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Kinetics of biodegradation of sewage due to addition of Chlorides

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ABSTRACT:- Presence of salinity 9 to 20 g/L of chlorides can cause osmotic stress or inhibit the reaction pathways in the organic degradation process. It results in a significant decrease in biological treatment efficiency or biodegradation kinetics. Research is carried out using glucose–glutamic acid and domestic wastewater to evaluate the amendment of chlorides on biodegradation of sewage at 20°C. The findings confirm the hypothesis of biological oxidation rate "k" has higher value under presence of up to 6 g/L of chloride concentrations, compared to that of fresh water medium. It was also noticed that improvement of "K" value was more pronounced during the first 3 days of BOD test, a fact that needs further detailing study. These values are of significance for co-treatment of sewage and industrial wastewater containing high salt concentrations.

Keywords: *osmotic stress; BOD; Reaction kinetics; up to 20 g/L of chlorides*;

I. INTRODUCTION

The urbanization, industrialization, and modernization of cities have resulted in faster growth rate across the world. As a result, adequate infrastructure is not available. There are 17 coastal megacities covering about 25% of the world's population. With intensifying population, the water demand has increased significantly resulting in the generation of an enormous quantity of domestic waste (Shivani S. et al., 2012).Those cities commonly have industries for seafood processing, vegetable canning, pickling, tanning, and chemical manufacturing. The effluent from these industries contains high salinity, which may be comparable to that of seawater (Dan N. P, 2001). The existence of a shoreline in coastal cities is not advantageous for the disposal of such wastewater. Presence of salinity over 20 g/L can cause osmotic stress or inhibit the reaction pathways in the organic degradation process thus these wastewaters are often difficult to treat with conventional treatment processes such as activated sludge, trickling filter and anaerobic processes (Dan N. P, 2001).This results in a significant decrease in biological treatment efficiency or biodegradation kinetics. In addition, high salt content induces cell lysis, which causes increased effluent solids (Kargi and Dincer, 1996).

The effect of inorganic salts on microbiological growth has been studied chiefly for the formulation of suitable growth media. Addition of salts, in most cases NaCl, was found to increase the respiration rate of microorganisms up to a specific salt concentration; thereafter a decrease was observed (Wodzinski and Frazier, 1960). Kincannon & Gaudy (1966) reported that lysis of bacterial cells occurs in a growth medium having sodium chloride. If the change in salt concentration was less than 10,000 mg/L the degree of lysis was negligible, but beyond it was extensive. Cellular constituents released following lysis are metabolized by the remaining microbial population in preference to the substrate present, thus yielding erratic BOD results.

In wastewater treatment field, there are contradictory reports on the influence of NaCl on the performance of biological process. Lawton and Eggert et al., (1957) reported adverse effect of high salinity or shocks of NaCl on organic removal efficiency and sludge settlability. Kincannon D. F. and Gaudy (1968) studied an activated sludge plant and reported the production of biological solids as maximum at a salt concentration of approximately 8,000-10,000 mg/L.

Dincer and Kargi (2000) reported that high salt concentrations (> 1%) caused disintegration of cells because of the loss of cellular water (plasmolysis) or recession of the cytoplasm, which is induced by an osmotic difference across the cell wall and caused outward flow of intracellular water resulting in the loss of microbial activity and cell dehydration. As a result, low removal performance of chemical, biological oxygen demands, and increase in the effluent suspended solids especially at high salt concentrations (> 2 %) occurred. Mills and Wheatland (1962) reported that constant application of NaCl to biological treatment system did not upset the organic removal efficiency and rather resulted in good flocculation of the biomass.

In addition, in a study on municipal wastewater Gotaas (1949), data indicate that presence of 6,000 mg/L of chlorides in wastewater showed the rate of biological oxidation "k' was 25 percent larger than in the fresh water, though the presence of 9 g/L of chloride concentrations reduced it to a lower value than fresh water medium. This led to the hypothesis that a low salinity may stimulate microbial activity and result in increased BOD values.

The aim of the present study was to determine BOD exertion of glucose–glutamic acid and domestic wastewater under chloride concentrations of 0 to 20 g/L at 20°C under controlled conditions, followed by Rami Reddy and Gupta (2014). The aim is to explore a possible co-treatment of domestic sewage with industrial wastewater containing high levels of salt.

Materials and methods

Grab samples of domestic wastewater were collected from the wastewater treatment facility of MNIT Jaipur, India. A glucose–glutamic acid (GGA) solution of 150 mg/L each was prepared and 6 mL of it was mixed with domestic wastewater in a controlled manner for making test samples. Samples having different chloride additions of up to 20 g/L (zero chloride sample means no NaCl added to the GGA-sewage sample) were prepared using analytical grade NaCl as a source of salt in the dilution water. The biochemical oxygen demand (BOD) tests were carried out by as per standard methods (APHA et al., 2010).Analytical grade chemicals were used during experiments to study the BOD exertion pattern under various salinities. Settled biomass from secondary settling tank of STP (Sewage Treatment Plant) Delawas, Jaipur (based on conventional activated sludge process) was used as “seed” to provide a heterogeneous population of microorganisms. All experiments were conducted at a temperature of 20°C ±2°C.

Theoretical calculations of BOD

The rate of BOD exertion is based on the assumption that the amount of organic material remaining at a time “t’ is governed by first order function. According to the first-order, equation of chemical kinetics (Sawyer et al., 2010) mathematically expressed as:

$$-dC/dt=kC \quad (1)$$

The BOD curve can be described by a first-order kinetics equation (Metcalf and Eddy, Inc. 2003):

$$dL_0 /dt = -k L_0 \quad (2)$$

Where L_0 replaces C

Integrating between the limits of Y and $L_{0,}$ and t = 0 and t= t yields as:

$$Y=L_0 (1-10^{-(kt/2.303)}) \quad (3)$$

Where:

y = Amount of oxygen consumed (or BOD) at time t

t = Time elapsed since the start of the assay

L_0 = Total amount of oxygen consumed in the reaction (or ultimate BOD)

k = Reaction constant

Ultimate BOD calculations

The samples for detailed studies were prepared by mixing a known volume of GGA solution with measured quantity of domestic sewage obtained from the sewage treatment plant of MNIT campus. The COD of sewage sample was measured by close reflux method as described in APHA (2010) and was considered as its ultimate BOD. The theoretical COD of 373 mg/L as determined from the chemical formula of GGA was considered as its ultimate BOD. The ultimate BOD of the experimental sample was computed by the mass balance shown below.

The ultimate BOD of the sample =

$$\frac{(373\text{ mg/L} * 6\text{ mL}) + (\text{ultimate BOD of sample mg/L}* \text{mL of Sample taken})}{(\text{mL of GGA (6)} + \text{mL of sample taken})}$$

Results and discussion

Experiments were conducted with wastewater of different chloride concentrations (0 – 20 g/L Cl). TheBOD exertion, rate constant (k) under varied chloride concentrations wasdetermined. The major objective of these experiments was to investigate the behavior of BOD exertion under high chloride concentrations. Salt-free wastewater was considered for baseline comparison.

In the first set of experiments, chloride concentrations of 0.0-0.8 g/L were used. The BOD exertion of samples is shown in table 1. The kinetic coefficient (k) values under these salt concentrations are shown in table 2.

TABLE 1: BOD observations at low chloride concentrations of 0 to 0.8 mg/L

Days	Average BOD (mg/L)				
	0 g/L Chlorides	0.2 g/L Chlorides	0.4 g/L Chlorides	0.60 g/L Chlorides	0.80 g/L Chlorides
1	45	51	64	Not observed	Not observed
2	55	62	72	Not observed	Not observed
3	87	85	90	Not observed	Not observed
4	115	117	120	Not observed	Not observed
5	126	134	143	147	147

Table 2: BOD exertion rate (k) of the samples at low chloride concentrations of 0 to 0.8 g/L

Days	Reaction constant (k)				
	0 g/L of Cl	0.20 g/L of Cl	0.40 g/L of Cl	0.60 g/L of Cl	0.80 g/L of Cl
1	0.17	0.19	0.24	Not observed	Not observed
2	0.11	0.12	0.14	Not observed	Not observed
3	0.12	0.11	0.12	Not observed	Not observed
4	0.12	0.13	0.13	Not observed	Not observed
5	0.11	0.12	0.13	0.15	0.15

The observations indicatethat assalinity increased, the BOD exertion rateincreasedsignificantly for chloride concentrations up to 0.80 g/L,at which it stabilized to a value of 0.15 per day asshown in table 2. This shows a significant increase in biological treatment efficiency or biodegradation kinetics due to stimulation by chlorides. These data add to the growing body of evidence for the presence of up to 0.60 g/L of chloride concentrations not upsetting the biological system. The sequential biodegradation removal can occur, when low concentrations of NaCl are present in wastewater containing carbonaceous organic and nitrogen matter (Kargi and Dincer, 1999). Low chlorides appeared to promote adaption to the change in chlorides and produce a more flocculent sludge (Ludzack and Noran, 1965).Rao and Gaudy (1966) have presented data which indicate that for heterogeneous microbial populations, sludge yield can vary for the same carbon source. It seems abundantly apparent from these results that the inorganic constituents of the carriage water can have pronounced effects on cell yield**.** It can be concluded that in spite of the detrimental effect of salt on microbial activity, moderate acclimation of activated sludge to high salinity is possible. Acclimation implies the exposure of non-salt-adapted microorganisms to increasing salt concentrations in order to permit the obtention of satisfactory effluent treatment performance at a given salt concentrations.

In the second set of experiments high concentrations of 0, 5, 10, 15, and20 g/L of chloride were selected, the BOD exertion values of which have been shown in table 3.The kinetic coefficient (k) values for these samples are shown in table 4. The observations indicate that as the salinity is increased, the BOD exertion rate decreases for samples having 10g/L and above of chlorides, but the BOD exertion rate improved marginally at 5 g/L of chlorides during test period. Thus, it was decided to explore the range of 5-10 g/L more closely as the stimulation was turning in to inhibition in this range. High salinity has been reported to cause osmotic stress, because of the severe osmotic shock caused in the cells grown in high salt-containing medium rather than fresh water medium. This results in a significant decrease in biological treatment efficiency or biodegradation kinetics. In addition, high salt content induces cell lysis, which causes increased effluent solids. Thus, conventional microbiological treatment processes do not efficiently function at high salt concentrations (Oren A et al, 1992; Woolard C. R, and Irvine R. L, 1995; Dan N. P, 2001).

Table 3:BOD exertion at high chloride concentrations of 0-20 g/L

Days	Average BOD (mg/L)				
	0 g/L Chlorides	5 g/L Chlorides	10 g/L Chlorides	15 g/L Chlorides	20 g/L Chlorides
1	52	60	30	Not observed	Not observed
2	85	93	71	Not observed	Not observed
3	142	115	129	Not observed	Not observed
4	167	186	137	Not observed	Not observed
5	194	200	180	131	104

TABLE 4: BOD exertion rate (k) of the samples at high chloride concentrations of 0 to 20 g/L

Days	Reaction constant (k)				
	0 g/L of Cl	5 g/L of Cl	10 g/L of Cl	15 g/L of Cl	20 g/L of Cl
1	0.16	0.19	0.09	Not observed	Not observed
2	0.14	0.16	0.11	Not observed	Not observed
3	0.18	0.13	0.15	Not observed	Not observed
4	0.16	0.19	0.12	Not observed	Not observed
5	0.16	0.17	0.14	0.09	0.07

A third set of experiments was performed with chloride concentrations of 0, 6, 9, and 12 g/L, the BOD values ofwhich have been shown in table 5 and the kinetic coefficient (k) values in table 6.

TABLE 5:BOD exertion at 0, 6, 9 and 12 g/L of chloride concentrations.

Days	Average BOD (mg/L)		
	0 g/L of Chlorides	6 g/L of Chlorides	9 g/L of Chlorides
1	82	92	48
2	120	140	107
3	189	183	129

TABLE 6: BOD exertion rate (k) of the samples at varied chloride concentrations of 0 to 12 g/L

Days	Reaction constant (k)			
	0 g/L of Cl	6 g/L of Cl	9 g/L of Cl	12 g/L of Cl
1	0.27	0.3	0.15	0.08
2	0.21	0.26	0.19	0.09
3	0.26	0.25	0.16	0.1

These results indicate that there was inhibition of the 3-day BOD values in all the samples, but an interesting observation was that an improvement of k value was recorded at 6 g/L of chlorides during 2- day period after which these values fell below that of zero chloride sample somewhat similar to what was observed by Shivani et al. (2012) at 5 g/L.Gotass, H. B (1949) reported that at 3 to 6.4 g/L of chloride concentrations the rate of biological degradation was higher than that of fresh water medium.Studies on toilet flushing conducted by Tang S.L. et al. (2002) reported that, when the used toilet flushing water (saline wastewater) was discharged in to the sewerage system, the salt concentration of the mixed wastewater was observed to be between 5,000 mg/L to 6,000 mg/L. At those salt concentration authors reported that the biodegradation rate of flushing toilet wastewater was more than that of the fresh water. It was concluded by them that the higher cell yield in the presence of sodium chloride in the range of 8,000-10,000 mg/L was due to changes in predominating species due to the presence of salt.

II. CONCLUSIONS

- The study revealed that a chloride concentration of 0.8 g/L was optimum for the K value, which attained its maximum of 0.15 per day. Chloride concentrations from 0.8- 5.0 g/L showed no inhibition of biodegradation, while at 6 g/L it was higher than that of freshwater medium during the first two day period and decreased thereafter. Beyond this concentration, all the values showed significant inhibition of the biological process. Thus, it can be concluded that in the presence of low salinities (5 to 6 g/L of chlorides) the cells exhibit a higher activity than in the freshwater medium. Further increase in salinity results in restriction of osmo-regulatory processes responsible for the breakdown of organic compounds within the cells of microorganisms. As a result, the kinetics and reaction rates of decomposition reactions suffer due to high chlorides.

- It appears that mixing high salinity (5 to 6 g/L of chloride concentrations) wastewater from industries with sewage in a controlled manner can be a good option for co-treatment of the two wastes without inhibiting the biological process significantly. More research is required to explore the short time stimulation followed by inhibition at chloride concentration near 6 g/L to assess its implications in actual field, where the retention times are of the order of few hours. Further research should also be carried out to explore the effects of chlorides in the full range of salt concentrations to attempt mathematical modeling of the process.

- Further studies are required to know theoccurrence behind the improvement of “k” value during two days period.

- The present study has demonstrated an additional way in which rapid changes in high salt concentration can cause the adversely effect of a biological treatment system.
- In the presented study has conducted on low strength of wastewater (MNIT JAIPUR CAMPUS). It would have resulted in to low BOD exertion under varied chloride concentrations. The present data vary useful for sewage treatments plants monitoring high strength of wastewater in coastal areas and non-coastal areas containing seafood processing, vegetable canning, and pickling, tanning and chemical manufacturing. Nevertheless, the calculated "k" values are very low in the present study, because the ultimate BOD of the experimental sample was computed by the mass balance equation. However, high dilution factor was considered for the BOD calculations.
- Based on above discussion the presence of 5 to 6 g/L of chloride concentrations in waste water causes; the improvement of biodegradation rates, improvement of volatile solid concentrations, higher cell yield, hydrophobic interactions improve inter bacterial interactions, and bridging to help in flocculation, compare than the freshwater medium condition.

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