SULFATE REDUCTION FROM SYNTHETIC WASTEWATER THROUGH MBBR TECHNOLOY – A LITERATURE REVIEW

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Abstract - *With reference to present day context Sulfate has became a serious threat for human society. Ever-increasing industrialization, severe level of wastes (effluents) from municipalities and industries are the prominently responsible causes for increased level of sulfate. Through sulfate, water bodies and water reservoirs are adversely affected and consequently Eutrophication of Lakes takes place on a greater extent. Due to this upper surface of water bodies becomes full of solid wastes and effluents which globally affects entire marine system and imbalances the hydrologic cycle. Sulfate has adverse effects on climate rather than human society. The main direct effect of sulfates on the climate involves the scattering of light, effectively increasing the Earth's albedo. This effect is moderately well understood and leads to a cooling from the negative radiative forcing of about 0.4 W/m² relative to pre-industrial values, partially offsetting the larger (about 2.4 W/m²) warming effect of greenhouse gases. The effect is strongly spatially non-uniform, being largest downstream of large industrial areas. Thus, we have opted to study on a Sulfate removal mechanism through MBBR technology by a cost-effective means. In our study we have used sponge based bio-carriers which have high porosity band low density. Our bio-carrier filling fraction is 1/5 by volume; through this filling fraction we could achieve satisfactory reduction of nitrate from effluent/wastewater. In this we have used a spontaneous Nitrification and Denitrification process (SND). This was done to make experiment study economically feasible. In our study it has been revealed that high concentration of sulfate restricts the bacterial growth in bio-carriers.*

Key Words: Sulfate, MBBR, Bio-film, Bio-carriers, PU, SND.

(A) INTRODUCTION

1. SULFATE

1.1 SULFATE

The sulfate (sulphate) ion is a polyatomic anion with the empirical formula SO^{2-}_4. Sulfate is the spelling recommended by IUPAC, but sulphate is used in British English. Salts, acid derivatives, and peroxides of sulfate are widely used in industry. Sulfates occur widely in everyday life. Sulfates are salts of sulfuric acid and many are prepared from that acid.

1.2 STRUCTURE

The sulfate anion consists of a central sulfur atom surrounded by four equivalent oxygen atoms in a tetrahedral arrangement. The symmetry is the same as that of methane. The sulfur atom is in the +6 oxidation state while the four oxygen atoms are each in the −2 state. The sulfate ion carries an overall charge of −2 and it is the conjugate base of the bisulfate (or hydrogen sulfate) ion, HSO^-_4, which is in turn the conjugate base of H_2SO_4, sulfuric acid. Organic sulfate esters, such as dimethyl sulfate, are covalent compounds and esters of sulfuric acid. The tetrahedral molecular geometry of the sulfate ion is as predicted by VSEPR theory.

1.3 BONDING

A widely accepted description involving pπ – dπ bonding was initially proposed by D. W. J. Cruickshank. In this model, fully occupied p orbitals on oxygen overlap with empty sulfur d orbitals (principally the d_{z^2} and $d_{x^2-y^2}$). However, in this description, despite there being some π character to the S−O bonds, the bond has significant ionic character. For sulfuric acid, computational analysis (with natural bond orbitals) confirms a clear positive charge on sulfur (theoretically +2.45) and a low 3d occupancy. Therefore, the representation with four single bonds is the optimal Lewis structure rather than the one with two double bonds (thus the Lewis model, not the Pauling model). In this model, the structure obeys the octet rule and the charge distribution is in agreement with the electro negativity of the atoms. The discrepancy between the S−O bond length in the sulfate ion and the S−OH bond length in sulfuric acid is explained by donation of p-orbital electrons from the terminal S=O bonds in sulfuric acid into the antibonding S−OH orbitals, weakening them resulting in the longer bond length of the latter.

1.4 PREPARATION

Methods of preparing metal sulfates include:

I. treating metal, metal hydroxide or metal oxide with sulfuric acid
   a. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
   b. $Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2\ H_2O$
   c. $CdCO_3 + H_2SO_4 \rightarrow CdSO_4 + H_2O + CO_2$

II. oxidation of metal sulfides or sulfites

1.5 PROPERTIES

Many examples of ionic sulfates are known, and many of these are highly soluble in water. Exceptions include calcium sulfate, strontium sulfate, lead (II) sulfate, and barium sulfate, which are poorly soluble. Radium sulfate is the most insoluble sulfate known. The barium derivative is useful in the gravimetric analysis of sulfate: if one adds a solution of, perhaps, barium chloride to a solution containing sulfate ions, the appearance of a white precipitate, which is barium sulfate, indicates that sulfate anions are present.

The sulfate ion can act as a ligand attaching either by one oxygen (monodentate) or by two oxygens as either a chelate or a bridge. An example is the complex $[Co(en)_2(SO_4)]^+Br^-$[7] or the neutral metal complex $PtSO_4(P(C_6H_5)_3)_2$ where the sulfate ion is acting as a bidentate ligand. The metal–oxygen bonds in sulfate complexes can have significant covalent character.

1.6 COMMERCIAL APPLIATIONS

Sulfates are widely used industrially. Major compounds include:

i. Gypsum, the natural mineral form of hydrated calcium sulfate, is used to produce plaster. About 100 million tonnes per year are used by the construction industry.
ii. Copper sulfate, a common algaecide, the more stable form ($CuSO_4$) is used for galvanic cells as electrolyte
iii. Iron(II) sulfate, a common form of iron in mineral supplements for humans, animals, and soil for plants
iv. Magnesium sulfate (commonly known as Epsom salts), used in therapeutic baths
v. Lead(II) sulfate, produced on both plates during the discharge of a lead–acid battery
vi. Sodium Laureth Sulfate, or SLES, a common detergent in shampoo formulations

1.7 ENVIRONMENTAL EFFECTS

Sulfates occur as microscopic particles (aerosols) resulting from fossil fuel and biomass combustion. They increase the acidity of the atmosphere and form acid rain. The anaerobicsulfate-reducing bacteria Desulfovibrio desulfuricans and D. vulgaris can remove the black sulfate crust that often tarnishes buildings.

1.7.1 PROMINENT EFFECTS ON CLIMATE

The main direct effect of sulfates on the climate involves the scattering of light, effectively increasing the Earth's albedo. This effect is moderately well understood and leads to a cooling from the negative radiative forcing of about 0.4 W/m^2 relative to pre-industrial values, partially offsetting the larger (about 2.4 W/m^2) warming effect of greenhouse gases. The effect is strongly spatially non-uniform, being largest downstream of large industrial areas.

The first indirect effect is also known as the Twomey effect. Sulfate aerosols can act as cloud condensation nuclei and this leads to greater numbers of smaller droplets of water. Lots of smaller droplets can diffuse light more efficiently than just a few larger droplets. The second indirect effect is the further knock-on effects of having more cloud condensation nuclei. It is proposed that these include the suppression of drizzle, increased cloud height, to facilitate cloud formation at low humidities and longer cloud lifetime. Sulfate may also result in changes in the particle size distribution, which can affect the clouds radiative properties in ways that are not fully understood. Chemical effects such as the dissolution of soluble gases and slightly soluble substances, surface tension depression by organic substances and accommodation coefficient changes are also included in the second indirect effect.

The indirect effects probably have a cooling effect, perhaps up to 2 W/m^2, although the uncertainty is very large. Sulfates are therefore implicated in global dimming. Sulfate is also the major contributor to stratospheric aerosol formed by oxidation of sulfur dioxide injected into the stratosphere by impulsive volcanoes such as the 1991 eruption of Mount Pinatubo in the Philippines. This aerosol exerts a cooling effect on climate during its 1-2 year lifetime in the stratosphere.

1.8. OTHER SULPHUR OXYANIONS

Molecular formula	Name
$SO^{2-}{}_5$	Peroxomonosulfate
$SO^{2-}{}_4$	Sulfate
$SO^{2-}{}_3$	Sulfite
$S_2O^{2-}{}_8$	Peroxydisulfate
$S_2O^{2-}{}_7$	Pyrosulfate
$S_2O^{2-}{}_6$	Dithionate
$S_2O^{2-}{}_5$	Metabisulfite
$S_2O^{2-}{}_4$	Dithionite
$S_2O^{2-}{}_3$	Thiosulfate
$S_3O^{2-}{}_6$	Trithionate
$S_4O^{2-}{}_6$	Tetrathionate

2. MBBR TECHNOLOGY/MECHANISM

Moving bed biofilm reactor (MBBR) is a type of wastewater treatment process which employs thousands of polyethylene biofilm carriers operating in mixed motion within an aerated wastewater treatment basin. Each individual biocarrier increases productivity through providing protected surface area to support the growth of heterotrophic and autotrophic bacteria within its cells. It is this high-density population of bacteria that achieves high-rate biodegradation within the system, while also offering process reliability and ease of operation.

This technology provides cost-effective treatment with minimal maintenance since MBBR processes self-maintain an optimum level of productive biofilm. Additionally, the biofilm attached to the mobile biocarriers within the system automatically responds to load fluctuations.

2.1 PROCESS DESCRIPTION/OVERVIEW

The MBBR system consists of an aeration tank (similar to an activated sludge tank) with special plastic carriers that provide a surface where a biofilm can grow. The carriers are made of a material with a density close to the density of water (1 g/cm^3). An example is high-density polyethylene (HDPE) which has a density close to 0.95 g/cm^3. The carriers will be mixed in the tank by the aeration system and thus will have good contact between the substrate in the influent wastewater and the biomass on the carriers.

To prevent the plastic carriers from escaping the aeration it is necessary to have a sieve on the outlet of the tank.

2.2 ADVANTAGES

The MBBR system is considered a biofilm process. Other conventional biofilm processes for wastewater treatment are called trickling filter, rotating biological contactor (RBC) and biological aerated filter (BAF). Biofilm processes in general require less space than activated sludge systems because the biomass is more concentrated, and the efficiency of the system is less dependent on the final sludge separation. A disadvantage with other biofilm processes is that they experience bioclogging and build-up of head loss.

MBBR systems don't need a recycling of the sludge, which is the case with activated sludge systems.

The MBBR system is often installed as a retrofit of existing activated sludge tanks to increase the capacity of the existing system. The degree of filling of carriers can be adapted to the specific situation and the desired capacity. Thus an existing treatment plant can increase its capacity without increasing the footprint by constructing new tanks.

When constructing the filling degree can be set to, for example, 40% in the beginning, and later be increased to 70% by filling more carriers. Examples of situations can be population increase in a city for a municipal wastewater treatment plant or increased wastewater production from an industrial factory.

Some other advantages compared to activated sludge systems are:

i. Higher effective sludge retention time (SRT) which is favorable for nitrification
ii. Responds to load fluctuations without operator intervention
iii. Lower sludge production
iv. Less area required
v. Resilient to toxic shock
vi. Process performance independent of secondary clarifier (due to the fact that there is no sludge return line)

(A) LITERATURE REVIEW

Libing Chu *et al.,* (2017)

As per this study, it has been observed that the types of Bio-carriers have significant effect on the reduction of many undesirable contents of wastewater. In this study they have compared biodegradable polycaprolactone (PCL) and polyurethane foam – a non biodegradable bio-carrier for the removal of organic as well as nitrogen based impurities i.e. ammonium, Nitrite, Nitrate with low C/N ratio with the help of moving bed biofilm reactor (MBBR).

The reactor with polyurethane (PU) has shown efficient TN removal (59%) at low level of Nitrate i.e. < 5 mg/l in effluent this is because of simultaneous nitrification and denitrification (SND) on the other hand reactor with polycaprolactone (PCL) has shown less TN removal in initial stage because it is a solid carbon source, its degradation rate is very slow due to which the microbial assimilation rate gets lower down, which causes low denitrification rate.

As per their conclusion, it has been figured out that if we want to use biodegradable Bio-carriers then we have to increase its porosity meanwhile we can develop improvised PU Bio-carriers (i.e. PU Bio-carriers impregnated with solid carbon substitutes).

Xinbo Zhang *et al.,* (2016)

This study is based on the effect of packing fraction on the working and efficiency of sponge based moving bed biofilm reactor (MBBR). Their experience has shown us that the simultaneous nitrification and denitrification (SND) increases with increase in the filling percentage i.e. SND were 85.5 ±8.7%, 91.3±9.4%, 93.3±10.2% in 10%, 20%, 30% filling fraction reactor respectively. In their study it has been observed by me that as per their experiment result, if a 12 l reactor fill up to 12% by sponge (15×15×15) mm Bio-carriers then the process would achieve maximum biomass accumulation per gram of sponge.

Nguyen *et al.,* (2016)

This experiment was conducted to study the effect of size and type of sponge Bio-carriers on the removal of micronutrients and other organic components from wastewater under aerobic conditions. Their observation has revealed that there has been no effect on removal efficiency of reactor with respect to variation in filling fractions i.e. we need to worry about the specification of sponge Bio-carriers like in the case of other Bio-carriers

Chu and Wang *et al.,* (2016)

According to this study, use of polyurethane sponge (PU) based Bio-carriers (20% filing fraction in MBBR) in case of low C/N ratio, has shown that TOC and ammonium removal has been 90% and 65% at HRT of 14 hrs respectively.

Luo *et al.,* (2016)

This study has revealed that there has been a variation in sorption capacity of polyurethane (PU) sponge based moving bed biofilm reactor (MBBR) for micro pollutants like removal efficiency of carbamazepine -22.9% & for b-

Brinkley, Johnson & Souza (2015)

According to this study, existing wastewater treatment facilities are being upgraded to cater for increased effluent flows, and that many such existing facilities. Have constraints on space for expansion. They identify MBBR as one wastewater treatment technology that has been developed which addresses both of these issues. They suggest that MBBR systems provide more treatment capacity within a given reactor volume compared to a conventional activated sludge (AS) process. They present a case study of a full-scale MBBR system that was installed on a space-constrained site to treat a planned increase in wastewater from a pharmaceutical production facility. They state that the MBBR system was the most cost-and space-effective treatment solution. The MBBR system is smaller than the existing aeration basin and can treat wastewater with a significantly higher organic load. They expect good performance from the MBBR system and less operator invention than the original AS process. They conclude that the MBBR process is ideal for expanding or upgrading existing treatment plants that have space constraints. (Brinkley, Johnson & Souza, 2015)

A.A.L.Zinatizadeh *et al* (2015)

The MBBRs filled with two types of carriers with different geometry, Ring form and Kaldnes-3 ,at packing rate of 50%(v/v) showed good performances in COD removal(>85%). The system with Ring form media could achieve more TN removal efficiency than that of the process with Kaldnes-3, indicating that anoxic condition is favored with Ring form.

Feng Quan, Wang Yuxiao *et al.,* (2015)

As per this study, the MBBRs filled with PUF carriers at packing percentage of 20%, 30%, and 40% (v/v) showed good efficiency in COD removal. The prosequencing analysis, predicted that the proteobacteria, Bacteriodetes and Verrucomicrobia were the three most abundant phyla.

Falletti and Conte (2014)

This experimental study presented a pilot-scale performance comparison of an AS treatment process and the same plant after the aerated tank was converted to an MBBR format. Following excellent results in the pilot phase, a full-scale AS wastewater treatment plant was converted to MBBR operation. The existing plant had been designed to service 3000 PE (person equivalent), but over time the waste stream had grown to 5800 PE, causing the system to be overloaded. Following successful operation of the converted plant, they conclude that MBBR is a suitable technology for upgrading overloaded AS plants without building new tanks. They report that the conversion of existing tanks to MBBR format can be done quickly, and that the main capital cost is related to the purchase of the proprietary MBBR attached-growth media. They note that no cleaning or emplacement of the media growth media is required in normal operation, and that the excess sludge produced is similar to that from conventional AS plants. They observe that the aeration requirement for MBBR systems is somewhat higher than for an AS (activated sludge) tank of the same volume, and that this contributes to higher operating costs, but that this is offset by the higher treatment flow rate possible with an MBBR system, and that automatic control of aeration based on pollutant concentration can optimize aeration costs. They make other observations about the practical operation of MBBR plants, and recommend that a pilot-scale test be performed to identify the optimal design parameters for a particular application. (Falletti & Conte, 2014)

Andreottola *et al.,* (2015)

This experimental study was performed to evaluate the application of an MBBR system for the upgrading of an overloaded municipal wastewater treatment plant (MWWTP). The MBBR solution was considered to offer several advantages including good potential in nitrification process, easiness of management and the possibility to use the existing tank with very few modifications. A pilot-scale experiment was undertaken to develop the design parameters for the full-scale upgrade. The final configuration was a two stage MBBR system. The upgraded configuration was able to handle a 60% increase in flow rate with good performance. (Andreottola et al., 2015)

Rodgers & Zhan *et al.,* (2015)

This research presented a review of four types of moving medium biofilm reactors for the treatment of wastewater. Review is based on published case studies and covers:
1. The rotating biological contactor (RBC);

2. The moving bed biofilm reactor (MBBR);
3. The vertically moving biofilm reactor (VMBR); and
4. The fluidized-bed reactor (FBR).

They conclude that the MBBR is a good process for upgrading existing wastewater treatment Systems.

Di Trapani et al. (2012)

This experimental study presented a pilot-scale comparison between a conventional AS treatment system and a MBBR treatment system. The aerobic reactor in both systems was of the same size. The MBBR system was able to treat twice as much wastewater as the AS system while maintaining similar performance in organic material removal. They conclude that the higher treatment capacity of the MBBR system demonstrates that it is an effective technology for the upgrading of overloaded wastewater treatment plants. (Di Trapani, Mannina, Torregrossa and Viviani, 2012).

Verma *et al.* (2015)

This experimented presented a survey of aerobic bio-filtration processes for wastewater treatment. They assess a range of conventional and advanced bio-filtration systems including MBBR systems. It concludes that the MBBR process is a good one for upgrading existing wastewater treatment systems. However, they also mentioned that for fluidized systems, generally (including MBBR systems), capital costs are comparatively low, operating costs are higher due to pumping/aeration requirements. (Verma, Brar, Blais, Tyagi & Surampalli, 2015)

McQuarrie & Boltz et al., (2012)

This experimental study provides an up-to-date overview of MBBR process design considerations. They observe that MBBR systems can be used for a wide range of wastewater treatment applications, and that they offer a range of benefits, including similar treatment performance as AS systems, and being a continuous flow process that does not require a special operational cycle. (McQuarrie & Boltz, 2012)

(C) CONCLUSIONS

MBBR systems are broadly reported in the research literature as having a range of desirable characteristics, including:

- **i.** Provides excellent pollutant removal performance;
- **ii.** Suitable for a wide range of effluent sources and types;
- **iii.** Ease of Management – Good stability and no sequencing;
- **iv.** Can be retrofitted with ease into existing tanks to extend asset life and performance;
- **v.** Required a smaller tank volume compared to AS systems for the same treatment flow rate;
- **vi.** Higher effluent treatment flow rates compared to similar capacity AS plants;
- **vii.** Lower capital cost compared to an AS plant with similar performance characteristics.

Particular capital costs of MBBR systems include the purchase of proprietary attached growth media, which may be offset against the typically reduced overall cost for the smaller plant size required compared to traditional treatment plant technology.

MBBR systems generally have an increased energy requirement for aeration on a tank unit volume basis, which may be offset against the typically smaller tank unit volume required for the same flow rate of effluent treatment compared to traditional treatment plant technology.

Many Researchers identified MBBR technology as appropriate for upgrading the performance and for treatment capacity of existing plants, particular if plant expansion is constrained by space limitations.

Many Researchers have recommended the use of a pilot-scale evaluation to determine suitable design and operating parameters for full-scale plant development.

After referring to research literatures pertaining to MBBR, it could be firmly drawn that there is broad range of advantages of MBBR. But bio-carriers being used in MBBR to treat wastewater are quite expensive and have less surface area for bacterial growth or say biofilm generation. Hence, we have decided to perform our nitrogen removal study using a cheap and feasible bio-carrier, for this we have opted a cubical shaped polyurethane (PU) sponge bio-carriers as in place of moving bed.

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