Journal of Water Process Engineering 19 (2017) 220–230

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

A hybrid super hydrophilic ceramic membrane and carbon nanotube adsorption process for clean water production and heavy metal removal and recovery in remote locations

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ARTICLE INFO

Keywords:
Wastewater
Filtration
Adsorption
Carbon nanotube
Functionalised membrane

ABSTRACT

A novel hybrid membrane-adsorption process has been developed for the production of clean water supplies. A 0.2 μm ceramic membrane has been functionalised to produce a super-hydrophilic surface on the microfiltration membrane capable of maintaining flux with little or no fouling under normal operating conditions. The adsorbent used is a supported epoxidised carbon nanotube material capable of removing heavy metals from solution. Both the membrane and the adsorbent can be easily cleaned when necessary using only a solution of readily available vinegar. The intended aim for this new water production system is for the production of clean water in remote locations, in disaster relief zones and for humanitarian purposes. Laboratory studies have shown that the membrane is capable of maintaining flux over a significant period of time and even when tested with an extreme foulant (used motor oil) performed admirably. The rejection properties of the membrane are as expected for small pore microfiltration, i.e. microbial contamination is easily removed. The adsorbent was shown to remove heavy metals (Cd, Hg, Ni, Co and Pb) to a very high degree ($>$ 99.3% in all cases) and was easily regenerated to almost complete adsorptive capacity. The hybrid-process was briefly deployed to the Rio Las Vacas (Guatemala) as part of a basic feasibility study and the unit performed as expected. No microbial contamination was detected in the permeate and the flux was maintained consistently at one third of the clean water flux. This demonstrates the system is capable of microbial removal and has good antifouling properties.

1. Introduction

The United Nations (UN) estimates that the world population reached 7.3 billion as of mid-2015, implying that the world has added approximately one billion people in the span of the last twelve years [1]. 60% of the global population lives in Asia (4.4 billion), 16% in Africa (1.2 billion), 10% in Europe (738 million), 9% in Latin America and the Caribbean (634 million), and the remaining 5% in Northern America (358 million) and Oceania (39 million). China (1.4 billion) and India (1.3 billion) are the two largest countries of the world representing 19 and 18% of the world's population respectively. The world population continues to grow, although at a slower rate than in the recent past. Ten years ago, world population was growing by 1.24% per year and this figure is currently 1.18% per year or approximately an additional 83 million people annually. The world population is projected to reach 8.5 billion by 2030 and to increase yet further to 9.7 billion by 2050. The predicted population increase will add further stress to current already oversubscribed infrastructure for water; either for drinking, sanitation or agricultural use and will particularly affect developing regions which will see the largest percentage increase in population.

The Joint Monitoring Programme (JMP) by the UN Children's Fund (UNICEF) and World Health Organisation (WHO) reported in 2015 that 9% (663 million) of the world's population have no access to an improved drinking water source, classified as unimproved and surface water [2]. The sub-Saharan Africa region makes up approximately 48% of the total population with no access to clean water, Southern Asia being the second highest with 134 million (20%). The same report also found that 2.4 billion people globally (1 in 3) have no access to improved sanitation facilities, 934 million (39%) of them defecate in open spaces. The majority of the population without access to clean drinking water and sanitation are from rural areas [3]. As a result, local sources and/or localised treatment are required. The most desirable source of drinking water for remote locations are from shallow or deep wells

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http://dx.doi.org/10.1016/j.jwpe.2017.08.006
Received 31 October 2016; Received in revised form 3 August 2017; Accepted 5 August 2017
2214-7144/

drawing fresh groundwater [4]. Shallow wells are considerably less expensive than deep wells as they can be hand dug and do not require any specialised drilling equipment [5]. However, they rely on an aquifer sources of less than 50 m below ground which can fluctuate seasonally. Shallow wells are also prone to contamination from surface water permeation, open space defecation being a prime example [6]. Deep water wells are also prone to contamination but the likelihood if greatly reduced when compared to shallow wells [7]. Deep water wells require expensive and heavy drilling equipment due to the hard rock basin that needs to be penetrated to reach the depths of the groundwater beneath [8]. Several technology platforms exist that can be used for the treatment of local water sources. These include physical processes, chemical treatment, thermal processes, light based treatments, integrated systems and membrane technology [9]. Several of these technologies have been coupled to local energy production systems for off-grid applications, such as solar stills, photo-voltaic driven systems, solar-thermal systems, biomass and geothermal energy [10,11]. Some future technologies have also been proposed that could come online for local water generation; these include new methods for disinfection using nanostructures, development of biosensors to confirm decontamination, deployment of hybrid membrane bioreactor systems and development of novel membranes based on bio-inspired systems [12]. However, due to simplicity and cost the Bio-sand filter is currently often deployed for the generation of water in local or remote regions. Bio-sand filters have been deployed as an alternative method for generating clean drinking water from rainwater or a contaminated local source [13–17]. The untreated water passes through a biological layer and multiple sized physical layers, pathogens are removed by microorganisms in the bio-layer, layers of fine sand and gravel of increasing size then remove any suspended solids. The negative aspects of bio-sand filters include the requirement for sufficient hydraulic head to force the water through the bed. As a result, the production rate of clean water can be slow and as the feed water level drops, the production rate slows further. Particles can accumulate in the sand filters clogging the filter, reducing the flow rate of clean water [18]. Typically, a bio-sand filter will be constructed of concrete, therefore, they are heavy and vulnerable to damage making them difficult units to transport to remote locations. Limited research has been conducted into the removal of heavy metals by bio-sand filters, results reported have varied considerably [19,20] Personal drinking water devices have been developed that are able to produce clean drinking water from an untreated fresh water supply. These devices have been made popular to the general public through advertisement campaigns on social media, in particular the personal filter brand *LifeStraw* (Vestergaard Frandsen). These units work well for bacteria, protozoa and viruses depending on the version of the filter used, LifeStraw (0.2 μm) and LifeStraw Family or Mission (0.02 μm). These units are reliant on a suitable local source of water being available and do not remove heavy metals.

The research group was approached by the clean water charity, Millions from One, to produce a filtration platform that could treat a local contaminated water source, the Rio Las Vacas in Guatemala, which contains a plethora of bacterial and heavy metal contaminants. The challenge was to produce water that meets the WHO drinking water quality, although a clear improvement in general water quality would be acceptable. One of the tributaries for the Rio Las Vacas river passes through the Guatemala City dump, Fig. 1a. This dump is notorious for unauthorised dumping of hazardous and toxic material into the local environment as witnessed during a tour of the surrounding area, Fig. 1b. Furthermore, the city cemetery is located directly above the dump and operates a plot lease scheme, i.e. if payment is no longer made the plots are exhumed and any remains are reburied in mass grave pits on site, coffins, rubbish and any other material is burned and cast over the cliff into the dump. Locals have alleged that human remains have also found their way over the cliff edge into the city dump. The raw sewage stream that forms part of the Rio Las Vacas tributary is eroding the cliff edge. As recently as May 2015, a large mudslide due to erosion carried 18 tombs from the edge of the cemetery down into the dump. Some 7000 people work in the dump, these workers or "Guajeros" known locally spend their lives collecting plastic, metal and old magazines from out of the trash heap to sell to recyclers. Around 1000 of these workers are children. Workers, local residents and children of Barrios (an area downstream) regularly play and wash laundry in the contaminated waters. Fortunately, they understand the water is not suitable for consumption.

In this work, a localised water purification system is developed that combines a sterilising pre-filter to remove bacteria and protozoa followed by a post filtration heavy metal removal unit. The sterilising pre-filter used was a super-hydrophilic functionalised ceramic 0.2 μm filter, 0.2 μm being the minimum international standard for sterilisation [21]. The permeate from the pre-filter is then passed through a heavy metal adsorption pack. The adsorption pack contains supported epoxidised carbon nanotubes (SENTs) and are highly efficient at removing heavy metals. The novel water purification system is extensively tested in the laboratory and briefly deployed to an extremely polluted river water in Guatemala City.

2. Experimental

2.1. Ceramic functionalisation

Virgin (unmodified) Atech ceramic membranes (19-3.3 version Atech-Innovations GmbH, Germany) with support and active layer manufactured from alpha alumina were initially washed with hot mains tap water (approx. 42 °C) to remove any alumina dust from the manufacturing process. The membranes were then rinsed with ultra-pure water (Millipore – Elix 5). The membranes were placed inside a stainless steel housing (Memtech Ltd – Membralox housing custom design) with an electrical heating tape (Electrothermal – HT95515 glass fibre heating tape) wrapped around the external surface of the housing, see Fig. 2. In addition to the intact membrane a small broken alumina membrane piece from an unmodified alumina membrane (Pall – Membralox 1.4 μm) was placed inside the housing on top of the whole membrane, this fractured piece will functionalise in-situ and is used for functionalisation analysis post treatment to avoid damaging the intact membrane. The membranes were submerged in a 150 g/l solution of L-cysteic acid anhydrous (Acros Organics) and left to effervesce until the air inside the membrane structure was removed. Once the membranes stopped effervescing a condenser (Axium Process Ltd – custom design) was attached to the housing and a coolant from a chiller unit (Huber) set at 4 °C was circulated through the condenser jacket. After the set point temperature was achieved the electrical heating tape controller (Electrothermal – MC242 1800W) was turned on and the cysteic solution was allowed to reach a steady reflux temperature of approximately 105 °C. The solution was maintained at reflux for 72 h. The heating tape was turned off and the solution was allowed to return to room temperature, the remaining cysteic acid solution was drained from the housing and stored for further functionalisation processes. The membrane and membrane piece were then thoroughly washed at least 3 times in hot water and deionised (DI) water respectively. The membranes were then stored in original packaging under ambient conditions prior to scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) and thermogravimetric analysis (TGA). This is a modified version of a patented fabrication process described previously [22].

2.2. SENT functionalisation

4.33 g of ferrocene was dissolved in 80 ml of toluene in a volumetric flask with the aid of sonication. The flask was then filled to produce a 0.233 M solution. 3.45 g of 12 μm diameter quartz wool for nanotube deposition was placed in a 34 mm inner diameter × 38 mm outer diameter × 500 mm long quartz tube, which was then inserted into an