International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:10, No:5, 2016

Bio-Electrochemical Process Coupled with MnO_2 Nanowires for Wastewater Treatment

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***Abstract*—**MnO_2 nanowires were developed as filtration media for wastewater treatment that uniquely combines several advantages. The resulting material demonstrated strong capability to remove the pollution of heavy metal ions and organic contents in water. In addition, the manufacture process of such material is practical and economical. In this work, MnO_2 nanowires were integrated with the state-of-art bio-electrochemical system for wastewater treatment, to overcome problems currently encountered with organic, inorganic, heavy metal, and microbe removal, and to minimize the unit footprint (land/space occupation) at low cost. Results showed that coupling the bio-electrochemical with MnO_2 resulted in very encouraging results with higher removal efficiencies of such pollutants.

***Keywords*—**Bio-electrochemical, nanowires, wastewater, treatment.

I. Introduction

RELIANCE on groundwater or desalinated potable water is the norm in Abu Dhabi, United Arab Emirates (UAE), resulting to high withdrawal rate of natural water resources. The World Bank puts the annual water withdrawal in the UAE, mostly from groundwater resources, as 4 billion m^3 [1]. The largest chunk of this amount (70.7%) is consumed for agricultural purposes while 15.4 and 1.7% are consumed for domestic and industrial purposes, respectively. On the other hand, the renewable water resource of the UAE is 83 m^3 per person per year, far below the UN minimum of 1000 m^3 per person per year – making the UAE one of the world's driest countries. These groundwater resources are fast depleting and have decreased by 18% since 2003 because the total consumption of water exceeds 24 times the capacity of the natural recharge [2]. Furthermore, the average water consumption in the country is expected to grow by 30% by 2030. Abu Dhabi would lose its natural water resource soon if the current abstraction of groundwater continues unabated. On the other hand, UAE is a world leader in desalination, contributing 11% of the total desalinated water in the world. The consumption of desalinated water rose from 873 Mm^3 in 2010 to 1,059 Mm^3 in 2012 [3] with further increases to 2014. However, due to its high energy requirements, water desalination results into the emission of deleterious pollutants and wastes into the environment. The use of treated wastewater would improve the conservation of groundwater resources and reduce the long-term imbalance of water demand vs supply in Abu Dhabi. Treated wastewater of high quality can also be used to recharge the depleting aquifers. The prediction of Abu Dhabi Sewerage Service Company (ADSSC) for treated wastewater production in 2016 is 600,000 m^3 per day and the production of treated wastewater in 2030 has been projected as 1435 Mm^3 [3], [4]. Currently, treated wastewater is most commonly used for irrigation and landscaping [5]. Lack of adequate infrastructure for the transmission of the treated wastewater to places of need have been identified as the major challenge of 100% wastewater reuse [4]. As a result, the Abu Dhabi government has started to execute the Strategic Tunnel Enhancement Program for the construction of a new 40-kilometer long wastewater tunnel to plan for the increased flows. Furthermore, modular technologies such as membrane bioreactors are increasingly used to produce treated effluents of higher quality, with less than 5% of total wastewater in Abu Dhabi being treated by MBRs currently [6]. Therefore, the overarching goal of this research was to investigate the feasibility of coupling the bio-electrochemical treatment with MnO_2 nanowires as advanced wastewater treatment system.

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II. Methodology

A bio-electrochemical cell [7] integrated with filtration via MnO_2 nanowires [8] has been used for preliminary investigation of removal efficiencies of contaminants from raw unscreened municipal wastewater from Masdar City, Abu Dhabi, United Arab Emirates. The set-up is shown in Fig. 1. Firstly, the bio-electrochemical cell (Fig. 2) was used to partially remove the pollutants via activated sludge treatment and electrocoagulation (EC). Two porous vertical electrodes were submerged in sludge suspension obtained from the MBR plant, Masdar City. Aluminum and stainless steel have been used as anode and cathode, respectively, and these electrodes were connected to a DC power supply with current density (CD) of 5, 8, 10, 15, and 20 A/m^2 and intermittent mode of 5 min ON: 15 min OFF.

Hydraulic retention time (HRT) was also varied at 15, 20, and 25 h (HRTs of 4, 6, and 8 h were also tested but results are not shown → i.e. long HRTs worked better), corresponding to effective reactor height of 7.5, 5.2, and 4.5 cm, respectively. CD and HRT have been varied to investigate the influence of current density on removal efficiencies. A batch system was

operated for 24 h and each operating condition was varied, while keeping the other condition constant. Although EC is a complicated process for which a number of mechanisms co-exist and function in sequences to remove pollutants from water, a number of interpretations exist in literature to explore the key steps.

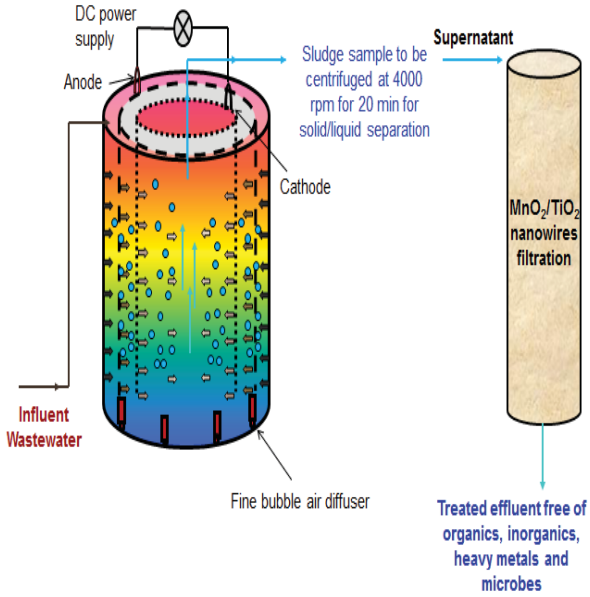

Fig. 1 Schematic diagram of the integrated technology

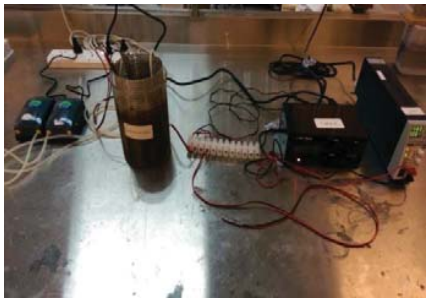

Fig. 2 Bio-electrochemical batch cell [9]

Removal of pollutants by electrocoagulation involves: the formation of coagulant as shown in (1)-(3), destabilization of the contaminants and particulate suspension, breaking of emulsions and aggregation of the destabilized phases to form flocs [10].

The oxidation reaction at the anode:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

The reduction reaction at the cathode:

$$3H_2O_{(l)} + 3e^{-} \rightarrow 3H_{2(g)} + 3OH^{-} \quad (2)$$

The hydrolysis reaction:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^{+} \quad (3)$$

The Al^{3+} and OH^{-} ions formed by the electrodes would give rise to various monomeric species such as $Al(OH)_2^{+}$, $Al(OH)_2^{2+}$ and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ which turn into insoluble amorphous $Al(OH)_3(s)$ through polymerization. Cationic $Al(OH)^{+}_2$ would be formed at low pH and anionic $Al(OH)^{-}_4$ would be formed at high pH [11]. A precipitate is formed by the aluminum hydroxide coagulant with the pollutants, thus promoting their electromigration, transport, and precipitation in reactor, as shown in (4).

$$nA^{-}(\text{pollutant}) + Al_x(OH)_y^{+} \rightarrow [Al_x(OH)_y^{+}]A_n \quad (4)$$

The pollutants are also removed by deposition of ions on opposite electrodes. Cationic polymeric hydroxyl aluminum species would combine with other anionic pollutants (colloidal species) to yield charged low density lighter particles (cationic/anionic) which would migrate by electrophoretic motion towards opposite electrodes depending on their net charges as well as electro-osmotic drift force that propels dewatering of smaller floc particles. These would be adsorbed on the respective electrodes. The heavier flocs precipitated down to form sludge due to gravity. The oxidation of water would produce hydrogen ions and oxygen gas at the anode whereas hydrogen gas and hydrogen oxide are generated due to water reduction at the cathode. Chlorine gas, hydrogen peroxide and hydroxyl radical which, as strong oxidizing agents, react with organic pollutants, would also be produced from oxidation [12].

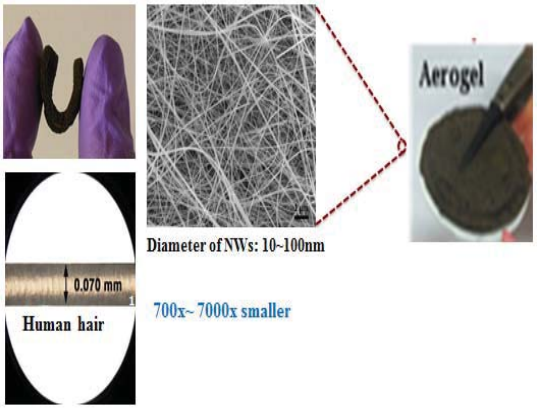

Fig. 3 MnO_2 nanowires with aerogel structures [8]

Secondly, a sample of mixed liquor from the reactor at each operating condition was centrifuged at 4000 rpm and 20 min to obtain the supernatant. The supernatant was then filtered through Whatman fritted glass filtration set with 1.5µm-pore and 47mm-diameter nanowire filter, and connected to WELCH 2546C-02A vacuum pump for further removal of organics, nutrients, heavy metals, and inorganics. The filtrate was obtained as the final effluent. The MnO_2 nanowire filter was fabricated at Massachusetts Institute of Technology (MIT), in which a method to enable a vast variety of materials to be made into aerogel structures was developed (Fig. 3).

Aerogels are porous solid materials with ultra-high surface area and low bulk densities and low thermal conductivities. It was through that effort that materials such as MnO_2 where hydrothermal synthesis can be used were found.

Previous results from MIT have shown that the aerogels can remove both organic dyes in water and heavy metal ions [8]. Thirdly, COD, ammonia (NH_4^+-N), and phosphate (PO_4^{3-}-P) concentrations in the influent and final effluent were determined via HACH LCK reagent vials and HACH DR3900 spectrophotometer with RFID technology.

These concentrations were compared to obtain the removal efficiencies in the integrated set-up for the matrix of operating conditions.

III. Results and Discussion

The concentrations of COD, NH_4^+-N, and PO_4^{3-}-P in the influent were obtained as 824 mgCOD/L, 13.5 mg PO_4^{3-}-P /L, and 269.5 mg NH_4^+-N/L respectively. The removal efficiencies obtained at different HRT and CD values for COD, NH_4^+-N, and PO_4^{3-}-P are provided in Figs. 4–6. 85 – 96% COD, 49 – 79% NH_4^+-N, and 71 – 89% PO_4^{3-}-P removal were obtained at the different conditions. From the results, as shown in Figs. 4–6, a CD of 15 A/m^2 and HRT of 25 h were selected as providing optimized removal efficiencies.

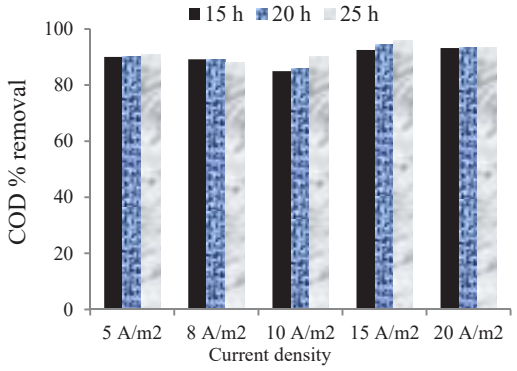

Fig. 4 COD removal efficiency at different conditions

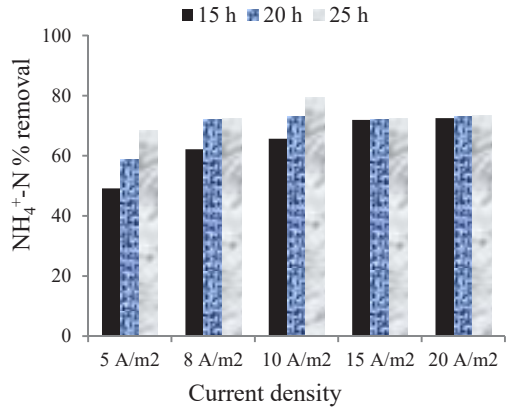

Fig. 5 NH_4^+-N removal efficiency at different conditions

Finally, more bio-electrochemical cell configurations were tested to determine whether there will be improvements in the final effluent water quality. Two other configurations were carried out, each involving two pairs of electrodes. These configurations were: anode-cathode-cathode-anode (A-C-C-A) and anode-cathode-anode-cathode (A-C-A-C). For these two additional configurations, the current density and HRT were maintained at 15 A/m2 and 25 h, respectively (the optimized values selected from the experiments involving a single pair of electrodes). These results obtained for removal efficiencies from these two configurations were then compared with the results obtained when a single pair of electrodes was used at 15 A/m2 and 25 h. It was observed that the A-C-A-C configuration produced effluent with lower COD, NH4+-N, and PO43--P concentrations, whereas the A-C-A-C configuration produced effluent with lower PO43--P concentration, much lower NH4+-N concentration, but higher COD concentration (Table I). Because of the marked differences obtained when different configurations were used, more characterization of the effluent streams was carried out by determining the composition of other pollutants such as nitrate, heavy metals, water hardness, and chlorine. The concentrations obtained, alongside those obtained when a single pair of electrodes was used at 15 A/m2 and 25 h are provided in Table I.

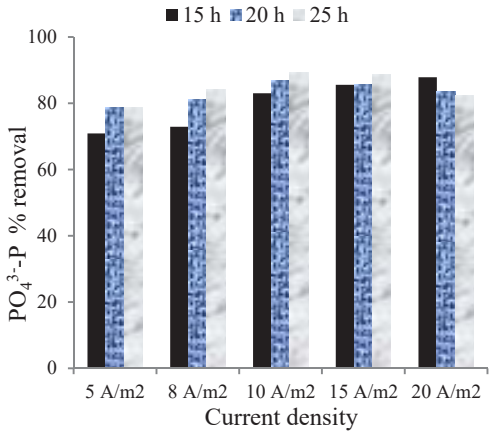

Fig. 6 PO_4^{3-}-P removal efficiency at different conditions

TABLE I
% Removal of Contaminants from Different Bio-Electrochemical Reactor Configurations at 15 A/m^2 and 25 h

Component	Raw wastewater (mg/L)	% Removal by A-C-C-A configuration	% Removal by A-C-A-C configuration	% Removal by A-C configuration
COD	824	94	97	96
NH_4^+-N	269.5	85	76	72
PO_4^{3-}-P	13.5	95	96	89
Fe	1.95	91	92	86
Cr	0.164	87	71	72
Cd	0.063	94	95	94
Cu	2.06	93	95	91
Pb	0.22	100	100	100

IV. Conclusion

An integrated system for wastewater treatment based on coupling bio-electrochemical process with MnO_2 nanowires was investigated. Different operating conditions such as electrodes' configuration, current density and hydraulic retention time were optimized. Results showed that 97, 85 and 96% removal of COD, NH_4^+-N, and PO_4^{3-}-P were achieved at 15 A/m^2 and 25 h. Furthermore, the integrated system showed a great potential in removing heavy metals accomplishing >90% removal of Fe, Cd, Cu and Pb.

Acknowledgment

Authors would like to thank Masdar Institute and MIT Deshpande Center for the financial support (Grant No. MM2014-000006).

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