Treatment of Industrial Wastewater by Organic Wastes

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Performance of the laboratory scale bioreactors containing different organic substrates has been tested for the treatment of acidic industrial wastes in terms of acid neutralization, sulphate and metal removal processes. Glass jars of 1.5 liter capacity (30 cm height) containing bacterial consortium of different organic substrates were inoculated with dairy whey to promote SRB culture. After incubation period of 17 days at room temperature the jars were introduced with 850 ml acidic industrial wastewater rich in ferric iron characterized by low pH, polluted with presence of metals like cobalt, zinc, copper, lead, manganese, nickel and iron. The experiment was run for three months. After retention period of four, twelve, nineteen, twenty five, thirty seven, fifty two, sixty six, eighty and ninety four days. The pH of the wastewater increased from 5.58 to 8.39, alkalinity from 0 to 712mg/l as CaCO₃, acidity removal was from 223.8 to 95 mg/l as CaCO₃, sulphate removal was 48.9%, lead removal was 91%, zinc 99.3%, copper 97.0%, cobalt 97.0%, manganese -55.6%, nickel- 99.7% and iron 99.87% were observed. The main aim of this study is to compare and interpret the best organic substrate for treatment of acidic wastewater in bioreactors and to be applied on commercial scale.

Key words- Industrial wastewater, substrate, bioreactor, sulphate reducing bacteria.

Introduction

Industrial revolution besides being the backbone for economy of the country has added to the widespread environmental pollution. Soils, ground water and surface waters have become contaminated, and there is increasing pressure on the industries to reduce the risks associated with this contamination. Industrial wastewater continues to be a serious water pollution problem around the world. Industrial processes in particular to name a few industries like metal processing, mining, tannery, galvanic processing, power plants, construction sites, paper and pulp as well as transportation corridors discharges and produce almost every other pollutant i.e. sulphates, acidity, heavy metals and sometimes toxic chemicals; requires further treatment before being discharged¹. It is well perceived that there is a permissible limit of each metal, above which they are generally toxic and some are even hazardous. It has also been observed that heavy metals can cause biochemical alterations, such as inhibition of enzymes, metabolic disorders, genetic damage, hypertension and cancer. Therefore it is essential to treat industrial wastewater safely to avoid contamination of terrestrial and aquatic life. Clearly, the problems associated with water pollution have the capabilities to disrupt life on our planet to a great extent²,³. Due to large volumes of effluents and presence of recalcitrant compounds, the treatment of these streams is rather challenging. The trend over the past centuries in the construction of water pollution control facilities has been towards concrete and steel alternatives employing various physical and chemical concepts⁴. Several physico-chemical treatment systems, most commonly used by most of the industrial units such as continual addition of chemicals like limestone, lime, hydrated lime, caustic soda, soda ash, ion-exchange, activated charcoal, chemical reduction and adsorption etc presents some limitations. There are some common problems associated with these methods such as these are costly and themselves produce other waste problems and additional costs, which has again limits to their industrial application⁵,⁶. With the rising capital and also operation and maintenance costs in chemical treatment technology, need for more eco-friendly, economical and simple (less skill demanding) treatment systems has been felt strongly. Recent years have witnessed a growing interest in the use of biological methods in the remediation of variety of wastewaters. Bioremediation of acidic
sulphate rich industrial effluents by bioreactors using microbial communities is a promising alternative to chemical remediation. It has been developed over the past few years by the developed countries to the stage where it can compete and replace successfully other technologies for full scale treatment of industrial effluents commercially.

The dissolved organic carbon content of metal-containing wastewater is very low but the bacterial colony needs supply of carbon source as food for sulphate reducing bacteria’s. Therefore, addition of a suitable carbon source and electron donor for sulphate reduction is necessary to promote biogenic H₂S production (eq.1). Various organic substrates and cellulosic wastes have been used as the energy sources for SRB, most being typical fermentation products, manures etc. Bacterial sulphate reduction in the bioreactors has been applied to remove metals, raise pH and various other toxicants from the industrial effluents. For heavy metal removal sulfide generated by sulphate reduction is used to chemically precipitate metals as sulfides. Extremely low solubility of metal sulfide formed allows the removal of heavy metals from the waste stream (eq. 2). The metal precipitation reaction releases protons, thus adding to the acidity of the water. Therefore, excess sulphate needs to be reduced to compensate for the acidity. Bicarbonate alkalinity or hydroxide ions produced in the sulfidogenic oxidation of electron donors (eq. 1) neutralizes the acidity of the water (eq. 3).

The biological transformation process is described in the following reactions,

\[ \text{CH}_3\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} (g) + 2\text{HCO}_3^- \quad \ldots (1) \]
\[ \text{H}_2\text{S} + \text{M}^{2+} \rightarrow \text{MS} (s) + 2\text{H}^+ \quad \ldots (2) \]
\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 (g) + \text{H}_2\text{O} \quad \ldots (3) \]

Where, \( \text{CH}_3\text{O} \) and \( \text{M}^{2+} \) represent the carbon source and heavy metal, respectively.

Different electron donors and acceptors can result in different bacterial biomass yields of SRB. The substrate consumption rate of the sulphate reducers is dependent on concentrations of both the electron donor and electron acceptor. As the economic constraints have a determining role in developing countries, the choice of carbon source selected is the use of waste, which is very much feasible. The goal of this research is to examine and recommended some easily available waste products for the treatment of industrial wastewater.

### Table 1—Glass jars (bioreactors) with their respective substrate compositions

<table>
<thead>
<tr>
<th>Glass jars (bioreactors)</th>
<th>Substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (AI, AII, AIII)</td>
<td>80% cow manure + 20% sugarcane</td>
</tr>
<tr>
<td>B (BI, BII, BIII)</td>
<td>90% horse manure + 10% sugarcane</td>
</tr>
<tr>
<td>C (CI, CH, CIII)</td>
<td>85% goat manure + 15% sugarcane</td>
</tr>
<tr>
<td>D (DI, DII, DIII)</td>
<td>95% camel manure + 5% sugarcane</td>
</tr>
</tbody>
</table>

### Material and method

#### Organic substrate

Five different organic waste materials i.e. cow manure, horse manure, camel manure, goat manure and sugarcane waste in four different compositions in four different reactors were used in this study (Table 1). Manures were collected from local farms and sugarcane waste was collected from different juice corners of the city. After collection all the samples were dried and then grinded manually to make fine powder. All the five organic substrates were considered to be potentially suitable with respect to economic characteristics compared to commercially available chemicals.

#### Wastewater

The experiments were conducted on the industrial wastewater collected from various industrial areas of Jodhpur city in Rajasthan state of India. Jodhpur city is enriched with number of industries like of stainless steel-500, textile industries-150 gwargum-15, chemicals-12 and miscellaneous 100 (Jodhpur Industrial Association). Most of the above industries use water in different processes and the wastewater drains out as an industrial effluents. The effluents from these industries are generated in large quantities and drained in natural drainage system without treatment covering a distance of about 10-15 kms. This drainage discharged is loaded with sulphate, metals and is of low pH thus contaminating both terrestrial as well aquatic ecosystems. The effluents of the industrial area contain the pollutant parameters far beyond the limits prescribed by Bureau of Indian Standard and Ministry of Environment and Forests.

Wastewater was collected from open drainages present in one of the industrial estates of the Jodhpur city which is located at Basni Phase (I & II).

#### Experimental setup

Twelve column glass jars each of 1.5 L capacity were used as bioreactors in group of four sets with each set comprising of three column jars (Table. 1). All the four sets had different substrate combinations to treat wastewater.
The total height of each jar is about 30 cm. Initially the bottom of each jar was filled with substrate up to a height of 8 cm, then filled with pebbles up to a height of 6 cm. It was followed with a layer of sand and crushed stones, thus increasing the surface area to volume ratio. Thereafter each jar was inoculated with 100 ml dairy whey to provide a medium for culture of SRB. Whey promotes SRB culture\(^\text{13,14}\). The bioreactors were capped with air tight lids to create anaerobic conditions for different retention periods for bacterial culture (Fig. 1). Sand and crushed stone proved to be of vital importance for the reduction by increasing the surface area. Whey was found to contain 50 g lactose, 6 g protein, 6 g ash and .03 g fat per liter\(^\text{15}\).

After an incubation period of 17 days at room temperature, the glass jars were filled with 850 ml of industrial wastewater. Formation of black film at the junction of substrate and sand stones layer with \(\text{H}_2\text{S}\) smell confirmed SRB culture. Afterwards, sampling and analysis of samples were carried out.

**Sampling and analysis**

Water sample of 50 ml were taken from each jar and each time and 50 ml wastewater was added to maintain the same level of wastewater in each bioreactor. Observations were taken after retention period of four, twelve, nineteen, twenty-five, thirty-seven, fifty-two, sixty-six, eighty and ninety-four days.

**Methodology**

The following chemical parameters were examined in the laboratory: pH, Acidity, Alkalinity, Sulphate and for the metal ions examinations filtered samples were preserved using nitric acid as detailed in Standard Methods for the Examination of Water and Waste water (APHA, AWWA, WEF 1992). The pH was measured immediately after wastewater collection with a pH meter (Make- RI, Model 151R). The sulphate concentration was measured using turbiditric method with a turbidity meter (Make- RI, Model -211R). The acidity and alkalinity of the water samples were measured using titration method. Prior to metal analysis effluent samples were filtered twice through Whatman filter no. 42 and adjusted to a pH less than 2 by adding concentrated \(\text{HNO}_3\). Metal concentrations were determined using Atomic Absorption Spectrophotometer (Make- Thermo electron corporation Ltd, Model S2). All the parameters were examined by Standard methods for the examination of Water and Wastewater (APHA- AWWA-WEF, 1992).

**Results and discussion**

The industrial wastewater collected from Basni phase I & II at Jodhpur was reddish in colour due to the presence of ferric iron and is characterized by low pH, polluted with presence of metals like cobalt, zinc, copper, lead, manganese, nickel and iron. The experiment was carried out on laboratory scale for different retention periods approximately for three months. The water chemistry of industrial wastewater treatment process in the bioreactors is summarized below.

**pH**

The pH of input industrial wastewater in the bioreactors was 5.58 and it increased up to 8.01, 7.98, 8.18 and 8.39 in the bioreactor A, B, C and D respectively. The organic substrate in the bioreactors plays a very important role in raising pH. Whey addition also improved pH neutralisation. Therefore, the pH increase in these reactors is likely to be influenced by SRB activity\(^\text{20}\) thus increasing effluent alkalinity. These organic substrates
provides source of carbon for bacterial culture which is capable of raising pH by reducing sulphate to sulphides thereby reducing acidity in industrial wastewater\textsuperscript{17,18}. The maximum increase was estimated in bioreactor D.

**Acidity**

It represents the pH and metal ions present in the industrial wastewater. The acidity of input industrial wastewater was 223.8 mg/l (as CaCO$_3$). The maximum acidity reduction observed in bioreactors was 125.3 mg/l in A, 111.1 mg/l in B, 95 mg/l in C and 99.9 mg/l in D (as CaCO$_3$) (Fig. 2). The maximum reduction in acidity was observed in the reactor containing goat manure and sugarcane waste followed by reactor containing mixture of camel manure and sugarcane waste. The findings are in conformity to the reportings of various authors\textsuperscript{19}.

**Alkalinity**

It is the acid neutralizing capacity of the wastewater. The alkalinity of input industrial wastewater in the different bioreactors (A, B, C and D) was zero. After treating them in sulphate reducing bioreactors the output alkalinity increased from zero to 572.17 mg/l as CaCO$_3$ in A, 503.47 mg/l as CaCO$_3$ in B, 471.3 mg/l as CaCO$_3$ in C and 712.67 mg/l as CaCO$_3$ in D. Sulphate reducers are clearly important for the alkalinity generation in all the cells and generation was quite substantial. In the first set of generation of alkalinity and their role in the bioremediation has been well reported\textsuperscript{20,21}.

**Sulphates (SO$_4^{2-}$)**

It is one of the most common pollutant of industrial wastewater. The sulphate concentration of input was 1350 mg/l. Sulphate removal rates in bioreactors was observed upto 48.9 % in A, 47.0 % in B, 46.7 % in C and 47.4 % in D. Sugarcane waste powder and various manures provide a substrate which is capable of removing sulphates by reducing them to sulphides, part of the sulphides escape to atmosphere as H$_2$S gas while part precipitates metals in forms such as FeS\textsuperscript{22}.

### Table 2—Change in metals concentration (mg/l) of industrial wastewater in the bioreactors with time

<table>
<thead>
<tr>
<th>Composition</th>
<th>Retention period</th>
<th>Pb (Avg ± SD)</th>
<th>Zn (Avg ± SD)</th>
<th>Cu (Avg ± SD)</th>
<th>Co (Avg ± SD)</th>
<th>Mn (Avg ± SD)</th>
<th>Ni (Avg ± SD)</th>
<th>Fe (Avg ± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0 Days</td>
<td>1.19 ± 0</td>
<td>2.03 ± 0</td>
<td>3.20 ± 0</td>
<td>2.11 ± 0</td>
<td>2.50 ± 0</td>
<td>3.60 ± 0</td>
<td>12.41 ± 0</td>
</tr>
<tr>
<td></td>
<td>50 days</td>
<td>0.14 ± 0.006</td>
<td>0.11 ± 0.01</td>
<td>0.13 ± 0.006</td>
<td>0.08 ± 0.006</td>
<td>1.68 ± 0.819</td>
<td>0.77 ± 0.187</td>
<td>0.32 ± 0.344</td>
</tr>
<tr>
<td></td>
<td>98 days</td>
<td>0.12 ± 0.036</td>
<td>0.04 ± 0.035</td>
<td>0.09 ± 0.072</td>
<td>0.06 ± 0.006</td>
<td>1.11 ± 0.181</td>
<td>0.01 ± 0.005</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>B</td>
<td>0 Days</td>
<td>1.19 ± 0</td>
<td>2.03 ± 0</td>
<td>3.20 ± 0</td>
<td>2.11 ± 0</td>
<td>2.50 ± 0</td>
<td>3.60 ± 0</td>
<td>12.41 ± 0</td>
</tr>
<tr>
<td></td>
<td>50 days</td>
<td>0.13 ± 0.06</td>
<td>0.18 ± 0.006</td>
<td>0.14 ± 0.046</td>
<td>0.10 ± 0.01</td>
<td>1.68 ± 1.556</td>
<td>0.02 ± 0.065</td>
<td>0.13 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>98 days</td>
<td>0.10 ± 0.006</td>
<td>0.07 ± 0.023</td>
<td>0.11 ± 0.012</td>
<td>0.06 ± 0.01</td>
<td>1.50 ± 0.006</td>
<td>0.03 ± 0.013</td>
<td>0.10 ± 0.005</td>
</tr>
<tr>
<td>C</td>
<td>0 Days</td>
<td>1.19 ± 0</td>
<td>2.03 ± 0</td>
<td>3.20 ± 0</td>
<td>2.11 ± 0</td>
<td>2.50 ± 0</td>
<td>3.60 ± 0</td>
<td>12.41 ± 0</td>
</tr>
<tr>
<td></td>
<td>50 days</td>
<td>0.14 ± 0.23</td>
<td>0.15 ± 0.025</td>
<td>0.13 ± 0.006</td>
<td>0.08 ± 0.012</td>
<td>2.40 ± 0.034</td>
<td>0.02 ± 0.037</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>98 days</td>
<td>0.11 ± 0.006</td>
<td>0.01 ± 0.006</td>
<td>0.10 ± 0.006</td>
<td>0.07 ± 0.07</td>
<td>1.44 ± 0.395</td>
<td>0.019 ± 0.01</td>
<td>0.11 ± 0.019</td>
</tr>
<tr>
<td>D</td>
<td>0 Days</td>
<td>1.19 ± 0</td>
<td>2.031 ± 0</td>
<td>3.20± 0</td>
<td>2.11 ± 0</td>
<td>2.50 ± 0</td>
<td>3.60 ± 0</td>
<td>12.41 ± 0</td>
</tr>
<tr>
<td></td>
<td>50 days</td>
<td>0.14 ± 0.021</td>
<td>0.11 ± 0.006</td>
<td>0.13 ± 0.05</td>
<td>0.06 ± 0.006</td>
<td>2.03 ± 1.363</td>
<td>0.06 ± 0.082</td>
<td>0.14 ± 0.022</td>
</tr>
<tr>
<td></td>
<td>98 days</td>
<td>0.12 ± 0.00</td>
<td>0.04 ± 0.035</td>
<td>0.10 ± 0.035</td>
<td>0.06 ± 0.01</td>
<td>1.28 ± 0.956</td>
<td>0.01 ± 0.009</td>
<td>0.12 ± 0.002</td>
</tr>
</tbody>
</table>

Fig. 2—Change in acidity (mg/l as CaCO$_3$) of industrial wastewater in the bioreactors with time

Table 2—Change in metals concentration (mg/l) of industrial wastewater in the bioreactors with time
Metals

Due to low pH industrial wastewater is loaded with dissolved metals. This polluted water is toxic when they are present in high concentration. Table 2 shows reduction in the metals concentration after treatment in all the four sets of bioreactors A, B, C and D respectively. Lead concentration reduced upto 89.5 %, 91 %, 90 % and 89.7 % in A, B, C and D bioreactors respectively. Zinc concentration reduced upto 97.8 % in A, 96.4 % in B, 99.3 % in C and 97.8 % in D respectively. Likewise the concentration of copper dropped to 97.0 % in A, 96.3 % in B, 96.7 % in C and 96.8 % in D respectively. Good results were observed in cobalt also; reduction was upto 96.5 % in A, 97 % in B, 92.5 % in C and 97.0 % in D respectively. Reduction in manganese concentration was 55.6 % in A, 39.8 % in B, 44.4 % in C and 48.4 % in D respectively. Similarly nickel concentration reduced upto 99.3 % in A, 98.7 % in B, 99.32 % in C and 99.33 % in D respectively. Iron concentration reduced in bioreactors upto 99.87 % in A, 99.83 % in B, 99.82 % in C and 97.8 % in D respectively. In order to have high reducing activity of the SRB so as to have the high metal removal capacity, they require a strict anaerobic environment with pH in the range between 5 to 8.23. The neutral pH enhanced activity of SRB, the production of sulphide, and the removal of metals as metal sulphide precipitation. The results obtained are in conformity to the reportings by Smul et al (2000)24, Bernoth et al, (2000),25 Whiteley and Lee (2006)19 while working on biotechnological studies for remediation and pollution control in the metal industry.

Although cow manure has been reported to be the most efficient organic carbon source to culture and sustain SRB18 but other manures and cellulosic wastes used for treating wastewater presented equally good results. The substrate regime after being moisturized with whey, was covered with a layer of sand and stones to improve growth conditions of SRB, and then covered with glass lid to provide anaerobic conditions at room temperature. Whey addition had a positive effect on sulphate removal and it is the most common way of assessing SRB activity.26,27 Whey provides an additional electron donor source to stimulate sulphate reducing bacterial activity while treating wastewater. A variety of chemical and biological processes are likely to take place and influence water chemistry when industrial effluents are added to inoculums (substrate moisturized with whey for growth and multiplication of SRBs). Black precipitate formation at the interface between the sand and crushed stone layer indicated that growth conditions for SRB were indeed more favorable here than free water phase. The use of sand layer in the bioreactors has a vital role to play in culturing SRB on laboratory scale for treating acidic wastewater.

While considering all the microbial reactions, it became evident that combination of hydrogen sulphide produced by SRBs with Fe$^{2+}$ generates iron sulphide conditions necessary for the stable metal sulphide deposition. Each metal in solution contributes a specific metal acidity to the acidic effluent; additionally, specific metal precipitate at specific pH levels. For example hydroxides of Fe$^{3+}$ precipitate at about pH 3 and of Al$^{3+}$ at pH 3.7 to 4.5. Divalent metal ions precipitate at alkaline range, Ni$^{2+}$ at pH 8, Fe$^{2+}$ at pH 7 to 9, and Zn$^{2+}$ at more than pH 9.28. The removal system showed an excellent sulphate removal performance. The results obtained in this study is in conformity with the results reported by Kuyucak, (2000)13, Christensen, (1996)29, Tsukamoto and Miller, (2004).17

Competing factors (surface area and pore size) needs to be taken care to check the treatment efficiency as well as longevity17. Overloading of the organic substrates should be avoided because high surface area to water volume ratio will probably be beneficial. Most of the bacterial activity took place in the crushed stone layer than in free water phase, thus it is recommended to design accordingly.30.

Conclusion

A preliminary economic viability study showed that there is no operational cost for this bioremediation process of wastewater when compared to chemical treatment processes. This research work was designed to examine the feasibility of bioreactors with organic substrates containing manures, and various cellulosic components for remediation and pollution control of industrial wastewater on laboratory scale. The broad goals were to assess the performance of the bioreactors for different substrate compositions. The performance of the system was evaluated in the laboratory scale study, resulting in the treated effluents with pollutants within the prescribed limits setup by ISI and CPCB and in some cases better than prescribed standards after the complete treatment except electric conductivity.

Bioremediation of industrial wastewater through bioreactors appears to be promising treatment technology. It is apparent that the technique is economically viable and the end product is disposable.
Bioremediation technology dealt here just provides proper conditions for the substrate which otherwise is a decomposable waste (carbon source) to generate microbes and alkalinity for the treatment of industrial wastewater. Negative effects of pollutants on the growth and activity of the microbes was not observed. The regular monitoring of industrial wastewater before and after treatment in bioreactors revealed efficient removal of heavy metals, sulphates and acidity, thus have a capacity to purify industrial wastewater loaded with acidity and metals.

References