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Mathematical model of biodegradation process of sewage due to addition of chlorides

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ABSTRACT

Biodegradation plays a key role in the environmental risk assessment of organic matter. The need to assess biodegradability of organic matter for regulatory purpose can be ably supported by the development of a model for predicting the extent of improvement or inhibition of the process. A mathematical model was developed in order to describe the ratios of BOD_5 exertion under varying chloride concentrations compared to those at zero additional chloride values, which indicated the best fit in a polynomial third order equation. It reflected closely both the stimulation as well as inhibition effects under varied chloride concentrations. The model was duly validated by both primary data, acquired through an organized set of controlled laboratory experiments, as well as secondary data reported in the literature. The results indicate a peak value of the ratio at 0.8 g/L, while inhibition started at 6 g/L of chloride concentration. The model can be used as an aid for the design and prediction of sewage treatment process under different salt concentrations. It may help develop strategies for the co-treatment of domestic sewage and R.O. rejects as well as high salt containing industrial wastewaters.

Keywords: Biodegradation; BOD_5 exertion; Stimulation; Inhibition; Mathematical model

1. Introduction

There are 17 coastal megacities covering about 25% of the world's population and with ever-growing population, the water demand in them has increased significantly resulting in the generation of an enormous quantity of domestic waste [1]. These cities commonly have industries of seafood processing, vegetable canning, pickling, tanning, and chemical manufacturing. The seafood-processing sector contributes serious organic pollution loads and high salinity to receiving waters leading to difficulty in biological treatment processes [2]. The fish processing industry with cooking and brine filling operations normally produces high salt content of up to (65 g/L) [3]. Wastewater from fish canning has been reported to contain 10–12 g/L NaCl [4]. The dried salted fish plant wastewater contains very high salt contents of 10–27 g/L [5]. Among other such operations the ranges of salt concentrations reported are- canned sardine (30–35 g/L), canned shrimp (20–30 g/L), canned mussel/oyster (21 g/L), tuna (23 g/L) [6]. Salt is used widely in vegetable canning processing to enhance flavor, to preserve, or for conditioning, therefore, this industry in general produces wastewater containing high salt content, e.g. Asparagus (21.5–24.0 g/L),

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Green bean (19.2–2.5 g/L), Cabbage (15.6–25.2 g/L), Beets (24.0 g/L), and Peas (21.5 g/L) [7].

Oil field exploitation uses "oil-field brine" of as high as (17.6 g/L) [8]. Hypersaline wastes are produced in significant quantities in chemical industries such as oil and gas production. High salinity is also found in landfill leachates; domestic waste landfill (5.8–6.25 g/L of TDS), Hazardous waste landfill (22.6–25.9 g/L of TDS) [9]. The tanning process, which turns raw hides and skins into finished leather products, is a lengthy process that involves several steps, many of which require addition of salt [10]. The potential environmental impact of tanning is significant. The tanning process is almost wholly a wet process that generates very large amounts of wastewater containing as much as 80 g/L of NaCl [11].

The effluent from these industries contains high salinity, which may be comparable to that of seawater [5]. 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 severe 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 [5]. 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 [12].

In wastewater treatment field, there are contradictory reports on the influence of NaCl on the performance of biological process. Lawton and Eggert [13] reported the adverse effect of high salinity or shocks of NaCl on organic removal efficiency and sludge settlability, Kincannon and Gaudy [14] studied an activated sludge plant and reported that the production of biological solids was maximum at a salt concentration of approximately 8,000–10,000 mg/L. In another study on municipal wastewater Seymour [15] found that an increase in salinity resulted in a corresponding decrease in BOD values. Using municipal sewage, degradation rate decreased as the salinity level increased, yet only the particulate fraction seemed to be more affected. Degradation of the soluble portion was not affected as adversely by the salt content. Davis et al. [16] reported that dilution of sewage seeded saline organic standards with standard dilution water resulted in BOD values higher than those of corresponding non-saline organic standards due to increase in bacterial populations and increased organic removal (BOD values) in the presence of low levels of salt. Thus, both improvement as well as decrease in the rate of biological process has been reported though the major stress has been on modeling the inhibition aspects of high salt concentrations.

Nitisoravut and Klomjek [17] developed a mathematical model to describe the system behavior and performance of a constructed wetland under salt affected conditions. They observed that the kinetic reaction rate was lower under high salt conditions and salts were detrimental to the system by causing plasmolysis or loss of cell activities as also observed by Glenn [18]. Another mathematical model developed by Kargi and Dincer [19] describing inhibition due to salts of the performance of RBC showed significant adverse effects on biological process at salt contents higher than 3% NaCl. Kargi and Dincer [20] further reported that high salt concentrations (>1%) caused disintegration of cells because of the loss of cellular water (plasmolysis) or recession of the cytoplasm, which was 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 increases of the effluent suspended solids especially at high salt concentrations (>2%) occurred. In a recent study by Choi et al. [21], the controlled addition of TDS to the wastewater samples was shown to result in varying the specific oxygen utilization rates in their bioreactor from 84.2–31.0 (56.2 ± 11.6) as compared to the value of 63.2 ± 4.9 mg O_2/g MLVSS h obtained for the sample without any additional salt. Thus, both stimulation at low additional concentration and inhibition at high concentrations have been discussed in the literature but no reports could be traced that fit both the effects into a single mathematical expression, which can be used for the design of reactors under varying salt values.

The aim of the present study was to determine BOD exertion of controlled samples of glucose–glutamic acid (GGA) and domestic wastewater for a large chloride concentration range of 0–20 g/L at 20˚C under laboratory conditions in order to describe the effect, both stimulation as well as inhibition, by a single mathematical equation. The model was further validated by fitting against secondary data reported in the literature. Such a model can help arrive at optimal conditions for application of reverse osmosis rejects for flushing in the sewerage system as well as for the co-treatment of saline industrial wastewater with domestic sewage in a controlled manner.

2. Materials and methods

Grab samples of domestic wastewater were collected from the wastewater treatment facility of MNIT Jaipur, India. A 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 0–20 g/L (zero chloride sample means no external 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 [22]. 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 ± 2˚C. For samples having 0, 10, 12, 14, 16, 18 and 20 g/L of additional chlorides concentrations BOD_5 exertion was monitored.

For developing the mathematical model, the experiments were conducted on four sets of samples. The detailed results of the first three sets covering the additional chloride ranges of 0–20 g/L have been reported elsewhere [23–25]. These were superimposed over the results of the above-mentioned experiment in terms of ratios of BOD_5 exertion under a specific chloride concentration to those at zero chloride values to develop best-fit equations. Trial version STATISTICA 2014 software was used for statistical analysis of the data.

3. 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 [26] mathematically expressed as:

$$-\mathrm{d}c/\mathrm{d}t = kC \quad (1)$$

The BOD curve can be described by a first-order kinetics equation [27]:

$$\mathrm{d}L_0/\mathrm{d}t = -kL_0 \quad (2)$$

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.

4. 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 [22] 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.

$$\text{The ultimate BOD of the sample} = \frac{(373\ \text{mg/L} \times 6\ \text{mL}) \pm (\text{ultimate BOD of sample mg/L} \times \text{mL of sample taken})}{\text{mL of GGA (6)} + \text{mL of sample taken}} \quad (4)$$

5. Results and discussion

Laboratory experiments were conducted in three phases for studying the effect of chloride concentration ranges of 0–0.8, 5–20, and 5–8 g/L, on BOD exertions for each day of the 5 d period of incubation of controlled samples of GGA and domestic sewage. The detailed results of these experiments are available elsewhere [23–25]. It was found that while the concentrations up to 0.8 g/L produced a significant improvement in the BOD_5 exertions, concentrations higher than 6 g/L produced inhibition of the biological process. Since these experiments were conducted at three different times by mixing GGA and domestic sewage from a STP situated in the institute, to account for any variability in the samples, these results were converted in to dimensionless terms of ratios of BOD_5 values at a specific chloride concentration to the BOD_5 values for the same samples at no external chloride addition. A summary of derived values from the aforementioned paper for 5 d BOD values are shown in Table 1.

Fresh experiments were conducted with wastewater of different chloride concentrations (10–20 g/L) in order to have a complete coverage of chloride values in the range of inhibition of the biological process for developing a single mathematical expression. Three samples were kept at every chloride concentration to avoid any experimental error. The BOD_5 exertion, rate constant (k), standard deviation, and percentage of variance under varied chloride concentrations were determined. Salt-free wastewater was considered for baseline comparison. The BOD exertion of samples and different derived parameters (k values and ratios of BOD) thereof shown in Table 2.

The observations indicate that as salinity increased, the BOD exertion rate decreased significantly for chloride concentrations of 10–20 g/L, with the k value reaching a minimum of 0.05 per day as shown in Table 2. This shows a significant decrease in biological treatment efficiency or biodegradation kinetics due to high salinity. 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 [5,28,29].

Data from Tables 1 and 2 were clubbed together in order to develop a single mathematical expression for the BOD ratios at different chloride concentrations to those at zero chloride values in the complete range of stimulation as well as inhibition of biological process due to chlorides as shown in Table 3. These are graphically represented in Fig. 1 along with the best-fit polynomial curve and the regression coefficient.

Table 1
Five-day BOD exertion ratios at different chloride concentrations derived from Rami Reddy & Gupta [23–25]

Chlorides (X) (g/L)	Mean values of BOD_5 of sample with X (g/L) chlorides	Standard deviation (SD)	Mean values of BOD_5 of same sample with zero chloride concentration	Standard deviation (SD)	Ratio (reaction constant (k) at X (g/L) chlorides/reaction constant (k) at zero chloride)
0.2	134	2.31	126	1.53	1.090
0.4	143	1.53	126	1.53	1.181
0.6	147	2.52	126	1.53	1.363
0.8	147	2.65	126	1.53	1.363
5	200	2.52	194	1.69	1.062
10	180	2.0	194	1.69	0.875
15	131	1.73	194	1.69	0.562
20	104	1.53	194	1.69	0.437
5	211	2.08	197	1.80	1.058
6	219	1.15	197	1.80	1.176
7	184	1.53	197	1.80	0.882
8	170	3.51	197	1.80	0.764

Table 2
BOD_5 exertion at different chloride concentrations of 10–20 mg/L

Chlorides (X) (g/L)	Average BOD_5 in (mg/L)	Standard deviation	k values
0	189	1.62	0.16
10	172	2.73	0.13
12	147	1.58	0.11
14	120	1.58	0.09
16	102	1.58	0.07
18	91	1.59	0.06
20	87	3.15	0.05

Table 3
Derived data of BOD exertion ratios at different chloride concentrations

Chlorides (*X*) (g/L)	Ratio (BOD_5 at *X* (g/L) chlorides/BOD_5 at zero chloride)
0	1
0.2	1.063
0.4	1.134
0.6	1.166
0.8	1.166
5	1.050
6	1.111
7	0.934
8	0.862
10	0.918
12	0.777
14	0.634
15	0.675
16	0.539
18	0.481
20	0.498

The observed ratios indicate that as salinity increases the BOD_5 exertion ratios decrease for samples having 7 g/L and above of chlorides, but the BOD exertion ratios improved up to 6 g/L of chlorides showing a value of more than 1.0 as shown in Table 3. The BOD_5 exertion ratios increased significantly for chloride concentrations up to 0.80 g/L, at which it stabilized to a maximum value of 1.166, thereafter a consistent decrease was observed up to 20 g/L of chlorides as shown in Fig. 1. Thus mixing high salt containing wastewater with sewage to reach up to 7 g/L concentration is acceptable from the point of view of biodegradation kinetics. These inferences may help in developing strategy for co-disposal of wastewater from industrial and domestic origin, especially in the coastal areas having industries, which discharge high salinity effluent making it difficult to treat those [5].

Fig. 1 shows that a polynomial cubic curve fitted the data quite closely, which represented the entire range of stimulation as well as inhibition of the biological process under varying concentration of salt up to 20 g/L by a single expression given below:

$$\text{Ratio}\,(\text{BOD}_5\text{ of }X\text{ g/L chlorides}/\text{BOD}_5\text{ of 0 g/L chlorides}) = 0.8801 + 0.1402 \times x - 0.0212 \times x^2 + 0.0007 \times x^3 \quad (5)$$

This expression can help predict the change in biodegradability of sewage due to mixing of industrial waste thus prove to be a good tool for taking decisions for their co-treatment. This equation was then used for predicting the changes in biodegradation rates due to the presence of different concentrations of chloride reported in the literature by different authors and both the predicted (using this expression) as well as observed data have been summarized in Table 4.

The results indicate that the percentage variation in the predicted and observed values was between −34.73 (under 5 g/L of Cl) to +37.71 (under 13.75 g/L of Cl) though most of the vales lied within ± 15%. The variation in prediction in a range of 5–6 g/L can be

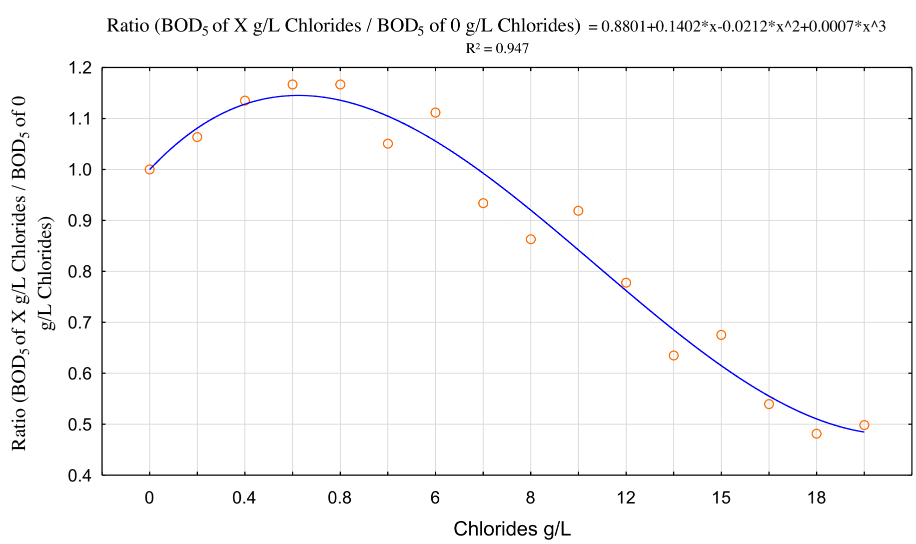

Fig. 1. Curve between BOD_5 exertion ratios and chloride concentrations.

Table 4
Model fitting on secondary data

Author	Chlorides (X) (g/L)	Observed values: BOD_5 value at X (g/L) of Cl	Observed values: BOD_5 value of 0 (g/L) Cl	Predicted values: Calculated value of BOD_5 (mg/L) using our model	Predicted values: % error ((obs − pre)/obs)
Dhage et al. [1]	5	285	337	384	−34.73
	10	255	337	291	−14.11
	15	200	337	194	3
	20	221	337	271	−22.62
Gotaas [30]	0.55	272	236	225	17.27
	1.65	240	236	250	−4.166
	3.65	250	236	270	−8
	6.4	243	236	258	−6.17
	9.2	215	236	218	−1.39
	13.75	236	236	147	37.71
	18.35	242	236	151	37.60

explained by the fact that we have ignored the salt already present in the sample, which may not be the case with that of other researchers, and it is sensitive range in which the stimulation converts to inhibition. The higher range of 18–20 g/L also showed high variation and needs further experimentation for probably the cell lysis phenomenon. Overall, the equation developed indicates a good fit with the observed values and hence can act as a good predictive tool.

6. Conclusion

A third order polynomial curve was developed using the results of controlled laboratory experiments for assessing the effect of chlorides on biodegradation rates of sewage. The equation so developed was able to explain both the stimulation (at low concentrations) as well as inhibition of the biological process due to the concentration of salt up to 20 g/L. The equation fitted well over the entire range of salt concentrations on secondary data reported in the literature. This equation can be used to predict of the biodegradation rates of high salt containing wastewater from different industries and hence carry out appropriate design of their biological treatment plants. This can further serve as a good tool for planning co-treatment of sewage and such industrial wastes, especially looking to the fact that the rate of biological oxidation rate "*k*" has higher values for additional chloride concentrations of up to 6 g/L compared to those for the fresh sewage.

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