"Sulphate Removal from Artificial Effluent by the Moving Bed Bio-Film Reactor Technology"

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ABSTRACT:- Since restricting sulfate discharged from industrial and municipal wastewater treatment plants is a vital factor in preventing Eutrophication of surface waters. Sulfate is one of the major nutrients which prominently take part in the increased Eutrophication of lakes and natural waters. Its presence may cause multiple water quality problems including increased purification costs, decreased recreational and conservation value of an impoundments, loss of livestock and the possible lethal effect of algal toxins on drinking water. After going through research literatures with reference to MBBR, it could be definitely being drawn that there is wide 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 bio-film generation. Hence, we have decided to perform our sulfate removal study using a cheap and effective bio-carrier, for this we have selected a cubical shaped polyurethane (PU) sponge bio-carriers as in place of moving bed.

Keywords – MBBR, Sulfate, Bio-Carrier, Eutrophication, SND

1. INTRODUCTION

As we all know that the crises of fresh water increases day by day and the quality of fresh water also decreases. The waste water generation increased from 7000 MLD in 1978-1979 to 17,000 MLD in 1994-1995 to 61,948 MLD sewage generation in urban areas of INDIA, Madhya Pradesh generated 3214 MLD (as per CPCB Bulletin, National status of waste water generation & treatment, July-2016). MBBR is technology becoming increasingly popular and widely used in the world for treating different kinds of effluents under different conditions because the idea of MBBR is to combine the two different processes - attached and suspended biomass. This study may be helpful to check possibility that the moving bed bio-film process can be used as an ideal and efficient option for the nutrients removal from waste water (*Borkar et al.* 2013). Thus, we have taken into consideration a Sulfate removal mechanism using MBBR technology by a cost-effective means (*Barwal, et al*, 2015). In our study we have used sponge based bio-carriers which have high porosity band low density. Our bio-carrier filling fraction is 20% by volume; through this filling fraction we could achieve satisfactory reduction of sulfate from effluent/wastewater (*Kiilerich, et al*. 2017). In this technology a bed of Bio-carriers has been provided for the growth of bio-film. Some specific features of the MBBR system are the less head loss, no packing bed channeling problem, periodic back washing and sludge recycle is not required, and a large surface area for colonization and high specific biomass activity.

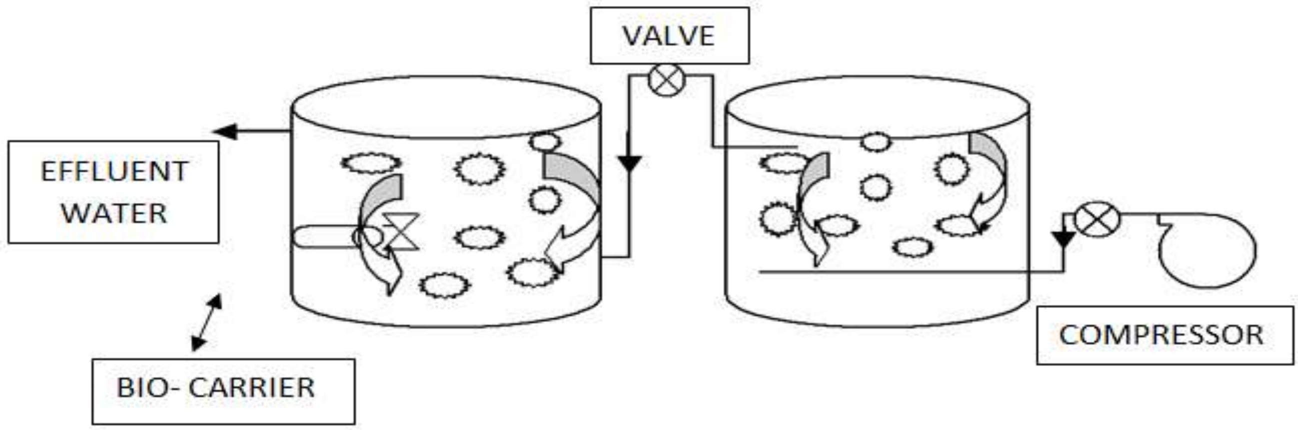

Figure 1.1 -Moving Bed Bio-film Reactor

2. EXPERIMETAL CONSTRUCTION

2.1 Moving Bed Bio-film Reactor assemble-

A single cylindrical tank/vessel has been used by us. The example is formed from polyvinyl chloride (PVC) besides this a model are additionally established by us for precise observations.

Some important data related to Moving Bed Bio-film Reactor setup-

2.1.1 Material of construction (MOC) -

- Prototype - PVC.
- Model - Pyrex glass cylindrical vessel
- Stirrer connected with mechanical motor
- Compressor
- Heater

2.1.2 Effluent / Raw material- Normal water added chemicals along with Shipra River water

2.1.3 Bio-carrier-

- -Material of construction- Polyurethane foam(PU)
- -Polyurethane foam sheets has been cut-out in the form of polymeric foam pads
- -Dimensions of a polymeric foam pad is 1cm * 1cm shown below-
- -Specifications of polymeric foam pad-[appendix 1]
- -Shape – Cuboidal

2.1.4 Aeration operation

An storage tank apparatus has been equipped with MBBR to supply a constant rate of aeration to aerobic zone throughout nitrification method. The apparatus /vacuum pump is supplied with stone based mostly diffuser. Aeration rate -2 LPM. (0.09m^3/ hr.)

2.2 Auxiliary equipment –

2.2.1 Natural draft drier-

The natural draft drier has been used to remove moisture from magnesium sulfate ($MgSO_4$), at 105 ^oC for 24 hours. It provides uniform heating to sample material for a long period of time, In general it has been used to remove the moisture from sample.

2.2.2 Centrifuge machine –

The centrifuge machine has been used to extract out bacterial from Moving Bed Bio-film Reactor, we will discuss about extraction process of bacteria in detail in the chapter named as ‘ Results and Discussion”.

The centrifuge machine works on the principle of specific gravity difference.

Rate of centrifuge – 10,000 RPM

2.3 Distillation Unit-

The purpose of distillation unit is to provide distilled water at a large quantity. The distilled water must have zero (nearby) electrical conductivity and TDS .

Salient features of distilled water-

- Odor- Odorless.
- Color- colorless.
- TDS- 0 ppm.
- PH - 7.0

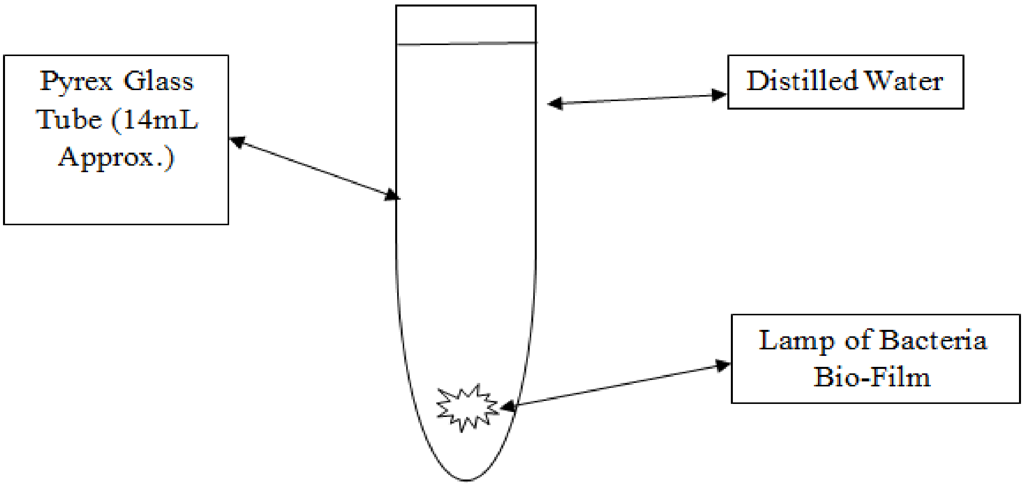

Figure 2.1- After centrifuge operation at 10,000 RPM

EXPERIMENTAL SETUP:-

Plate 2.1 – Experimental setup

3. Materials and Methods –

In this section, we will discuss about the procedures for analysis of Sulfate and bacterial growth. (*Mudakavi, 2010)*

3.1 Chemicals used –

Sodium Chloride, Hydrochloric Acid, Barium Chloride, Glycerol, Isopropyl alcohol

3.2 Procedure of Sulfate determination in waste water using a calibration curve method.

3.2.1 Reagent Preparation -

1. **Sodium Chloride – Hydrochloric Acid reagent**: Dissolve 24 gm. of analytical reagent (Sodium Chloride) in 80 ml distilled water. Add 2 ml of concentrated hydrochloric acid, dilute to 100 ml in a volumetric flask.

2. **Glycerol – Alcohol Solution**: Dissolve 10 ml of glycerol in 20 ml of isopropyl alcohol (or ethyl alcohol).

Sulfate ion precipitated in an acetic acid medium with barium chloride so as to form barium sulfate crystals of uniform size. Light absorbance of barium sulfate suspension is measured by a spectrophotometer and the sulfate ion concentration is determined by comparison of the reading with a standard curve.

3.2.2 Procedure

Pipette out .5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 6.0 ml standard sulfate solution (100 ppm) into ten different 10 ml volumetric flasks. Add 1 ml sodium chloride-hydrochloric acid reagent and then add 200 µl of the glycerol alcohol solution followed by 1ml. (10%) barium chloride solution. Make up the volume to the 10 ml. by adding de-ionized water. Close the lids and mix by inverting 20 times.

Measure the absorbance of each solution at 420 nm using 1 cm cuvettes, taking care to again shake the solution vigorously just before taking readings.

Recommended sample volume – 1 ml.

For the analysis the Shimadzu Recording Spectrophotometer UV-1800 has been used & all the measurement has been read against distilled water set at zero absorbance as a blank by us.

3.3 Significance of Reagents in Sulphate Estimation:

1. **Sodium Chloride-hydrochloric Acid reagent** – To regulate the PH of the solution.
2. **Barium Chloride** – When the sulfate present in our synthetic wastewater come in contact with barium chloride, double displacement chemical reaction takes place. In this sulfate displaces the chloride from barium and produces a cloudy precipitation of barium sulfate.
3. **Glycerol Reagent** – It helps to make suspension of Barium sulfate.

Instructions for the preparation of the Sulfate dilute samples.

1. Separate into 7 groups, this will increase your precision in drawing calibration curve.
2. Out of every groups , concentration should be maintain at the 100 mg sulfate stock solution as prescribed in above and prepare 1, 2, 4, 5, and 7 mg standard sulfate solutions for the calibration curve from the stock solution as instructed below.

Preparation of 7 mg SO^{2-}_4 /L standard solution.

- Take volumetric flask of 50 ml.
- Apply ratio equality equations

Desired ratio = Known ratio

x / 7 mg/L = (50 ml) / (100 mg/L), and

Then solve for x:

x = ((7 mg/L) ⨯ (50 mL))/ (100mg/mL) = 3.5 ml.

- Take 3.5 ml from stock solution into 50 ml of volumetric flask and makeup with distilled water up to 50 ml mark on volumetric flask .

Preparation of 1 mg SO^{2-}_4 / L standard solution .

- Take volumetric flask of 50 ml.
- Apply ratio equality equation

Desired ratio = Known ratio

x / 1 mg/L = (50 mL) / (100 mg/L), and

Then solve for x:

x = ((1 mg/L) ⍰ (50 mL)) / (100 mg/mL) = 0.5 ml.

- Take 3.5 ml from stock solution into 50 ml of volumetric flask and makeup with distilled water up to 50 ml mark on volumetric flask.

Repeat this procedure to make standards of 2, 4, and 5 mg $SO^{2-}{}_4$/L standard solutions.

- Analyze each of the 5 standard solutions 3 times each using the UV-VIS (shimadzu 1800 series) as described below.
- Analyze distilled water and tap water 3 times each as your samples.

4. RESULT AND DISCUSSION

1. Removal of Sulfate from wastewater (Synthetic)

We have established a Moving Bed Bio-film Reactor setup, which has started work on April 20, 2019. We suppose the starting date as the reference point i.e., zero days for the ease of calculation.

Our whole experiment has been divided into 3 phases –

1st Phase- It has taken more HRT, to cultivate and grow the desired bio-film first time.

2nd Phase- It has been a moderate phase during which the HRT is 12 hours.

3rd Phase- It is the final phase in which we observe maximum removal of sulfate.

Phase	Time duration (day)	pH	HRT (Hours)
I	0-30	7.1	24 hours - for 15 days
			12 hours - for next 15 days
II	31-45	7.11	12 hours
III	46-60	7.1	12 hours

Result analysis of prepared sample

2. **Effect of Time on PH**

, Below figure shows the effect of time on pH of the waste water sample. pH is one of the affecting parameter of waste water sample.

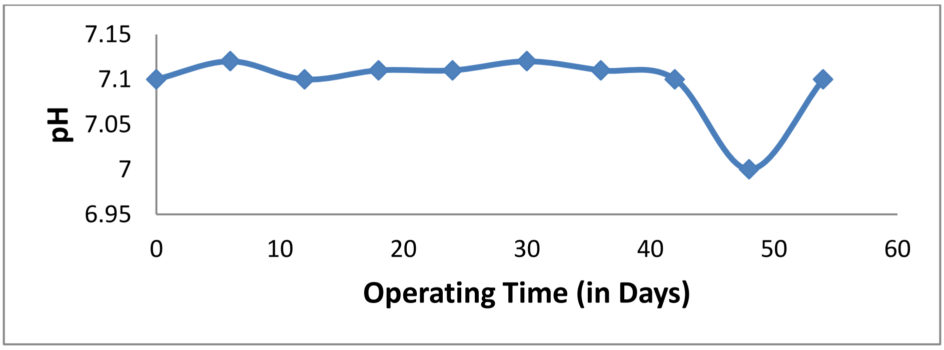

Chart 4.1

Variation in pH with time

We have observed that the PH has been not varying with operating duration i.e., days. We predicted that this was happened due to auto PH regulating abilities of bacterial colony which has grown in bio-carrier pores. The bacterial colony has been of two types-

1. Auto-trophs bacterial colony
2. Hetero-trophs bacterial colony

The Autrophic bacterial colony results-

The acidic medium in reactor

$SO^{-}_{3} + H_2O \rightarrow SO^{2-}_{4} + H^{+}$

Which causes decrease in PH but on the other hand the heterotrophic bacterial colony causes the increase in PH value.

During SND - Simultaneous Nitrification & De-nitrification

Neutralize the environment of auto PH regulation that's why PH remains constant during experiment.

3. **Effect of Temperature on pH**

Below figure shows the effect of temperature on pH of the waste water sample. Temperature prominently affects the pH value of the waste water sample.

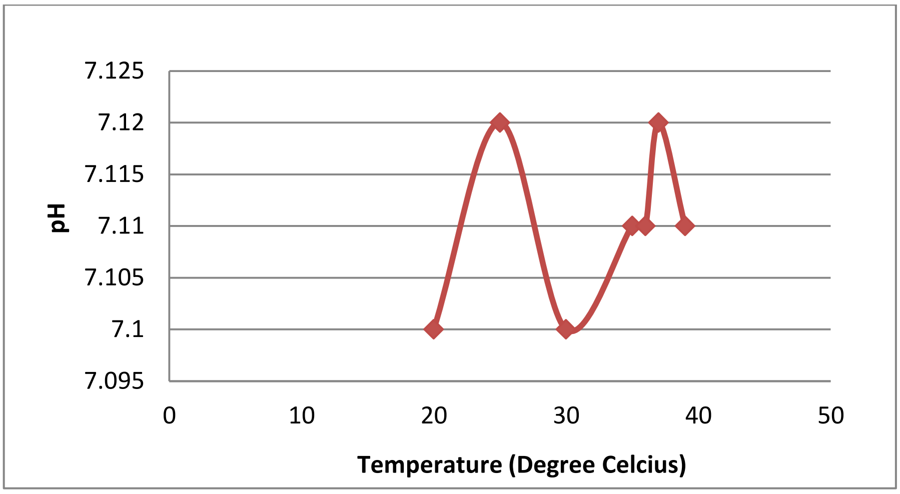

Chart 4.2

Variation in pH with temperature

Our reactor has been operated at the temperature range of 20°C to 39° C, from the experimental data we have observed that the temperature has affected the pH value of the sample. When we increased the temperature from 20C to 35C the pH value has increased from 7.1 to 7.11 and afterward the value of pH has attained at 7.11 at the temperature of 39C.

We can conclude that if the operating temperature goes below 20°C, then the conversion of sulfate gets lower which mean we have to increase the hydraulic retention time (HRT) which is not at all feasible.

Analysis of Sulfate sample -

Table 2 Analysis of Sulfate calibration curve of unknown sample

S. No.	Concentration In PPM	Absorbance	K*Abs	Wavelength
1	1	0.057	0.106061	420
2	2	0.064	0.212121	420
3	3	0.071	0.318182	420
4	4	0.077	0.409091	420

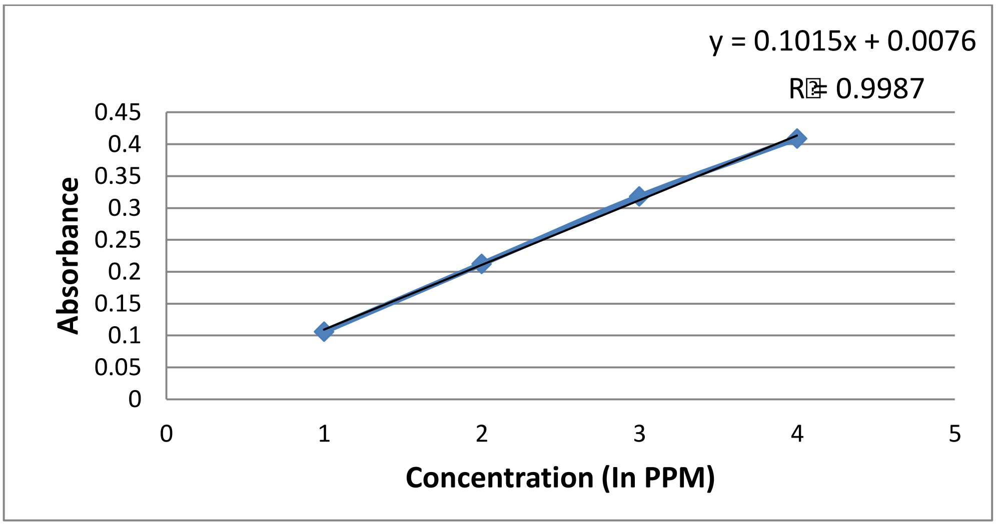

Chart 4.3 - Analysis of Sulfate Calibration Curve of Unknown Sample

2. Reduction in Sulfate concentration

Sulfate present in prepared synthetic sample varies with operating time. The below figure shows that how sulfate concentration varies with time. With the help of this figure we can find sulfate reduction at any day. The highest efficiency 78.22% has been achieved in 60 days after that efficiency is constant due to reduction in bacterial activity.

Total reduction in sulfate concentration = Initial concentration – Final concentration

= 6.8181 mg/l – 1.4848 mg/l

= 5.3333 mg/l

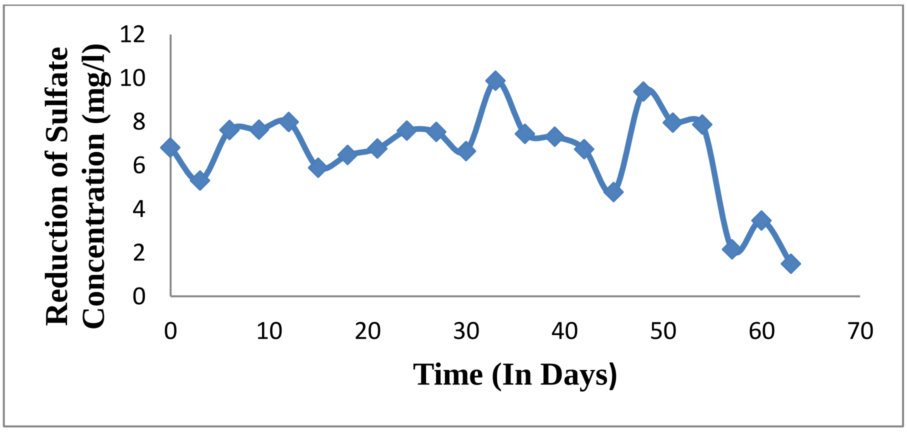

Chart 4.4 -Reduction in Sulfate Concentration

Taking into consideration that higher concentrations of substrates ($SO^{2-}{}_4$) were thermodynamically favorable for the SRAO reaction and that higher consumption of NH_4 was experimentally observed than it could be predicted by the extent of $SO^{2-}{}_4$ reduction based on the influent NH_4 content was approximately doubled while $SO^{2-}{}_4$ content remained unchanged in days 0–60 days for the MBBR. For reactors, had no significant effect on the $SO^{2-}{}_4$ removal.

During the mentioned period, the average $SO^{2-}{}_4$ loading rate was 0.15 kg-N/m3/day (0.64 g-N/m2/day), $SO^{2-}{}_4$ removal efficiency 18% and $SO^{2-}{}_4$ removal rate 0.03 kg-N/m3/day (0.11 g-N/m2/day)

During the entire experimental period, the average $SO^{2-}{}_4$ loading rate was 0.13 kg-N/m3/days (0.52 g-N/m2/day in the MBBR). The average $SO^{2-}{}_4$ removal efficiencies for the entire experimental study were 24% for the MBBR. The corresponding $SO^{2-}{}_4$ removal rates were 0.03 kg-N/m3/ day (0.13 g-N/m2/day) for the MBBR. These results are significantly lower than those achieved in MBBRs fed with reject water using $SO^{2-}{}_4$ as the terminal electron acceptor for anammox reaction. In the latter reactors the average total Sulfate (SO^{2-}_4) removal efficiency was 78.22% and the SO^{2-}_4 removal rate 0.50 kg-N/m3/day (1.25 g-N/ m2/day).

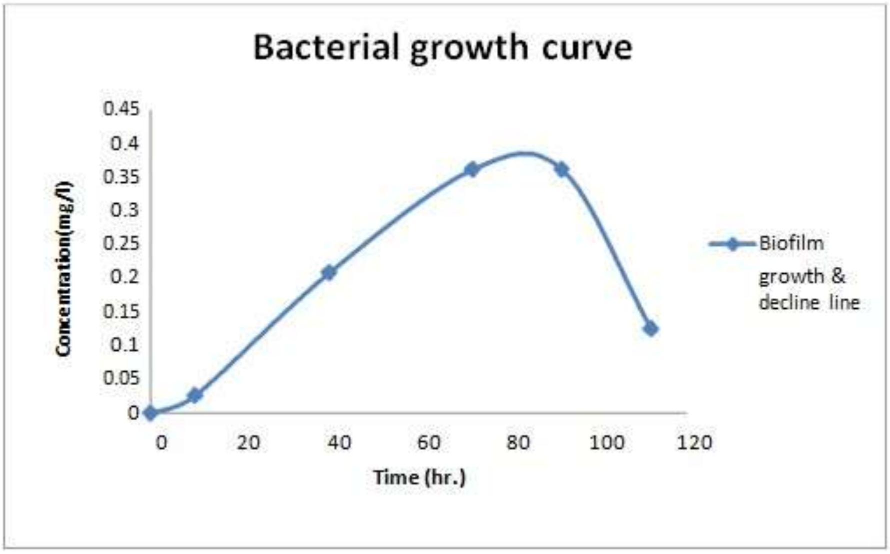

Chart 4.5 -Bacterial Growth Curve

Bacterial growth curve using optical density method

The wavelength for bacterial estimation is 600nm.

To study the bio-film generation rate, we have used the bacterial cell mass determination method. For bacterial growth curve we know that Monod kinetics has been used to study the bacterial growth.

Above figure shows bacterial growth curve. It has been observed that the bacterial colony developed on the PU based polymeric foam pads has a time period of 118 hrs, the bacterial growth curve give the evidence how the bacterial life is changing with respect to time.

The physical observation of bio-carrier has shown that the color of the bio-carrier change from pink to pink brown.

CONCLUSION

With aid of this experimental study, MBBR (Moving bed bio-film reactor) tested to be a cheap and eco-friendly alternative for the reduction of sulfate from artificial waste water. Specifically, this experimental study analyzed the reduction of sulfate from the artificial waste water using MBBR. This analysis discovered that MBBR with polyurethane media (PE) as bio-film support carrier may be economical for sulfate reduction from waste water.

Some specific findings of this study are as below:

1. It's been determined that the microorganism colony developed on the element primarily based compound foam pads features a fundamental quantity of 118 hours.
2. High Accumulations of biomass within the bio-film method once hooked up with smart gas transfer capability of the system make sure the high treatment capability and operational stability. This could build the MBBR method engaging and promising to use for sulfate reduction from waste water.
3. The result of pH on removal efficiency isn't considerable, throughout the method it's been determined that the pH has been well maintained itself within the reactor.
4. It established to be economically possible as a result of the number needed of sponge bio-carriers is a smaller amount with relevance typical plastic primarily based bio-carriers.
5. PU sponge primarily based bio-carriers are in the least appropriate for sulfate reduction because of its high porosity still as high specific surface area.

6. We have a tendency to achieved sulfate reduction by 78.22% in 60 days with the assistance of Moving Bed Bio-film Reactor.
7. We will also perform kinetic and model based study.

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