds using a Vibratory Shear Enhanced Process (VSEP) that uses a microfiltration membrane module with a specific construction for high temperature use. The use of vibrating polymer membranes is an advantage over the use of filter presses and other conventional methods of clarification. Patent WO2013133684A1 has developed a process for the purification of phosphoric acid by nanofiltration. This process requires a step of clarification by the coagulation-flocculation pre-nanofiltration in order to avoid problems related to scaling and clogging of the NF membrane and those of the quality of phosphoric acid produced. Regardless of the scope of application, membranes must frequently undergo cleaning and/or disinfection procedures in order to eliminate the clogging which results from the filtration. These cleanings are responsible for accelerating the aging of materials, which directly affects the technical and economic performance of membrane processes. The sustainability of the latter depends on the identification of the main factors responsible for aging and the understanding of the mechanisms that govern it. Therefore, it is possible to recycle spent RO membranes to ultrafiltration or microfiltration membranes by removal of the active layer using a strong stripping agent. It highly likely that these membranes are capable of filtering solids and macro-impurities that presented in wet-process phosphoric acid. This study involves a process, which allows the recycling of spent membranes taken from seawater desalination plants or similar plants and reuse them as microfiltration or ultrafiltration membranes. The recycling is based on the removing of both fouling and the active layers of spent membrane using a suitable stripper to avoid damaging the microporous layer of the membrane [13]. The regenerated membrane was subjected to clarification of wet process phosphoric acid to access its performance in terms of flux and rejection of suspended particles and the organic matter.

The goal of this work is to assess the chemical treatment of spent RO membranes discarded from industrial seawater desalination plant. Four strong strippers named $KMnO_4$, NaOH, H_2O_2 and TBP were investigated to remove chemically both active layer and fouling layer of spent membrane. The converted membrane was applied for clarification of wet-process phosphoric acid.

2. Materials and Methods

2.1 Chemicals

In this study, several end-of life RO membranes discarded after nine years of service from seawater desalination plant of OCP group located in Lâayoune, southern of Morocco. The used RO membrane is energy saving polyamide (ESPA) with 8″ spiral wound module manufactured by Hydranautics, US. Flat-sheet membrane pieces of 0.15 m^2 were taken out from spent ESPA RO membranes.

Wet-process phosphoric acid (29 wt% of P2O5) produced via dihydrate process of OCP group Jorf Lasfar, Morocco. Sodium bisulfate ($NaHSO_3$, 93 wt%), hydrogen peroxide (H_2O_2, 33 wt%), potassium permanganate ($KMnO_4$, 99,4 wt%), tributyl phosphate (TBP) ($C_{12}H_{27}O_4P$, >97 wt%) and sodium hydroxide (NaOH, 98 wt%) were purchased from SNEP company. The water used for preparation of solutions and filtration experiments is distilled water.

2.2 Striping of spent membrane

In this study, both fouling layer and active layer of spent ESPA RO membrane were chemically removed using four strong strippers notably $KMnO_4$, NaOH, H_2O_2 and TBP. Initially, the spent membrane was cleaned with pure water and followed by cleaning using sodium bisulfate solution (200 mg $NaHSO_3$/L). Thereafter, the membrane was completely soaked in stripper solution during 1 and 7 days. Finally, the stripping solution was neutralized by using Sodium Bisulfate (SBS). The obtained membrane was rinsed several times with water and then it is kept in water until the use for characterization or filtration.

2.3. Filtration of wet process phosphoric acid

The MF experiments were conducted on a dead-end stainless steel stirred cell with effective filtration area of 43 cm^2 and feed volume of 1 L. The cell placed on an anti-vibration table and connected with compressed nitrogen gas to control transmembrane pressure (TMP) by mean of a needle-point valve. All filtration experiments were carried out in an air-conditioned room at 25 °C. The permeate flux Jv (L h^{-1} m^{-2}) and permeability Lp (L h^{-1} m^{-2} bar^{-1}) and hydraulic resistance of the membrane Rm (0,0235 m-1) of the membrane were calculated according to Eqs. (1-3), respectively [14].

$$J_v=V/(A\times t) \qquad (1)$$

$$L_p=J_v/TMP \qquad (2)$$

$$R_m=1/(\mu\times L_p) \qquad (3)$$

Where V (L) is the volume of permeate, A (m^2) is effective filtration area, t (h) is filtration time, TMP (bar) is transmembrane pressure and μ (2,84 Pa s) is the viscosity of the permeate.

Industrial phosphoric acid with a concentration of 29% P_2O_5 was filtered under pressure of 4 bar at room temperature. The efficiency of the recycled membrane was evaluated by the measurement of permeate flux and the rejection of suspended materials and organic matter.

The rejection R (%) is calculated according to Eq. (4) [15].

$$R=(1-C_p/C_f)\times 100 \qquad (4)$$

Where Cf is the concentration in the feed and Cp is the concentration in the permeate.

2.4. Instruments and analyses

The set of doses performed to quantify: the acid (UV visible spectrophotometry), the suspended solids (dissolution by attack with $HClO^4$), the organic materials (infrared spectrophotometry) were made with ± 1% accuracy.

The number of cultivable bacteria per membrane's surface was determined according to the incubation method in rich nutrient agar medium at 22 °C during 72 h.

The determination of pore size and characterization of the active layer were performed consecutively by the capillary flow porometer, the X-ray diffractometer and the SEM/EDS/EDX.

In this study, an autopsy was proceeded on the active layer (skin + deposition of fouling), the size separation and the deposition of fouling. Full examination of the membrane was performed by chemical and microbiological analysis of the deposit, chemical oxidation tests (Fujiwara Test), and scanning electron microscopy (SEM) analysis using energy dispersive analysis (EDS/EDX).

3. Results and Discussion

3.1. Autopsy of spent RO membrane

3.1.1. Visual inspection

The external inspection shows that the general aspect of outer wrap of spent ESPA membrane is in good conditions (Figure 1a). It is worthy of note that no cracks and or any other physical damages have detected indicating that spent membranes could reused. The internal examination spent ESPA membranes reveal the presence of brown deposit on the outer membrane surface while the inner surface of membrane (brine side) and the conductive mesh are clean (See Figure 1b-d).

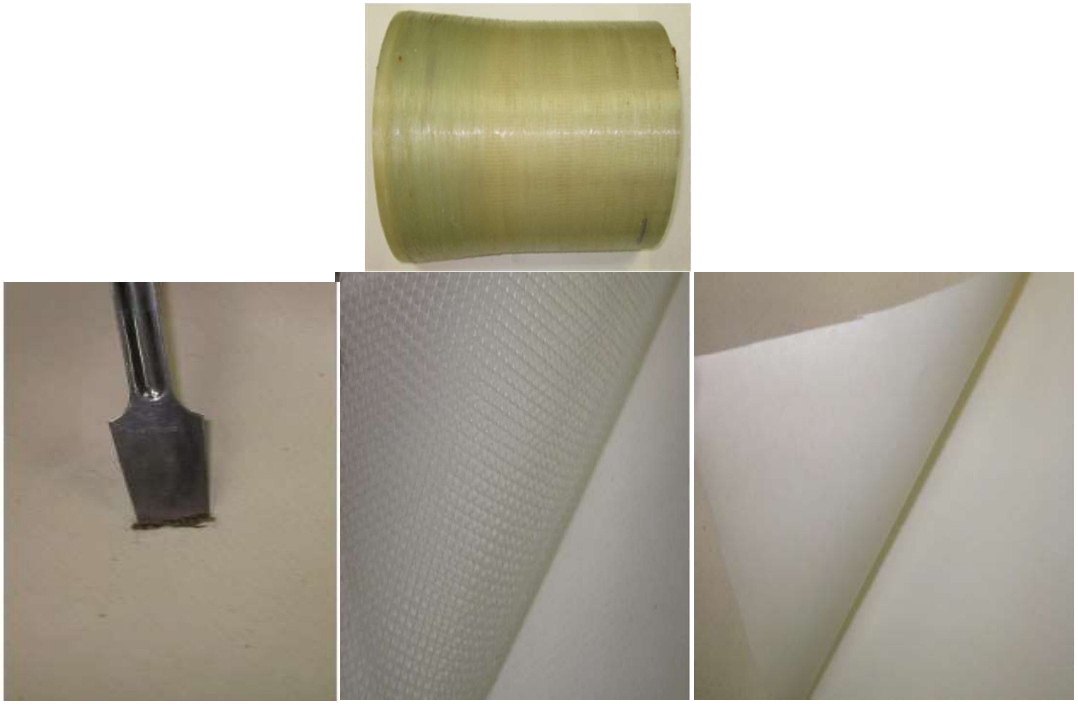

Figure 1. a) Photo of ESPA reverse osmosis membrane and internal view of the membrane: (b) surface of the membrane (active layer), (c) plastic mesh 'power-discharge' and (d) conductive mesh.

3.1.2. Chemical composition

The deposit collected from the surface of spent membrane was characterized to quantify the moisture and to analyze the organic and inorganic materials. It was found that deposit contains about 67.90% of moisture. While the dry deposit (residue after drying at 105 °C) with density of 0.12 mg/cm2 was then analyzed and the chemical composition of dry deposit is given in Table 1. It can be revealed that the dry deposit is mainly composed of organic matter with a content of 62.33% identified by solubilization in HCl and the insoluble fraction which presents 31.03% of the deposit. The insoluble fraction is identified by EDX. The inorganic impurities are about 4% of iron and phosphate (Table 1).

Table 1. Composition of the dry deposit collected from the membrane surface.

Compound	Organic matter	Insoluble in HCl	Fe_2O_3	P_2O_5	CaO	MgO	CO_2	Others
Wt.%	62.33	31.03	3.02	0.89	<0.10	<0.10	<0.10	2.73

3.1.3. Microbiological characterization

The number of cultivable bacteria per surface was determined according to the incubation method in rich nutrient agar medium at 22 °C during 72 h. Microbiological analysis of the spent membrane revealed the presence of microorganisms in different membrane parts. It was found that the amounts of biogrowth in active membrane layer, feed-rejection mesh and permeate conductive mesh are respectively 192, 62 and 10 CFU/cm2. It can be concluded that bacteria are less abundant in the feed-rejection mesh and tend to disappear in the permeate conductive mesh.

3.1.4. SEM examination

Figure 2 corresponds to a topographical image of spent RO membrane obtained by SEM analysis at low magnification (50×). As clearly observed, three regions could be distinguished: (i) black area is corresponded to membrane surface, (ii) gray area is deposit layer on the surface of the membrane and (iii) white areas are just particles at the level of the deposit present on the membrane. The EDX analysis of regions is illustrated in Figure 3 in order to investigate their elementary chemical composition. The sulfur detected is in black area is assigned to polyether sulfone of active layer of the membrane. The chemical composition of white area mainly consists of Al and Si elements beside low amount of Na and K suggesting the presence of alumino-silicate in the form of clay [16]. The gray area shows the presence of Si, Al, Mg, Ca and Na elements due to acculturation of inorganic impurities on membrane surface.

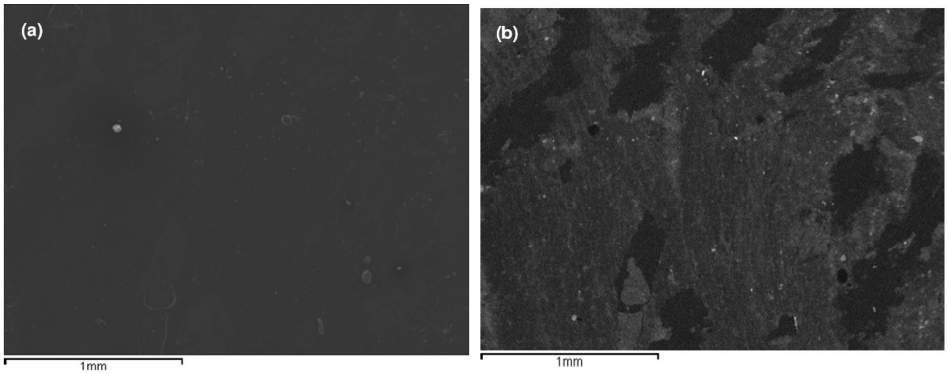

Figure 2. SEM micrographs of spent RO membrane: (a) Topographic image and (b) 'Z-Contrast' image.

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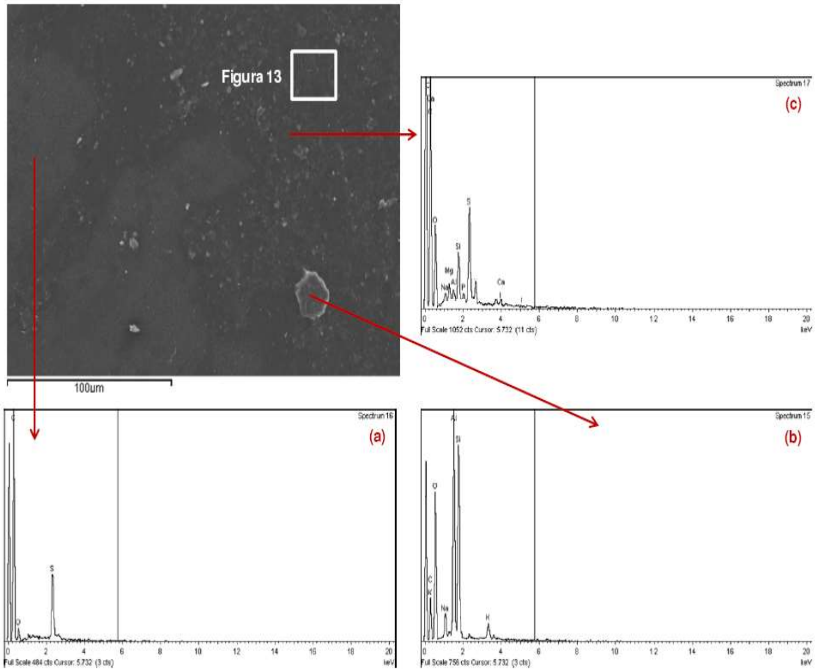

Figure 3. Topography image (550X) and spectra of EDX analyses.

3.2. *Characterization of regenerated spent membrane*

The preliminary tests allowed to select the stripping agents suitable for the degradation of the active layer of spent membrane are presented in Table 2.

Table 2. Preliminary tests for the selection of the stripping agent.

Stripper	Visual Remarks during first day
NaOH	Partial degradation of the active layer
$KMnO_4$	Appearance of the blisters + degradation of the active skin
H_2O_2	No effect on active skin
TBP	No effect on active skin
NaOH (50%) +H_2O_2 (50%)	No effect on active skin
NaOH (50%) + $KMnO_4$ (50%)	Partial degradation of the active

Figure 4 shows the degradation of the active skin of the ESPA membrane by adding NaOH.

Figure 4. Photo of ESPA *plus* NaOH membranes.

3.2.1. XRD

XRD analysis (Figure 5) shows that the spectra of three membranes stripped by different strippers are almost identical. By comparing these spectra with those of the non-stripped membrane, it can be noted the quasi-total disappearance of the peak at 16.8°, confirming the degradation of the active layer, made of polyamide, of the membrane by the various used strippers.

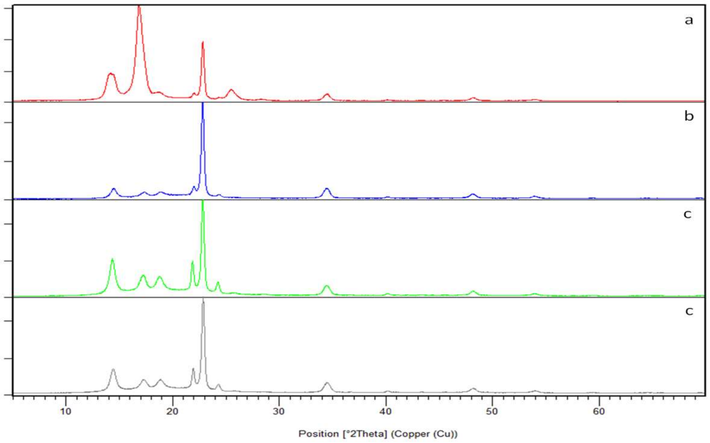

Figure 5. XRS diffractograms of the stripped and non-stripped membranes. (a) ESPA non-stripped, (b) ESPA + NaOH, (c) KMnO4 and (d) ESPA + KMnO4/NaOH.

3.2.2 Hydraulic permeability

Table 3 shows the hydraulic permeability of the spent membrane and regenerated membranes using NaOH, $KMnO_4$ and $KMnO_4$/NaOH. Stripping of the ESPA membrane by NaOH increases about 26 times the hydraulic permeability of the spent membrane. As for oxidant $KMnO_4$, there is a large increase in hydraulic permeability which reaches 27 times compared to the initial state. This can be attributed to the composition of the solid deposits on the membrane. More importantly, the results show that the hydraulic permeability does not increase during the next 7 days. This indicates the chemical stability of regenerated membranes.

Table 3. Permeability of new, spent and regenerated membranes.

Membrane	Lp (L h^{-1} m^{-2} bar^{-1}) 1 day	Lp (L h^{-1} m^{-2} bar^{-1}) 7 days
New membrane	15	15
Spent membrane	0.9	0.9
Regenerated membrane using NaOH	40	40
Regenerated membrane using $KMnO_4$	45	47
Regenerated membrane using $KMnO_4$/NaOH	43	43

3.3. Clarification of wet process phosphoric acid

3.3.1. Flux

Table 4 shows that the phosphoric acid (29 % P2O5) flux from the membrane regenerated using NaOH is considerably lower than those regenerated using $KMnO_4$ and $KMnO_4$/NaOH for the same operating conditions. The difference in acid flux shows that the dominant cutoff effect.

Table 4. Phosphoric acid flux of regenerated membranes.

Membrane	Jp l/h/m^2 1 day	Jp l/h/m^2 7 days
New membrane	25	25
ESPA + NaOH	43	44
ESPA + $KMnO_4$	54	56
ESPA + $KMnO_4$/NaOH	51	51

3.3.2 Rejection of suspended particles

We observed that the rejection of suspended particles using regenerated membrane under NaOH treatment is considerably superior to that regenerated using $KMnO_4$ for identical operating conditions (Table 5). The difference in rejection rates confirm that the pore size of the membrane controls the rejection.

Table 5. Suspended particles rejection of regenerated membranes.

Membrane	Abatement % 1 day	Abatement % 7 days
ESPA + NaOH	70	69
ESPA + $KMnO_4$	54	56
ESPA + $KMnO_4$/NaOH	65	65

3.3.3 Rejection of organic matter

We also observed that the organic material rejection using the membrane regenerated using NaOH are close to that the membrane regenerated using $KMnO_4$ for identical operating conditions (Table 6).

Table 6. Organic matter rejection of regenerated membranes.

Membrane	Rejection (%) 1 day	Rejection (%) 7 days
ESPA + NaOH	61	54
ESPA + $KMnO_4$	61	53
ESPA + $KMnO_4$/NaOH	59	59

4. Conclusions

The purpose of this study was to examine:

- Regeneration of membranes by chemical stripping of the active layer (skin + deposit of fouling) of spent ESPA RO membranes.

- The application of the regenerated membranes for the treatment of industrial phosphoric acid, particularly for the rejection of suspended particles and organic matter.

All together our results demonstrate that the autopsy of the used RO membrane showed the presence of external and internal clogging deposition of silicates in the form of clay. The comparison of the hydraulic permeability with water after degradation of the active layer is a good criterion for the rejection of suspended particles and organic matter. Furthermore, the regenerated membranes made it possible to achieve a rejection of 70% of the suspended materials and 61% of the organic material. These results clearly show the potential of our process with these materials and will pave the way for the application of these membranes in the treatment and clarification of phosphoric acid expanding therefore the applicability of this technology in the phosphate industry.

4. Conclusions

A certified reference material of industrial fluosilicic acid was developed in this study, with homogeneity and stability testing studies, the establishment of metrological traceability, the assignment of reference value, as well as uncertainty evaluation. The H_2SiF_6 mass fraction of the developed CRM was determined by UV-VIS as a primary method of measurement. The accuracy of the results that were obtained by the primary analytical method (UV-VIS) was evaluated by comparing the results with those obtained with a second analytical method (AAS). As demonstrated, both results were in good agreement. In addition, a pure 34% (w/w) fluosilicic acid was analyzed with the first method and presented satisfactory results. The developed CRM showed good homogeneity and high stability for at least one year. The uncertainty of the certified value was estimated by combining the uncertainties due to the analytical method, homogeneity, and stability. The certified value of CRM developed in this study is traceable to the International System of Units (SI). Since there is no available CRM fluosilicic acid in the market, this material will be useful for routine testing in the laboratory, especially for the validation and/or verification of internally developed analytical methods, for analytical instrument calibration, or for quality control.

Author Contributions: Conceptualization, KK and RB; validation, KK, RB and BA; investigation, KK, RB and J.P.; data curation, KK and BA; writing—original draft preparation, KK. RB, BA and RB; writing—review and editing, RB and RB; visualization, KK and BA; project administration and supervision, RB.; funding acquisition, KK, RB and RB. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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