Removal of organics and metal ion nanoparticles from synthetic wastewater by Activated Sludge Process (ASP)

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Abstract— Adsorption technique is widely used for removal of toxic organic contaminants from aqueous streams. Owing to the hazardous or otherwise undesirable characteristics of phenolic compounds in particular, their presence in wastewater from municipal and industrial discharge is one of the most important environmental issue. The discharge of poor quality effluents by the chemical-based laboratories and refineries in India is posing a serious threat to water sources and wastewater treatment installations alike. Our study was set up in the *Indo-French Unit* for Water & *Wastewater Technologies* (IFUWWT), IIT Delhi. The main objective of this study was to assess the efficiency of a laboratory-scale activated sludge treatment process in producing a final effluent conforming to regulatory standards of Central Pollution Control Board, India with regards to COD and metal ion loads. The study was conducted in three principal stages: characterization of wastewater containing nanoparticles; treatability studies of laboratory generated discards and investigations of heavy metal ions before and after treatment. The raw effluent parameters analyzed were COD, BOD, F/M ratio, Sludge Value Index, Total Solids and concentrations of Cu, Ag and Zn.

MLSS of the aeration basin was calculated to be 7180±261.3 mg/L while the F/M ratio was kept down to 0.1560±.0149; besides, an SVI of 107.24 mL/g complied with the state of bioreactor's sludge. These set of values suggested to set an extended aeration processes for the reactors. The results showed over 98% influent COD reduction and nearly 100% removal of metal ions. The sample used was operated on sludge collected from Vasant Kunj Wastewater Treatment plant. Based on the results from waste characterization and treatability studies, it was decided that the mixed liquor discharged in the activation tank should have glucose solution and laboratory discarded sample in 1:1 ratio. The reactor was operated on a glucose fed batch basis for 30 days. For metal analysis, the digested water samples were analyzed for the presence of copper, silver and zinc using Atomic Absorption Spectrophotometer. The biosorption capacities were found to be over 95% in all the cases. Such a high sludge yield is suggestive of the fact that heavy metals are in very low concentrations in the considered carboy sample. Because of these insignificant values, the amount of metal ions introduced to the system gets adsorbed almost completely, hence leaving behind no metal ion within the supernatant. Well-treated wastewater has enormous potential as a source of water for crops, households and industry.

Keywords— Nanoparticles, Activated Sludge Process, Adsorption, Bioreactor, Sludge yield, BOD_5 & COD, Metal Ion Analysis

1. INTRODUCTION

In many arid and semi-arid countries water is becoming an increasingly scarce resource and planners are forced to consider any sources of water which might be used economically and effectively to promote further development. The wastewater that is generated by the laboratories is characteristically high in both organic and inorganic content. The ability to reclaim wastewater for discharge or reuse would be a giant step toward over-all waste reduction.

The conventional methods for treatment of effluents contaminated with heavy metals involve physicochemical processes such as flocculation, precipitation, electrolysis and crystallization. However, these processes are very expensive and generate new products, merely resulting in a transfer of the metal from one medium to another, but not providing a definitive solution. The search for cheaper and definitive solutions led to the development of new technologies based on the utilization of organic substrates for removal of heavy metals by the process of sorption using bioreactors.

A bioreactor (BR) may refer to any engineered device or system that supports a biologically active environment. The aim of the study was to set up a vessel in which a chemical process can be carried out, which involves organisms or biochemically substances derived from such organisms. The sludge used was obtained from Vasant Kunj wastewater treatment plant. To keep the process aerobic, the sludge was kept on aeration throughout. This process is functioned to treat waste water using bacteria which is helped by its food.

2. CHARACTERIZATION OF CARBOY NANOPARTICLES (NPs)

In order to design onsite wastewater treatment systems, we must consider the nature of the wastewater because the effluent quality depends upon the influent characteristics. The treatment capacity and treatment efficiency of systems are calculated based upon the influent concentrations and the effluent requirements.

The source of the wastewater influences the characteristics of the waste stream. In general, we can categorize the source as residential, municipal, commercial, industrial or agricultural. The sample for the purpose of our study was a carboy whose constituents were the discarded materials of our laboratory. The components of influent-characterization would be:

a. TS (Total Solid)

Suspended Solid (SS) parameter/Non-Filterable Residue refers to the dry weight of particles trapped by the Whattman Filter Paper of 45 micron pore size while Dissolved Solid (DS) refers to the dry mass left behind on the filter paper. Their summation gives the net Total Solid content of the waste-water.

b. BOD_5

According to CPCB, the maximum permissible limit of suspended solids for irrigational land is 200mg/L while that for inland surface water is 100mg/L. CPCB guidelines state that those water bodies having BOD more than 6 mg/l are identified as polluted water bodies.

Biological oxygen demand (BOD) is a measure of the amount of oxygen that is consumed by bacteria during the decomposition of organic matter. Having a safe BOD level in wastewater is essential to producing quality effluent. If the BOD level is too high then the water could be at risk for further contamination, interfering with the treatment process and affecting the end product. By comparing the BOD of incoming sewage and the BOD of the effluent water leaving the plant, the efficiency and effectiveness of sewage treatment can be judged.

c. COD

The COD (Chemical Oxygen Demand) test represents the amount of chemically digestible organics (food). COD measures all organics that were biochemically digestible as well as all the organics that can be digested by heat and sulfuric acid.

For our purpose, COD was determined using Closed Reflux method ((APHA, 1989); (González, 1986); (Jirka & Carter, 1975)). In this case, a small volume of sample is heated with concentrated dichromate solution in presence of silver sulphate and mercuric sulphate. The reaction takes place in culture tubes with PTTE-lined screw caps at 150° *C*. Heating proceeds for usually shorter times, at higher temperatures than in the open reflux method; the COD is estimated by titrating the digested sample against ferrous ammonium sulphate solution (FAS) in the presence of Ferroin indicator.

d. Mixed Liquor Volatile Suspended Solid (MLVSS)
e. pH
f. Calcium and Magnesium content (to check for hardness)
g. Metal Analysis

3. DETERMINATION OF TRACE METAL IONS BY ATOMIC ABSORPTION SPECTROMETER

This is done after pre-concentration and subsequent concentration reduction on adsorption by sludge

Fig. 1: Culture tubes with PTTE-lined screw caps

<u>Samples Tested for presence of heavy metal ions</u>: Our aim was to characterize the carboy nanoparticle sample taking the concentration of three heavy metal ions, namely Cu, Ag and Zn, into consideration. Furthermore, we needed to check if the process of sludge-based-adsorption can prove to be an effective measure to remove these hazardous heavy metals. Hence the metal analyses were done for (a) carboy (b) sludge and supernatant for both reactors.

Sample Digestion: To ensure the removal of organic impurities from the samples and thus prevent their interference in analysis, the samples were digested with concentrated nitric acid. 10ml of nitric acid was added to 50ml of sample to be analyzed in a 250ml conical flask. The mixture was evaporated to volume of 5mL by keeping it over a heating plate chamber after which it was allowed to cool and then filtered.

Fig. 2: Heating Plate Chamber

Standard Preparation

(a) Copper: Dissolve 3.7980g of Cu $(NO_3)_2.3H_2O$ in 250ml. of deionized water. Dilute to 1 lt. in a volumetric flask with the water.
(b) Silver: Dissolve 1.5750 of silver nitrate in 200ml. of deionized water. Dilute to 1 lt. in a volumetric flask with deionized water.
(c) Zinc: Dissolve 1.2450g of zinc oxide (ZnO) in 5ml of deionized water followed by 25ml. of 5M hydrochloric acid. Dilute to 1 lt. in a volumetric flask with deionized water.

Sample Analysis: The digested water samples were analyzed for the presence of copper, silver and zinc using the ElementAS AAS4141 Atomic Absorption Spectrophotometer (by Electronics Corporation of India Ltd). The calibration plot method was used for the analysis. Air-acetylene was the flame used and hollow cathode lamp of the corresponding elements was the resonance line source, the wavelength for the determination of the elements were 217.9nm, 327.5nm and 212.6nm for copper, silver and zinc respectively. The digested samples were analyzed in duplicates with the average concentration of the metal present being displayed in mg/L by the instrument after extrapolation from the standard curve.

Fig.3: Atomic Absorption Spectrometer

4. EXPERIMENTAL SETUP

a. BIOLOGICAL REACTOR SETUP

The sludge which provided biomass was obtained from Vasant Kunj Wastewater Treatment plant. To prepare the feed/food for biomass-generation, 1 gram of D-Glucose was added to a liter of water kept on aeration for roughly an hour. This served the purpose for influent COD. 1ml each of $MgSO_4.7H_2O$, $CaCl_2$, $FeCl_3.6H_2O$ and phosphate buffer was next added to the vessel. 1 gram of glucose corresponds to a COD of 1066.67 mg/L of O_2. This solution was added by an amount equal to the supernatant decanted from each reactor. The reactors were kept on aeration overnight. Next day, the COD of the supernatant/effluent would be calculated using the closed-reflux-method. The biomass used wasn't discarded throughout the duration of the study.

b. RUNNING ADSORPTION EXPERIMENTS TO STABILIZE COD AND BOD_5

The overall goal of the activated sludge was to reduce or remove organic matter, solids, ions nutrients, and other pollutants from wastewater. More specifically, the activated sludge process involved blending settled primary effluent wastewater with a culture of microorganisms into fluid called "mixed liquor". The mixed liquor was discharged in an activation tank, in which air was introduced into the system to create an aerobic environment that kept the activated sludge properly mixed. The bacteria stabilized the substances that had a demand for BOD, while oxidizable chemicals (reducing chemicals) were responsible for consuming COD before being discharged in a clarifier where suspended solids and liquid were separated.

Oxidizable material + bacteria + nutrient + O2 → CO2 + H2O + oxidized inorganics

A number of treatment technologies are in use for the treatment of wastewater contaminated with organic substances. Among them, adsorption process is considered as a promising method for removing COD, heavy metals, colour, odour and ions. This method has aroused considerable interest during recent years for cleaning the wastewater specifically due to its cost-effectiveness.

Adsorption in Bioreactor B had been carried out in two stages. For an initial length of 20 days, only glucose-based organic feed was added to the reactor. The aim was to acclimatize the microorganisms residing in the reactor to glucose, which served as food for the microorganisms. After this initial set of 20 days, it was seen that the percentage reduction in COD didn't witness any changes. Hence, it was concluded that the bacteria had become acclimatized. Carboy nanoparticles were now introduced alongside the glucose to the bioreactor B. The ratio for carboy sample to glucose feed was kept at 1:1. This step was prompted due to small concentration of metal ions and had the ratio been kept smaller, the difference between CODs of mixed liquor and Bioreactor A would have been too small. The setup was studied for duration of one week.

5. RESULTS

a. CHARACTERIZATION DATA OF CARBOY NANOPARTICLES (NPs)

TABLE 1: TOTAL SOLID CONCENTRATION (in mg/L)

Date	16/5/2013	29/5/2013	26/6/2013	Average
DS (mg/L)	140	120	100	120
SS (mg/L)	400	460	560	473.33
TS (mg/L)	540	580	660	593.33

The BOD_5 during our study came out to be 697.9949mg/L. The high content of microorganisms and other organic matter lead to consumption of the available oxygen.

For the purpose of experiment, we had proceeded with COD monitoring instead of BOD_5 because of following reasons:

BOD_5 /COD ratio for June 3, 2013 was 0.373; the result indicated that COD readings are significantly greater than those of BOD_5. Secondly, for COD calculation, the sample needs to be kept in the digestor for only 2 hours. BOD calculation requires duration of 5 days, hence being inconvenient. By the time we have results from a 5-day test; the plant conditions would no longer be same. Hence, real time monitor and control cannot be relied upon BOD.

TABLE 2: COD VALUES OF CARBOY NANOPARTICLE SAMPLE

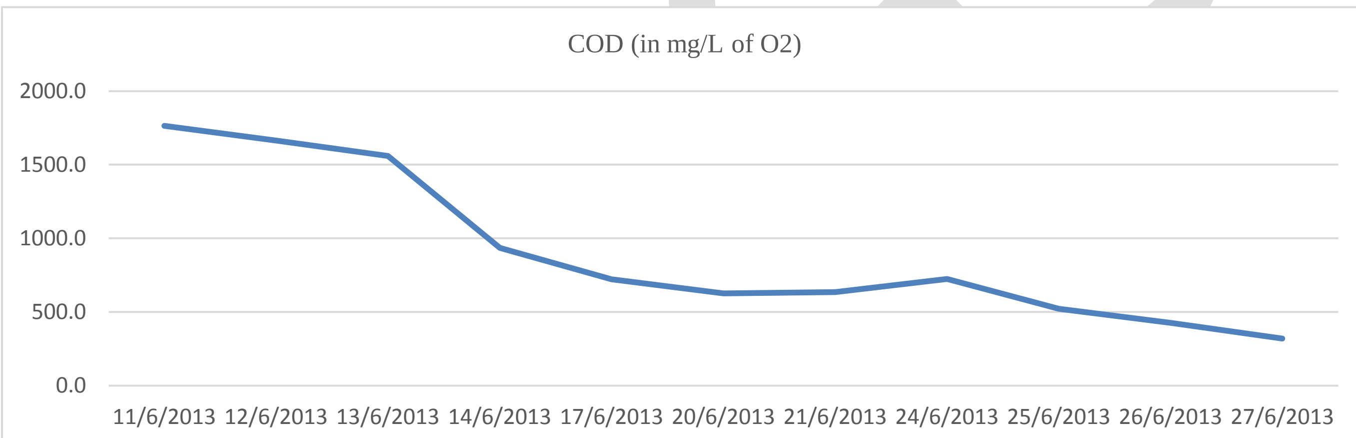
Date	Blank	1st	2nd	3rd	Average	Blank-Average	Molarity	COD
3/6/2013	1.453	1.42	1.36	1.4	1.393	0.060	0.0975	1871.3
4/6/2013	1.437	1.4	1.4	1.4	1.400	0.037	0.0978	1148.1
5/6/2013	1.437	1.42	1.41	1.4	1.410	0.027	0.0975	831.7
6/6/2013	1.447	1.42	1.44	1.43	1.430	0.017	0.0975	519.8
7/6/2013	1.467	1.46	1.45	1.45	1.453	0.013	0.0971	414.2
11/6/2013	1.473	1.42	1.42	1.41	1.417	0.057	0.0973	1763.9
12/6/2013	1.447	1.41	1.39	1.38	1.393	0.053	0.0975	1663.4
13/6/2013	1.500	1.44	1.47	1.44	1.450	0.050	0.0975	1559.5
14/6/2013	1.460	1.43	1.44	1.42	1.430	0.030	0.0975	935.7
17/6/2013	1.470	1.43	1.44	1.47	1.447	0.023	0.0967	722.1

20/6/2013	1.450	1.42	1.42	1.45	1.430	0.020	0.0977	625.0
21/6/2013	1.450	1.43	1.43	1.43	1.430	0.020	0.0990	633.7
24/6/2013	1.463	1.45	1.41	1.46	1.440	0.023	0.0971	724.9
25/6/2013	1.433	1.4	1.44	1.41	1.417	0.017	0.0978	521.9
26/6/2013	1.417	1.4	1.4	1.41	1.403	0.013	0.1000	426.7
27/6/2013	1.440	1.43	1.42	1.44	1.430	0.010	0.0996	318.7

After June 6, a certain amount of laboratory discarded waste was again feeded to the aging carboy to regenerate it. This explains the visible bump in COD readings. The constant decrement in the COD values can be attributed to decomposition of organic wastes and oxidation of chemical waste.

In accordance with the (CPCB, 2007) guidelines, the maximum permissible Chemical Oxygen Demand of Inland Surface Water could be 250mg/L and for drinking purposes, it comes down to 3 mg/L. With respect to these values, the given carboy sample can be categorized to be highly contaminated as its initial COD value is over 1500 mg/L. This result was expected as the constituents of the carboy are formed by laboratory-discards.

GRAPH 1: REDUCTION OF CHEMICAL OXYGEN DEMAND (in mg/L) OF CARBOY



COD values for the initial phase (June 3 to June 7) varied between 1871 mg/L to 414.2 mg/L.

Before examining metal-ion analysis, it is important to understand the primary role of activated sludge i.e. the reduction of chemical oxygen demand (COD) from domestic wastewater.

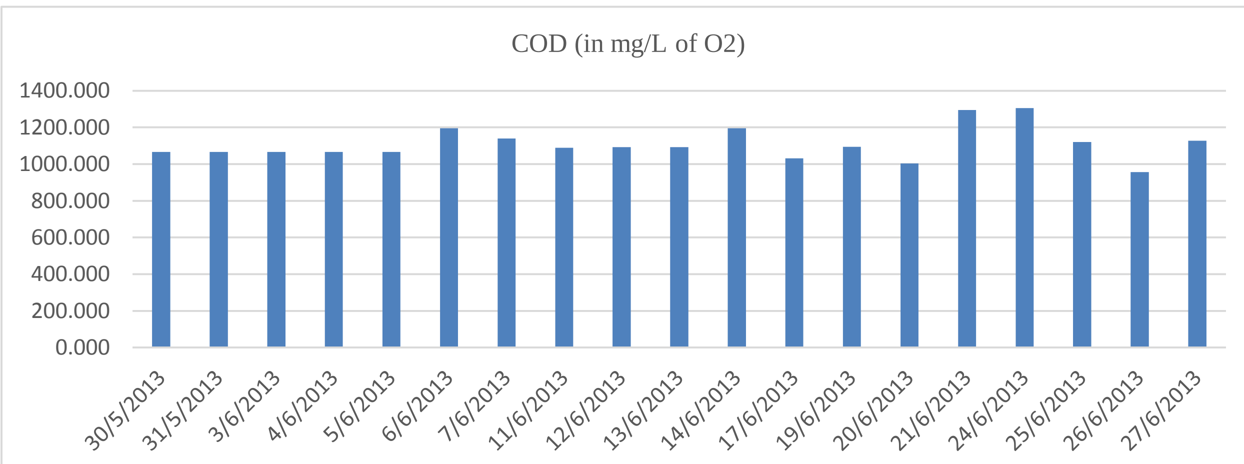
b. ATTRIBUTES OF NORMAL REACTOR (BIOREACTOR A)

TABLE 3: STRENGTH OF INFLUENT ADDED TO THE REACTORS (in mg/L)

Date	Blank	1st	2nd	3rd	Average	Blank-Average	Molarity	Influent
30/5/13	1.463						0.0969	1066.667
31/5/13	1.427						0.0990	1066.667
3/6/13	1.453						0.0975	1066.667
4/6/13	1.437						0.0978	1066.667
5/6/13	1.437						0.0975	1066.667

6/6/13	1.447	1.38	1.37	1.36	1.370	0.077	0.0975	1195.582
7/6/13	1.467	1.39	1.39	1.4	1.393	0.073	0.0971	1139.159
11/6/13	1.473	1.38	1.42	1.41	1.403	0.070	0.0973	1089.494
12/6/13	1.447	1.38	1.37	1.38	1.377	0.070	0.0975	1091.618
13/6/13	1.500	1.37	1.46	1.46	1.430	0.070	0.0975	1091.618
14/6/13	1.460	1.37	1.39	1.39	1.383	0.077	0.0975	1195.582
17/6/13	1.470	1.4	1.4	1.41	1.403	0.067	0.0967	1031.593
19/6/13	1.447	1.39	1.37	1.37	1.377	0.070	0.0977	1093.750
20/6/13	1.450	1.34	1.39	1.43	1.387	0.063	0.0990	1003.300
21/6/13	1.450	1.36	1.37	1.37	1.367	0.083	0.0971	1294.498
24/6/13	1.463	1.38	1.36	1.4	1.380	0.083	0.0978	1304.631
25/6/13	1.433	1.37	1.36	1.36	1.363	0.070	0.1000	1120.000
26/6/13	1.417	1.34	1.37	1.36	1.357	0.060	0.0996	956.175
27/6/13	1.440	1.35	1.38	1.38	1.370	0.070	0.1006	1126.761

GRAPH 2: STRENGTH OF INFLUENT ADDED TO THE REACTORS (in mg/L)



COD removal and sludge yield

Simply due to the high number of microorganism in bioreactors, the pollutants uptake rate can be increased. This leads to better degradation in a given time span; also the required reactor volumes are smaller. In comparison to the conventional activated sludge process (ASP (Trussel, 2006)) which typically achieves 95 percent removal, average COD removal by Reactor-A over a course of 30 days came out to be 98.186%. Such a high sludge yield could be attributed to high MLSS concentration.

F/M ratio and dissolved oxygen (DO) concentration has a big influence to on microorganism growth in activated sludge process. A rapid growth causes bulking sludge which is indicated by a High SVI value.

Calculating F/M ratio

The term Food to Microorganism Ratio i.e. F/M ratio, as per (DEP), is actually a measurement of the amount of incoming food (kg of Influent CBOD) divided by the kg of microorganisms in your system. In our calculations, the volume of activated sludge in our clarifiers has been taken as the total amount of microorganisms exposed to the incoming food.

Volume of supernatant removed everyday = 500ml/L

⇒ Volume of microbial-sludge exposed = 500ml/L

Volume of feed added to each reactor = 500ml (net volume of feed prepared = 1L)

TABLE 4: TSS VALUES FOR REACTOR A

DATE	Suspended Solids in mg/L	Dissolved Solids in mg/L	Microorganism (M) available in mg/L
May 28, 2013	6685	680	7365
May 29, 2013	6285	710	6995
Average	6485	695	7180

Aeration system volume = 500ml ⇒ M = (7180 mg/L)*(.5 L) = 3590 mg
F = Flow * Influent COD = (500 mL/day)*(1066.67 mg/L) = 533.335 mg/day
⇒ F/M = 533.335/3590 = 0.148

Normally, we prefer a low F/M ratio due to the following advantages: (i) High degree of elimination of BOD5 and COD (ii) Good nitrification/de-nitrification (iii) Good settle-ability to sustain shock and toxic loading.

Extended aeration processes generally operate within the following ranges:

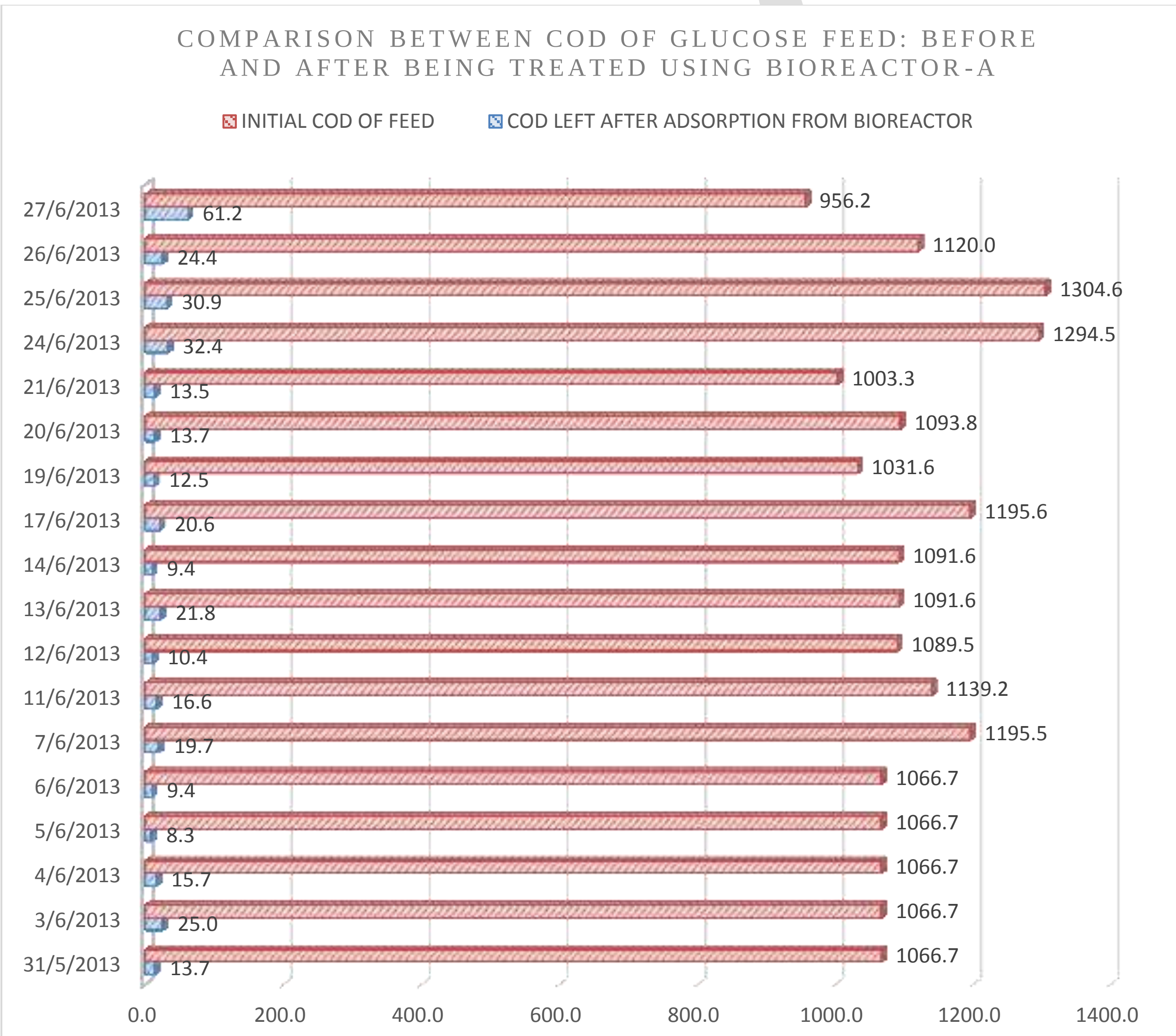
- Detention time in aeration basin = 12-24 hrs.
- MLSS in aeration basin = 2000-5000 mg/L
- System F: M Ratio = 0.05 – 0.15: 1
  Hence the setup is within the permissible limits.

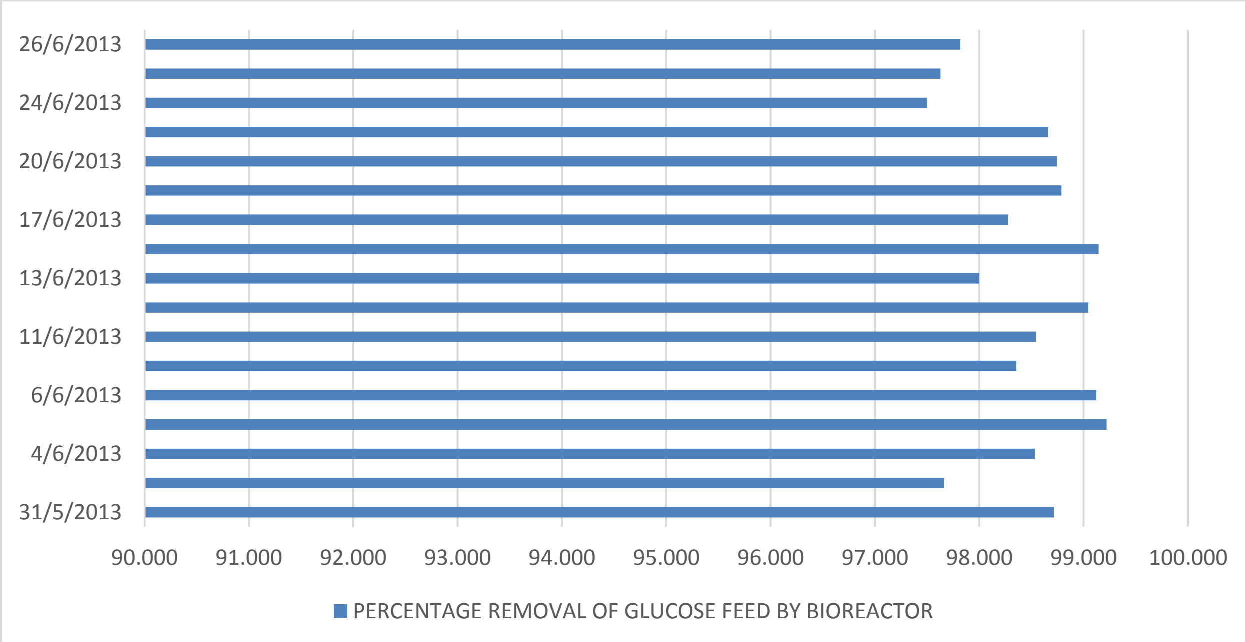
TABLE 5: PERCENTAGE COD REMOVING CAPACITY OF REACTOR-A

Date	Blank	1st	2nd	3rd	Average	Blank-Average	Molarity	COD left	% Removal
5/29/2013	1.470	1.38	1.37	1.38	1.377	0.093	0.0975	29.110	
5/30/2013	1.463	1.40	1.35	1.40	1.383	0.080	0.0969	24.806	
5/31/2013	1.427	1.37	1.38	1.40	1.383	0.043	0.0990	13.729	98.713
6/3/2013	1.453	1.39	1.34	1.39	1.373	0.080	0.0975	24.951	97.661
6/4/2013	1.437	1.39	1.37	1.40	1.387	0.050	0.0978	15.656	98.532
6/5/2013	1.437	1.41	1.41	1.41	1.410	0.027	0.0975	8.317	99.220
6/6/2013	1.447	1.42	1.43	1.40	1.417	0.030	0.0975	9.357	99.123
6/7/2013	1.467	1.41	1.39	1.41	1.403	0.063	0.0971	19.676	98.354
6/11/2013	1.473	1.40	1.43	1.43	1.420	0.053	0.0973	16.602	98.543
6/12/2013	1.447	1.42	1.41	1.41	1.413	0.033	0.0975	10.396	99.046
6/13/2013	1.500	1.45	1.39	1.45	1.430	0.070	0.0975	21.832	98.000
6/14/2013	1.460	1.43	1.44	1.42	1.430	0.030	0.0975	9.357	99.143
6/17/2013	1.470	1.39	1.42	1.40	1.403	0.067	0.0967	20.632	98.274
6/19/2013	1.447	1.41	1.40	1.41	1.407	0.040	0.0977	12.500	98.788

6/20/2013	1.450	1.42	1.39	1.41	1.407	0.043	0.0990	13.729	98.745
6/21/2013	1.450	1.38	1.42	1.42	1.407	0.043	0.0971	13.463	98.658
6/24/2013	1.463	1.36	1.34	1.38	1.360	0.103	0.0978	32.355	97.501
6/25/2013	1.433	1.33	1.32	1.36	1.337	0.097	0.1000	30.933	97.629
6/26/2013	1.417	1.34	1.34	1.34	1.340	0.077	0.0996	24.436	97.818
6/27/2013	1.440	1.26	1.24	1.25	1.250	0.190	0.1006	61.167	93.603

The abnormal reductions in removing capacity towards the end can a result of overburdening of the sludge biomass, indicating the need to replace the sludge.





GRAPH 3 & 4: BEHAVIOUR OF GLUCOSE FEED ON BEING TREATED BY BIOREACTOR-A

Calculating Sludge Volume Index (SVI) ratio

Sludge Volume Index as per (SacrementoState) is an extremely useful parameter to measure in a wastewater treatment process. In simple terms, SVI is the result of a mathematical calculation. It takes into account the 30-minute settle-ability test result and the activated sludge mixed liquor suspended solids (MLSS) test result to come up with a number (or index) that describes the ability of the sludge to settle and compact. Value of Sludge Volume Index can then be calculated from the formula SVI = (SV/MLSS)*1000

TABLE 6: SLUDGE VOLUME INDEX CALCULATION

SV (Volume of settled solids in one-liter graduated transparent measuring cylinder after 30 minutes settling period) in mL/L	770 mL/L
MLSS (Mixed liquor Suspended Solids) in ppm	7180 mg/L
SVI (Sludge Volume Index) in mL/g	107.24 mL/g

According to *(IDEM, 1986) tpo (treatment plant operator)* guidelines, cases wherein SVI is in the range of 100 to 200 mL/g, activated sludge plants seem to produce a clear, good-quality effluent which supports the observation of 98.186% removal of COD feeded. Such sludge typically settles more slowly and traps more particulate matter as it forms a uniform blanket before settling. It also supports the growth of microbial culture.

Fig. 4: Reactor when kept on aeration

Fig. 5: Reactor with settled sludge

c. ATTRIBUTES OF MIXED LIQUOR REACTOR (BIOREACTOR B) & EFFECT OF NANOPARTICLE WASTEWATER ON COD

TABLE 7: CHEMICAL OXYGEN DEMAND OF EFFLUENT FROM BIOREACTOR B

Date	Blank	1st	2nd	3rd	Average	Blank-Average	Molarity	COD (in mg/L of O_2)
29/5/2013	1.470	1.38	1.37	1.38	1.377	0.093	0.0975	29.110
30/5/2013	1.463	1.39	1.39	1.38	1.387	0.077	0.0969	23.773
31/5/2013	1.427	1.39	1.37	1.37	1.377	0.050	0.0990	15.842
3/6/2013	1.453	1.42	1.39	1.45	1.420	0.033	0.0975	10.396
4/6/2013	1.437	1.39	1.37	1.40	1.387	0.050	0.0978	15.656
5/6/2013	1.437	1.40	1.39	1.40	1.397	0.040	0.0975	12.476
6/6/2013	1.447	1.31	1.28	1.40	1.330	0.117	0.0975	36.387
7/6/2013	1.467	1.41	1.39	1.39	1.397	0.070	0.0971	21.748
11/6/2013	1.473	1.43	1.44	1.45	1.440	0.033	0.0973	10.376
12/6/2013	1.447	1.40	1.39	1.41	1.400	0.047	0.0975	14.555
13/6/2013	1.500	1.47	1.47	1.47	1.470	0.030	0.0975	9.357
14/6/2013	1.460	1.42	1.43	1.45	1.433	0.027	0.0975	8.317
17/6/2013	1.470	1.41	1.45	1.43	1.430	0.040	0.0967	12.379
19/6/2013	1.447	1.40	1.40	1.40	1.400	0.047	0.0977	14.583
20/6/2013	1.450	1.41	1.41	1.35	1.390	0.060	0.0990	19.010
21/6/2013	1.450	1.42	1.44	1.36	1.407	0.043	0.0971	13.463
24/6/2013	1.463	1.45	1.41	1.43	1.430	0.033	0.0978	10.437
25/6/2013	1.433	1.39	1.39	1.38	1.387	0.047	0.1000	14.933
26/6/2013	1.417	1.38	1.40	1.39	1.390	0.027	0.0996	8.499
27/6/2013	1.440	1.37	1.42	1.39	1.393	0.047	0.1006	15.023

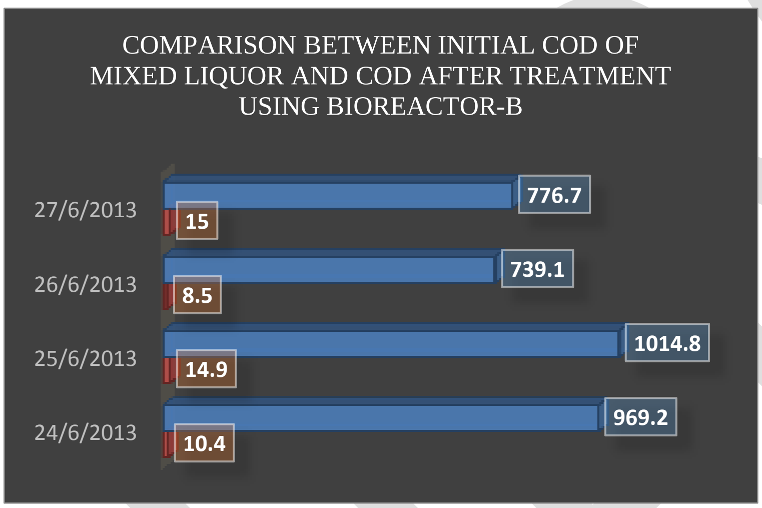
From June 21 onwards, the mixed liquor feeded to Bioreactor B consisted of 250 mL each of Glucose and Carboy sample, while Bioreactor A was continued to be fed with 500 mL of glucose feed only. The COD of mixed liquor supplied to the bioreactor B for June 25 is calculated by taking the mean of (a) carboy's COD for June 24 and (b) COD of glucose feed prepared on June 25. COD of mixed liquor for other days was similarly calculated.

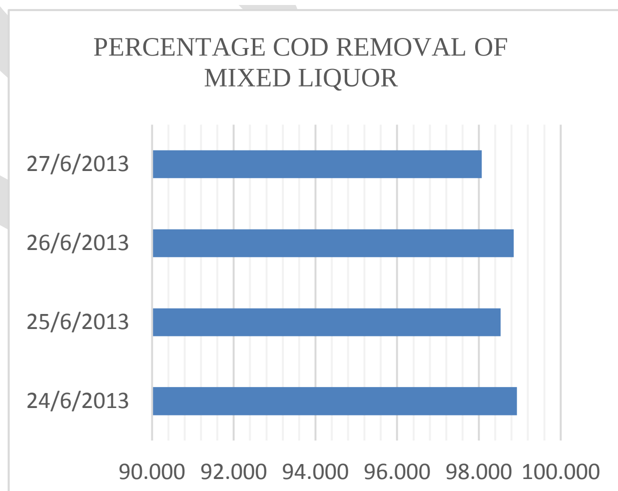
TABLE 6: COD OF INFLUENT AND EFFLUENT ASSUMING BIOREACTOR AS TREATMENT UNIT AND MIXED LIQUOR AS DISPOSAL WHICH REQUIRES TREATMENT

DATE	COD of carboy	COD of glucose	COD of mixed liquor Added to the Bioreactor		COD after treatment	Percentage Removal Efficiency
21/6/2013	633.7					
24/6/2013	724.9	1304.6	633.7/2 + 1304.6/2 =	969.2	10.4	98.927
25/6/2013	521.9	1120	724.9/2 + 1304.6/2 =	1014.8	14.9	98.532
26/6/2013	426.7	956.2	521.9/2 + 956.2/2 =	739.1	8.5	98.850
27/6/2013		1126.8	426.7/2 + 1126.7/2 =	776.7	15	98.069

GRAPH 5: COD OF SUPERNATENT RECOVERED AFTER TREATMENT IN BIOREACTOR B

The fluctuation in values aren't of importance as the significantly less as compared to the influent COD. The importance of the graph is to deduce that COD values in the range of 750mg/L to 1250 mg/L are brought down to 40 mg/L. This indicates significant sludge yield of the bioreactor as could be seen in the below graph.





GRAPH 8 & 9: EFFLUENT COD IS NEARLY INSIGNIFICANT AS COMPARED TO INFLUENT COD. THIS INDICATES HIGH ADSORPTION CAPACITY OF THE ACTIVATED SLUDGE.

It is evident that the domestic wastewater remains polluted with organic load plus the dissolved and suspended matter. Organic load is reflected in terms of the COD and the BOD values. In the present investigations only reduction of the COD was discussed. The COD concentrations, 739mg/L to 1014mg/L, in the wastewater were substantially higher than that of the permissible limit: 100–200 mg/l, for irrigation and horticultural uses, according to the Central Pollution Control Board, India (CPCB norms).

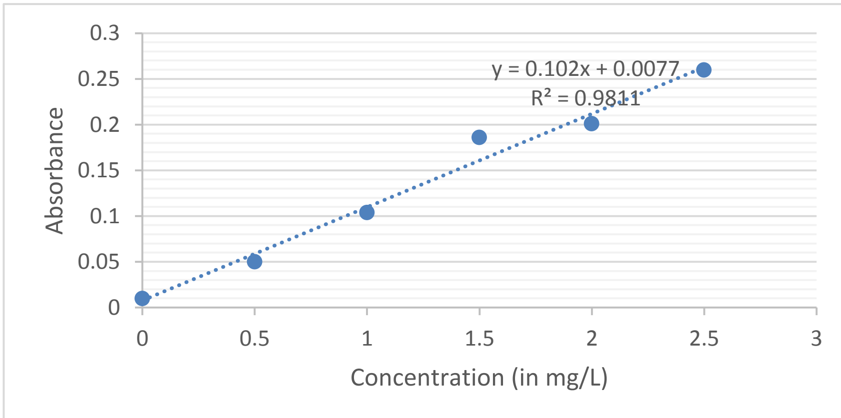
d. FATE OF METAL-ION NANOPARTICLES IN BIOLOGICAL REACTOR

TABLE 7: CONC. v/s ABSORBANCE VALUES FOR Ag (λ=327.5 nm)

Concentration (ppm or mg/L)	Absorbance
0.00	0.010
0.50	0.050

1.00	0.104
1.50	0.186
2.00	0.201
2.50	0.260

GRAPH 10: CONC. v/s ADSORBANCE VALUES FOR Ag



Silver nanoparticles were found to be absent from carboy and glucose solution. Concentration of copper nanoparticles in the carboy was found out to be 0.064 mg/L. This reading is very insignificant when compared to CPCB parameters.

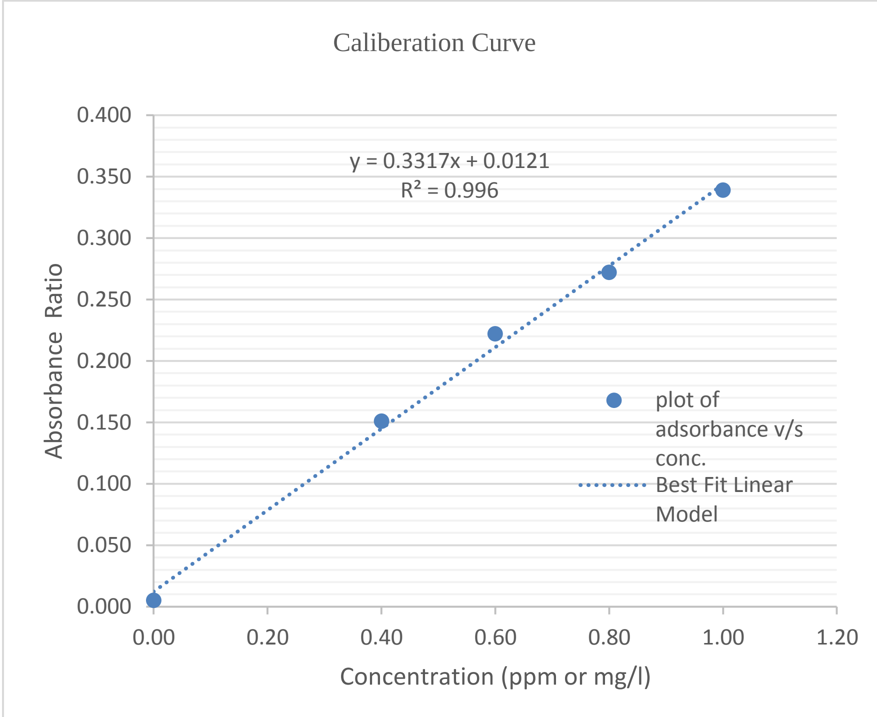
TABLE 8: STUDYING EFFICIENCY OF BIOREACTOR A TO ABSORB Zn HEAVY METAL

Concentration (ppm or mg/L)	Carboy	glucose	Sludge	Supernatant	Sludge + Supernatant	Biosorption Capacity of sludge (in percentage)
21/6/2013	0.645	0	0.371	0.027	0.398	
24/6/2013	0.612	0	0.589	0.030	0.619	95.35
25/6/2013	0.576	0	0.704	0.000	0.704	100.00
26/6/2013	0.561	0	0.934	0.000	0.934	100.00
27/7/2013	-	0	1.109	0.016	1.125	97.15

TABLE 9: CONC. v/s ADSORBANCE VALUES FOR Zn (λ=212.6 nm)

Concentration (ppm or mg/L)	Absorbance
0.00	0.005
0.40	0.151
0.60	0.222
0.80	0.272
1.00	0.339

GRAPH 11: CONC. v/s ADSORBANCE VALUES FOR Zn



Another set of readings suggest that when on glucose-based feed was added to the Bioreactor-B, no notable changes were noticed in metal ion's concentration of both supernatant and sludge.

6. CONCLUSIONS

Calibration curves were obtained using a series of varying concentrations of the standards for both the metals. The two calibration curves were linear with correlation coefficients of 0.996 and 0.9811. The initial biosorption capacities were 95.35% and 100%. The subsequent sludge yield continues to be very high owing to aging of sludge and the fact that we are dealing with heavy metals having very low concentrations. Because of these insignificant values, the amount of metal ions introduced to the system gets adsorbed almost completely, hence leaving behind no metal ion within the supernatant.

For the protection of human health, guidelines for the presence of heavy metals in water have been set by different International Organizations such as (USEPA), (WHO) and European Union. Thus, heavy metals have maximum permissible level in water as specified by these organizations. Maximum contaminant level (MCL, 2003) is an enforceable standard set at a numerical value with an adequate margin of safety to ensure no adverse effect on human health. It is the highest level of a contaminant that is allowed in a water system. The two elements that were studied in this research namely: Zinc and Silver have Maximum Contaminant Levels of 5mg/L and 0.10 mg/L for drinking purposes, according to National Secondary Drinking Water Regulations (NPDWR, 2009).

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