COMPLETE NITRATE REMOVAL USING A NOVEL ION EXCHANGE AND ENCAPSULATED BACTERIA SYSTEM

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I.INTRODUCTION

1.1 General Background

Nitrate pollution is a serious problem across industries, and severe ecological damage can occur when discharging to sensitive waterways. Many regions of the world have begun mandaring strict discharge limits of 1 mg/L of nitrate, especially to sensitive waterways and drinking water catchments.

Nitrate is often present in groundwater and surface water in agricultural areas from fertilizer use and is often present in municipal and industrial waste streams following the aerobic degradation of ammonia. Even moderate nitrate concentrations can lead to eutrophication of natural water bodies, causing algal blooms that severely harm the aquatic environment. In 2020 alone, the Harmful Algae Event Database (HAEDAT) reported almost 600 harmful algal bloom events globally [1], and the US EPA's 2013-2014 National Rivers and Streams Assessment rated 43% of rivers and streams as having poor quality in regard to their nitrogen content [2].

Infant methemoglobinemia (blue baby syndrome) has well-established links to high nitrate levels and is one of the main reasons for nitrate concentration limits being set for drinking water around the world [3]. Recent literature reviews of over 30 global epidemiologic studies have found increasing links to various forms of cancer, even when concentrations are below the current drinking water limits [4]. For these reasons, governments and water authorities around the world are placing increasingly strict regulations on nitrate concentrations in waters for discharge to the environment, and for drinking. These stricter limits are appearing at the same time as nitrate levels in water-stressed areas are increasing, leading the need to urgently upgrade water treatment infrastructure [5]. For too long, nitrogen issues have been growing unnoticed, and governments and authorities are now acting to avoid long-term knock-on effects to their critical and ever-declining clean water resources.

1.2 Conventional Nitrate Removal Methods

Conventional bacteria treatment methods such as CAS (conventional activated sludge), BNR (biological nutrient removal), MBBR (moving bed bio-reactor), and MBR (membrane bio-reactor) can struggle to reduce effluent nitrate concentrations below 1 mg/L, especially in cold climates [6]. While reverse osmosis and ion exchange can treat to these concentrations, they produce large volumes of waste that can be difficult to manage. Wetlands can be effective for nutrient reduction but have large footprints and can struggle to meet the nitrate limits at low temperatures.

Clean TeQ Water's BIONEX™ technology is specifically designed to deal with these nitrate issues in an environmentally friendly and cost-effective manner. By combining two of our innovative water treatment technologies, Continuous Ionic Filtration (CIF®), and lens encapsulated bacteria

(BIOCLENS®), the process electively removes nitrate/nitrite from water sources and converts it to harmless nitrogen gas.

1.3 Continuous Ion Exchange

Clean TeQ Water's CIF technology is well suited to treat difficult mine water streams. It can selectively remove contaminants through ion exchange while simultaneously performing physical filtration, tolerating suspended solids in the feed. The ion exchange resin is periodically moved around the system for reconditioning. Additional information about CIF can be found in the VIII .

1.4 Encapsulated Bacteria

Clean TeQ Water's BIOCLENS lenses contain living bacteria which are encapsulated in a stable, porous polymer gel matrix. As the lenses are stirred in a reactor, water and dissolved impurities diffuse through the lenses and encounter the bacteria, where targeted reactions occur. Specifically selected bacteria with high nitrification or denitrification activity are used in the lenses, resulting in high removal activity. The encapsulation protects bacteria in saline environments and from potentially toxic compounds in the feed.

The compact and regulated conditions of the bioreactor also promote complete reactions which means potentially lower nitrous oxide emissions. A diagram of a BIOCLENS lens can be seen in Figure 1.

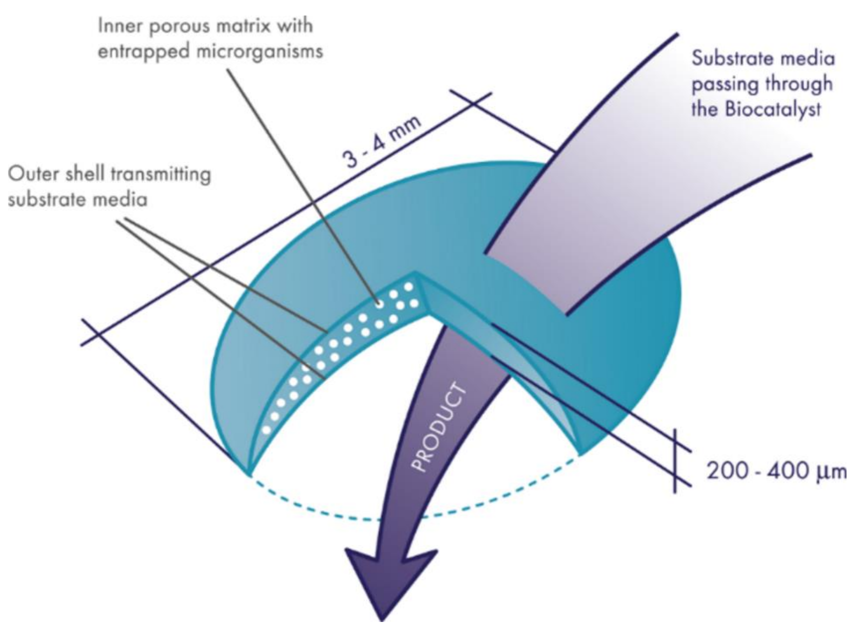

Figure 1. Diagram of a BIOCLENS® Lens

Since bacteria are encapsulated, as opposed to being free cell like in traditional treatment technologies, they remain protected in harsh environments and can cope with high ammonia and nitrate concentrations and osmotic pressures that are seen in salt-laden brines. Testing has shown that extremely high activity rates are still observed in the presence of high salt concentrations of 50,000 mg/L.

BIOCLENS can be used to retrofit existing treatment systems by adding an additional reactor vessel on the plant effluent for polishing, on a side stream, or they can be submerged in a box within existing activated sludge reactors to intensify ammonia and/or nitrate removal.

1.5 BIONEX Technology

BIONEX combines CIF and BIOCLENS in a complementary fashion to remove nitrate and convert it to nitrogen gas. The process diagram of a BIONEX system can be seen in Figure 2. The concentrated nitrate brine stream from ion exchange resin desorption is treated by lens encapsulated bacteria, typically removing nitrate to under 10 mg/L. The brine is then filtered, and returned to the desorption column, where it is reused for resin regeneration.

Less than 1% of the feed flow is purged from the brine loop in order to prevent build-up of contaminants. The waste stream typically has a TDS of 10,000 mg/L with 10 mg/L nitrate. In most cases, the small waste stream can either be returned upstream to the front of the wastewater treatment plant and/or can be blended with the product as a zero liquid discharge (ZLD) solution.

Salt usage is minimised since most of the brine is reused and not discharged. This is often a downfall of batch ion exchange processes where high volumes of nitrate-bearing brines are discharged from the system and need to be managed. The recycling of the brine typically saves 90-95% of the salt consumption compared to traditional batch ion exchange, resulting in typically operating costs US$0.10–0.15/m3 water treated.

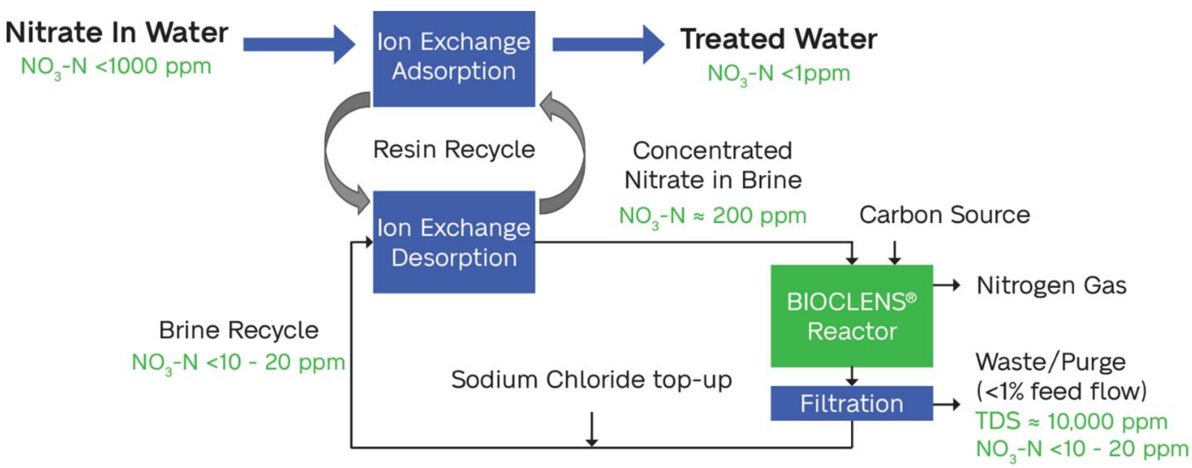

Figure 2. BIONEX™ Flowsheet

II.RESEARCH OBJECTIVES

The aim of the research conducted was to provide a proof of concept of the BIONEX technology by confirming:

1. CIF can consistently remove nitrate from feedwater to <1 ppm using ion exchange
2. BIOCLENS can remove nitrate from the salt brine to a level suitable for resin regeneration
3. The salt brine can be reused to regenerate the ion exchange resin

Laboratory testing and site piloting were undertaken to determine whether BIONEX is suitable to polish the nitrate from the discharge from a municipal water treatment plant.

III. METHODOLOGY

3.1 Initial Laboratory Testing

A range of lab-scale experiments were initially undertaken to assess the performance of BIOCLENS in relation to a range of operating conditions such as temperature, hydraulic residence time, salinity, pH, dissolved oxygen, mass-to-volume ratio of catalyst, carbon source type, and carbon-to-nitrogen dosing ratio. Results have shown that activity rates of the biocatalyst are consistently high, depending on influent nitrogen levels, and at low levels of catalyst loading can yield even higher activity rates of greater than 5,000 mg NOx/kgh which is otherwise unheard of in conventional technologies.

Further process development and testing that we carried out has resulted in the ability of BIONEX to be tuned to provide a unique sulphate desorption step to ensure low nitrate levels can be maintained consistently when sulphate-to-nitrate ratios in the feed are high, enabling a high degree of nitrate polishing to be sustained during long-term operation, without producing any additional waste.

3.2 Pilot Plants

A pilot-scale project was carried out in Taiping, China, treating up to 100 kL/d of industrial wastewater containing 15 ppm NO3-N and reducing it to less than 1.5 ppm. For this plant a fixed-bed ion exchange system was used, and the waste brine was treated with lens encapsulated bacteria. It was found that the fixed bed resin quickly suffered from extensive fouling and the flow was severely restricted.

A second pilot plant operated for 6 months in Tianjin, China from early 2021 to provide proof of concept to the client whose current wetland treatment plant was unable to achieve <3 ppm nitrate concentrations. The pilot plant shown in Figure 3 treats up to 100 m3/d and consists of a CIF® skid, and two stages of BIOCLENS® reactors. A proprietary self-cleaning screen keeps the lenses within the reactor whilst allowing treated water to pass through (right of Figure 3). The bioreactors have a two-hour residence time, and the temperature of the water is kept at 25 °C. Carbon dosing is controlled to optimise the activity of the lens encapsulated bacteria reactors. The pH and temperature of the system were controlled automatically during operation.

Figure 3. Photo of the Pilot Plant Equipment, CIF® (left), BIOCLENS® Reactors (middle), Self-Cleaning Screen (right)

IV RESULTS AND DISCUSSION

Piloting of the BIONEX system was successfully completed, and all of the research objectives were met. The results in Figure 4 show the nitrate is consistently removed to less than 1 ppm (undetectable levels) using CIF, apart from three instances during periods of maintenance/shutdown. After desorbing the resin this resulted in a brine containing 200 ppm nitrate at an EC of 50-60 mS/cm being fed to the BIOCLENS reactors.

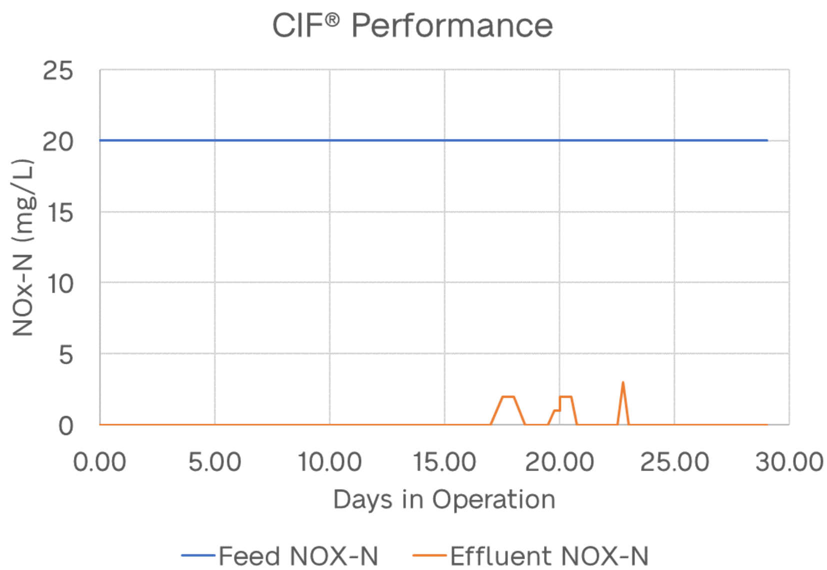

Figure 4. Feed and Effluent Nitrate Concentrations of the Pilot Plant

Figure 5 shows the activity of the BIOCLENS reactors operating at an EC of 50-60 mS/cm over time. After a few days for bacteria to acclimatise from cold storage, the two-staged reactor system consistently removed nitrate in the desorption brine to <10 ppm, while producing nitrogen gas. The nitrate removal allowed for efficient regeneration of the loaded resin in CIF. The two-stage system was optimised by reducing the carbon-to-nitrogen ratio, with the activity rates seen across both reactors peaking at around 1,000 mg NOx-N/kgh at higher carbon levels.

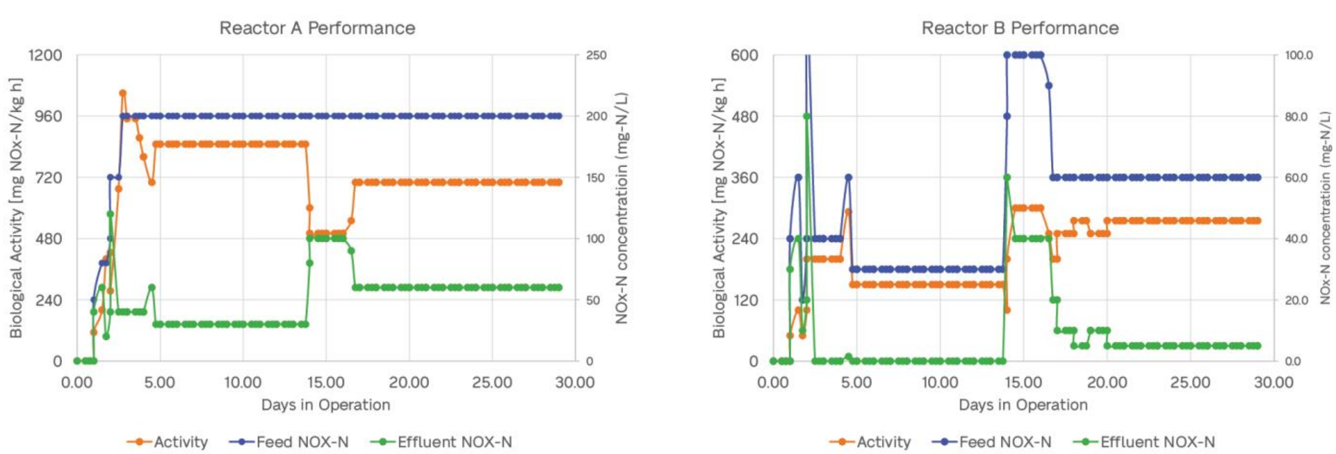

Figure 5. Biological Activity of BIOCLENS® Reactors (In Series) During Piloting

Piloting confirmed that the BIONEX™ system was able to consistently achieve <1 ppm nitrate in the effluent, and that lens encapsulated bacteria removes sufficient nitrate from the brine for it to be reused with minimal salt top-up required. These results form the basis for large-scale water treatment plants that can polish nitrate to very low levels with low chemical consumption, low waste production, and with small footprints.

V. CURRENT APPLICATIONS

Clean TeQ Water is currently delivering a flagship first-of-its kind 12 MLD BIONEX plant in Ordos, Inner Mongolia, China which will reduce the total nitrogen concentration of a wastewater treatment plant effluent from a coal mine from 5 ppm to less than 1 ppm. As at 15 June 2022 the plant is in the hot commissioning phase. A photo of the plant can be seen in Figure 6.

Figure 6. Photo of the BIONEX Nitrate Removal Plant in Ordos, China

VI. CONCLUSIONS

Results of BIONEX piloting prove that novel technologies such as BIONEX can offer treatment to achieve stricter regulatory requirements (<1 ppm TN) for discharge to the ocean and surface water, with biological treatment able to manage highly saline brines with minimal resource consumption and waste production. BIONEX™ plants typically operate with >99% recovery, with significantly lower waste and operating costs than batch ion exchange or reverse osmosis plants, meaning brine evaporation ponds and liquid waste handling can be eliminated when a zero liquid discharge approach is possible. It is a key enabler for reuse of wastewater for irrigation, industrial, mining, agriculture, and aquaculture purposes, reducing demands on clean drinking water, whilst reducing harmful algal blooms and eutrophication of sensitive water bodies. BIONEX has the potential to be the missing piece for existing water treatment plants looking to intensify their nitrate removal capacity.

VII REFERENCES

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VIII APPENDIX

Clean TeQ Water's CIF® (Continuous Ionic Filtration) technology is well suited to treat difficult mine water streams. It can selectively remove contaminants through ion exchange while simultaneously performing physical filtration, tolerating suspended solids in the feed, and allowing for cheaper reagents such as sulphuric acid and lime to be used. These usually cannot be used in conventional batch ion exchange systems since the precipitates that form cause the system to block up during desorption. CIF® is also more resistant to resin bed fouling compared to conventional ion exchange approaches since the ion exchange resin in periodically moved around the system. Higher removal efficiencies are also achieved in CIF® due to the counter-current movement between the feed solution and ion exchange resin. The system can also tolerate up to 150 mg/L of suspended solids in the feed and perform physical filtration if required.

In CIF®, ion exchange resin is continuously moved around the system for regeneration. Water treatment occurs in the adsorption column, which uses a moving packed bed of ion exchange resin. It can be likened to the continuous sand filtration process; however, the ion exchange resin continuously removes dissolved ions through ion exchange while simultaneously filtering solids if required. CIF® consists of a series of vertical columns, as seen in Figure 7, with one column treating the water, and the rest used to recondition the ion exchange resin as part of a continuous process.

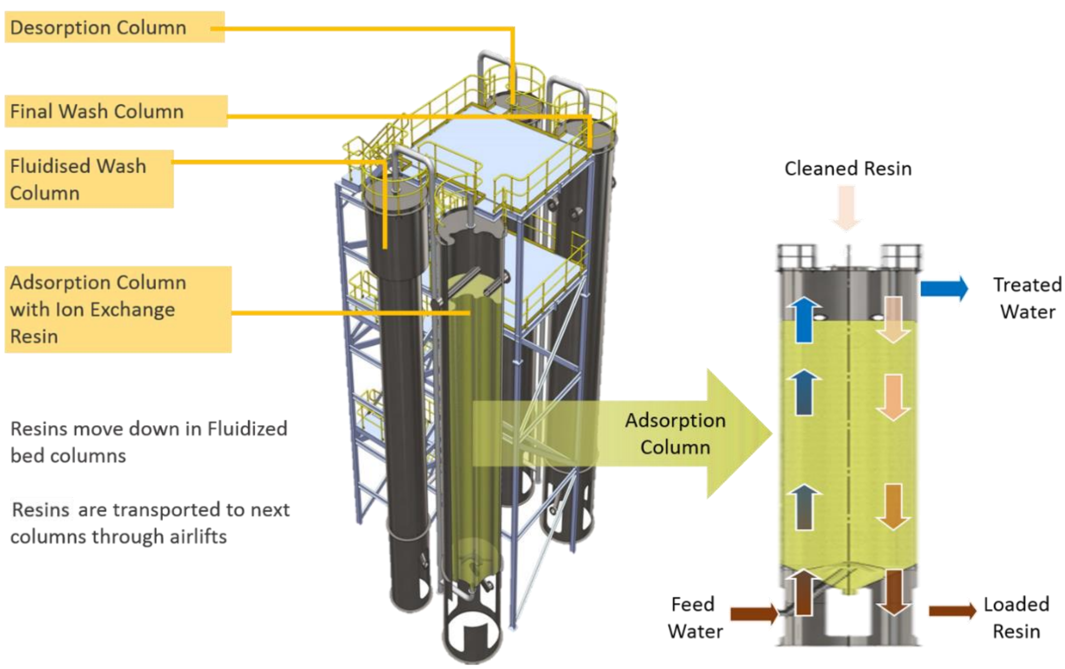

Figure 7. Diagram of a Typical CIF® System