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REMOVAL OF COD AND TDS FROM INDUSTRIAL WASTE WATER

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ABSTRACT

Physico-chemical analyses of Rice Mill Waste Water (RMWW) indicate these to have high COD (Chemical Oxygen Demand) and TDS (Total Dissolved Solids) values. Six chemical treatments were employed for COD and TDS removal using two representative RMWW samples (viz., treatment T-1 with added bleaching powder, T-2 with added ferric alum, T-3 with added lime, T-4 with bleaching powder, ferric alum and lime added together, T-5 with activated charcoal followed by bleaching powder, ferric alum and lime added together, and T-6 with rice husk charcoal followed by bleaching powder, ferric alum and lime added together). The observed results indicate that the treatment T-5 and to a slightly lesser extent treatment T-6 were found to be very effective in reduction of COD and TDS (as also removal of colour and odour) from RMWW. The kinetics of COD or TDS decrease by single reagent additives (e.g., T-1, T-2 & T-3) were smooth, mono-phasic and first order and the kinetics in the case of multiple additives (e.g. T-4, T-5 & T-6) exhibited bi-phasic first-order patterns. While the single phase kinetics may most probably correspond to a slow process of growth/precipitation, the bi-phasic kinetics most likely involve an initial step of nucleation/ sol formation, followed by a relatively slower step of growth/precipitation.

Key words: COD/TDS removal, Chemical treatments, Kinetics, Rice mill waste water treatments.

INTRODUCTION

Paddy is one of the major crops all over the world. Out of the total rice, 21.4% are produced in India, and 28.5% of the total area world wise where paddy is cultivated in India. The state of Orissa lies on the east coast of India. Its economy is mostly agro-based where 76% people depend on agriculture. There are 8.75 million hectors of gross cropped area, out of which 1.88 million hectors are irrigated. Paddy is the major crop in Orissa. The state contributes one tenth of the rice production in India. The par-boiled variety of rice is

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produced from the paddy in rice mills. Rice mills are water intensive industries and hence, require large quantities of water during their operations and allied activities. The process of producing the par-boiled rice involves steam heating of paddy, followed by treatment with hot water. After a retention time of several hours (e.g. 8 h), the water is drained out as effluent[1].

The rice mill effluents are turbid, coloured, foul-smelling, acidic and have high COD and TDS values, badly needing treatment prior to letting them off into the open[2]. This communication reports on our efforts on the treatment of such rice-mill effluents.

EXPERIMENTAL

Materials and methods

Physico-chemical analyses

Two samples (A and B) of rice mill waste effluents water were collected from the discharge outlet of two par-boiled rice producing mills. Physico-chemical (viz., COD and TDS) parameters were analysed in the laboratory in accordance with standard methods[3,4]. Detailed physico-chemical particulars of the RMWW samples are listed in Table 1. The values cited in this work refer to the averages obtained from several replicates.

Table 1: Physico-chemical analyses of RMWW samples

Physico-chemical parameters	Sample-A	Sample-B
Appearance	Turbid	Turbid
Odour	Fowl	Fowl
pH	4.81	5.19
Suspended solids (mg/L)	284	289
BOD (mg/L)	520	695
COD (mg/L)	1894	2365
TDS (mg/L)	2324	2145
Conductivity (micro ohm^{-1} cm^{-1})	3575	3570

Cont…

Physico-chemical parameters	Sample-A	Sample-B
Chloride (mg/L)	542	1882
Sulphate (mag/L)	166	220
Phosphorous (mg/L)	7.8	7.3
Fluoride (mg/L)	0.95	0.82
Sodium (mg/L)	562	311
Potassium (mg/L)	880	850
Total Hardness (mg/L)	522	1012
Ca-Hardness (mg/L)	461	914
Mg-Hardness (mg/L)	61	98
Total (KJ) -Nitrogen (mg/L)	24	28

Treatment methods

Aliquots of 1 L each of the rice mill waste water (RMWW) sample (A and B) were taken in separate shakers and were subjected to chemical treatments at room temperature (33 ± 1^{0} C). Six different chemical treatment methods were carried out on both the samples (A and B), with vigorous shaking initially/after each operation.

Treatment 1 : Effluent (1 L) + Bleaching powder (1 g)

Treatment 2 : Effluent (1 L) + Ferric alum (1 g)

Treatment 3 : Effluent (1 L) + Lime (1 g)

Treatment 4 : Effluent (1 L) + Bleaching powder (1 g) + Ferric alum (1 g) + Lime (1g).

Treatment 5 : Effluent (1 L) + Activated charcoal (5 g) and then after 24 h, Bleaching powder (1 g) + Ferric alum (1 g) + Lime (1 g).

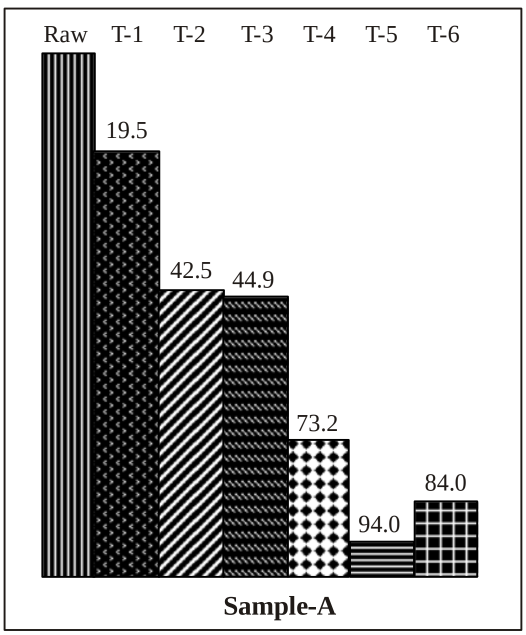
Treatment 6 : Effluent (1 L) + Rice husk charcoal (5 g) and then after 24 h, Bleaching powder (1 g) + Ferric alum (1 g) + Lime (1 g).

RESULTS AND DISCUSSION

Treatment of rice mill waste water with lime neutralizes the acidic components in order to have better precipitation (i.e. reduction in TDS or COD)[5], that with ferric alum coagulates[6] the colloidal/partly dispersible sols (reduction in TDS or COD), with charcoal brings about adsorption/removal of coagulated precipitated solids (reduction in TDS or COD), and that with bleaching powder removes organic impurities (reduction of TDS or COD). The bleaching action also removes colour and odour[7,8] by bleaching/oxidizing all organic impurities/colours/dyes and fowl smelling thiols present in the mentioned waste water[9].

The results also indicate that out of the six treatment methods discussed here, treatment-5 (i.e., the treatment with activated charcoal followed by bleaching powder, ferric alum and lime) was the most effective in reducing COD and TDS; for example, about 94% removal of COD and 75% removal of TDS after 96 hours were noticed in the case of sample-A. Similarly, the removal of COD and TDS were 94.5% and 74.5%, respectively for sample-B. Treatment T-6 with low cost rice husk charcoal adsorbent had more or less similar or slightly less effect as compared to T-5 employing activated charcoal as the adsorbent (Figs. 1-4).

Removal of COD



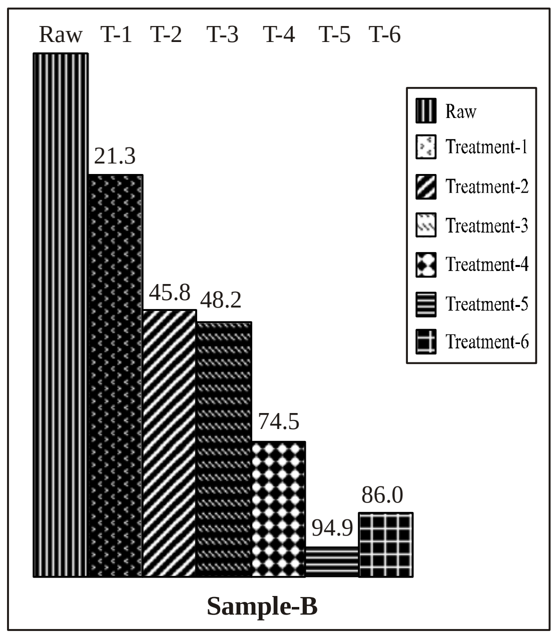
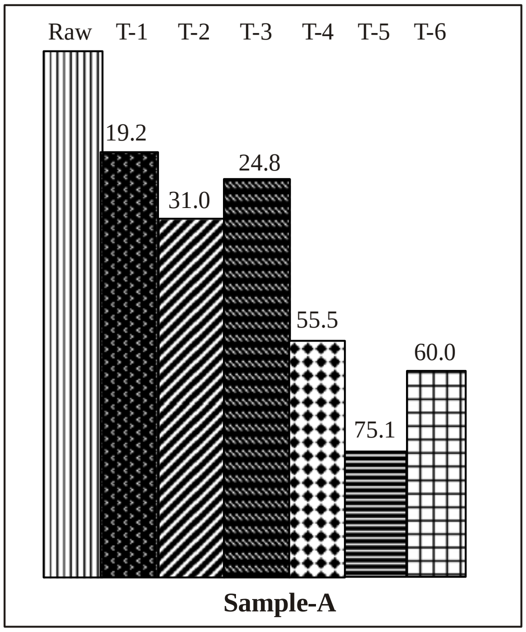


Fig. 1: % of COD removal after 96 hrs

Fig. 2: % of COD removal after 96 hrs

Removal of TDS



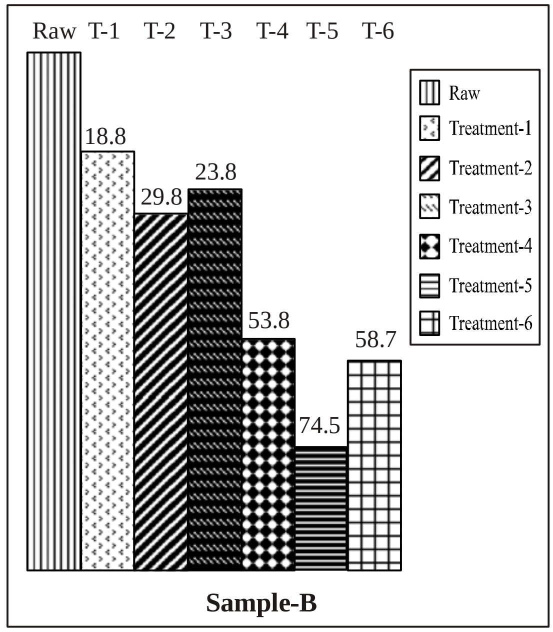


Fig. 3: % of TDS removal after 96 hrs **Fig. 4: % of TDS removal after 96 hrs**

Kinetics of the COD or TDS removal presents interesting observations. Treatments with single additives as in T-1, T-2 and T-3 exhibited regular and smooth exponential decrease of COD or TDS with respect to time. Plots of $\log_{10}$ COD or $\log_{10}$ TDS vs time (t) were linear, from the gradients of which k_s values can be calculated (Tables 2, 3 and 4). On the other hand, treatments with multiple additives as in T-4, T-5 and T-6 showed bi-phasic decreases (marked I and II in Figs. 5-8); the corresponding plots of $\log_{10}$ COD or $\log_{10}$ TDS vs time plots are also shown (Fig. 5-8). The first order rate constants for the slower phase-II (k_s) were calculated using the gradient(s) of such plot(s) (Tables 5, 6 and 7). The first order rate constants for the initial faster phase (k_f) were computed using standard procedures[10] from linear plots of $\log_{10}$ (concentration differences corresponding to I and the extrapolated part of II) vs time. The k_f values are also listed in Tables 5, 6 and 7.

It appears clear by from the observations that chemical treatment(s) T-1, T-2 and T-3 tried with single additive(s) can remove COD or TDS from the rice mill waste water (RMWW) through a slow process of precipitation/growth. On the other hand, multiple additives are able to remove COD or TDS in bi-phasic manner through an initial step of

Table 2: Measured COD and TDS values (mg/L) before and after treatment-1 (with bleaching powder 1 g/L)

Sample No.	Parameter	Raw effluent	After treatment for				% Removal				Rate constant	
			24 h	48 h	72 h	96 h	24 h	48 h	72 h	96 h	k_f (h^{-1})	$10^3 k_s$, (h^{-1})
A.	COD	1894	1856	1720	1587	1524	2.1	9.2	16.3	19.5	-	2.3
	TDS	2324	2238	1992	1908	1878	3.7	14.3	17.9	19.2	-	2.2
B.	COD	2365	2290	2156	1968	1862	3.2	9.9	16.8	21.3	-	6.3
	TDS	2145	2071	1848	1779	1742	3.5	13.9	17.1	18.8	-	3.6

Table 3: Measured COD and TDS values (mg/L) before and after treatment-2 (with ferric alum 1 g/L)

Sample No.	Parameter	Raw effluent	After treatment for				% Removal				Rate constant	
			24 h	48 h	72 h	96 h	24 h	48 h	72 h	96 h	k_f (h^{-1})	$10^3 k_s$, (h^{-1})
A.	COD	1894	1802	1422	1208	1102	4.9	24.9	36.3	42.5	-	5.6
	TDS	2324	1958	1733	1674	1605	15.8	25.5	28.0	31.0	-	3.8
B.	COD	2365	2233	1722	1417	1282	5.6	27.2	40.1	45.8	-	6.8
	TDS	2145	1821	1611	1551	1506	15.1	24.9	27.7	29.8	-	2.8

Table 4: Measured COD and TDS values (mg/L) before and after treatment-3 (with lime 1 g/L)

Sample No.	Parameter	Raw effluent	After treatment for				% Removal				Rate constant	
			24 h	48 h	72 h	96 h	24 h	48 h	72 h	96 h	k_f (h^{-1})	$10^3 k_s$, (h^{-1})
A.	COD	1894	1798	1378	1144	1045	5.1	27.3	39.6	44.9	-	6.2
	TDS	2324	1949	1862	1794	1748	16.2	19.9	22.9	24.8	-	2.9
B.	COD	2365	2218	1682	1284	1226	6.3	28.9	45.7	48.2	-	6.8
	TDS	2145	1813	1723	1668	1635	15.5	19.7	22.3	23.8	-	2.8

Table 5: Measured COD and TDS values (mg/L) before and after treatment-4 (with bleaching powder + ferric alum + lime 1 g/L each)

Sample No.	Parameter	Raw effluent	After treatment for				% Removal				Rate constant	
			24 h	48 h	72 h	96 h	24 h	48 h	72 h	96 h	k_f (h^{-1})	$10^3 k_s$, (h^{-1})
A.	COD	1894	824	668	576	508	57.5	64.8	69.6	73.2	0.11	6.4
	TDS	2324	1288	1136	1075	1044	44.6	51.2	53.8	55.5	0.14	4.1
B.	COD	2365	994	827	688	603	58.0	65.1	71.0	74.5	0.10	6.7
	TDS	2145	1222	1065	1010	992	43.1	50.4	53.0	53.8	0.14	2.7

Table 6: Measured COD and TDS values (mg/L) before and after treatment-5 (with activated charcoal 5 g/L, after 24 hours of which bleaching powder + ferric alum + lime 1 g/L each)

Sample No.	Parameter	Raw effluent	After treatment for				% Removal				Rate constant	
			24 h	48 h	72 h	96 h	24 h	48 h	72 h	96 h	k_f (h^{-1})	$10^3 k_s$, (h^{-1})
A.	COD	1894	216	164	128	114	88.6	91.4	93.3	94.0	0.14	8.4
	TDS	2324	697	636	602	580	70.0	72.7	74.1	75.1	0.13	3.1
B.	COD	2365	250	200	156	122	89.5	91.6	93.4	94.9	0.15	8.7
	TDS	2145	665	604	568	547	69.0	71.9	73.6	74.5	0.13	3.2

Table 7: Measured COD and TDS values (mg/L) before and after treatment-6 (with rice-husk charcoal 5 g/L, after 24 hours of which bleaching powder + ferric alum + lime 1 g/L each)

Sample No.	Parameter	Raw effluent	After treatment				% Removal				Rate constant	
			24 h	48 h	72 h	96 h	24 h	48 h	72 h	96 h	k_f (h^{-1})	$10^3 k_s$, (h^{-1})
A.	COD	1894	406	354	316	302	78.6	81.3	83.4	84.1	0.12	3.8
	TDS	2324	1050	1002	961	929	54.9	56.9	58.7	60.0	0.14	1.4
B.	COD	2365	442	391	345	332	81.4	83.5	85.5	86.0	0.13	3.8
	TDS	2145	977	938	938	886	54.5	56.3	57.7	58.7	0.14	1.9

nucleation/sol formation, followed by a slower step of precipitation/growth. Treatment with activated charcoal (T-5) or with low cost rice husk charcoal (T-6) offers an added advantage as the initial step of nucleation/sol formation is probably encouraged by surface adsorption.

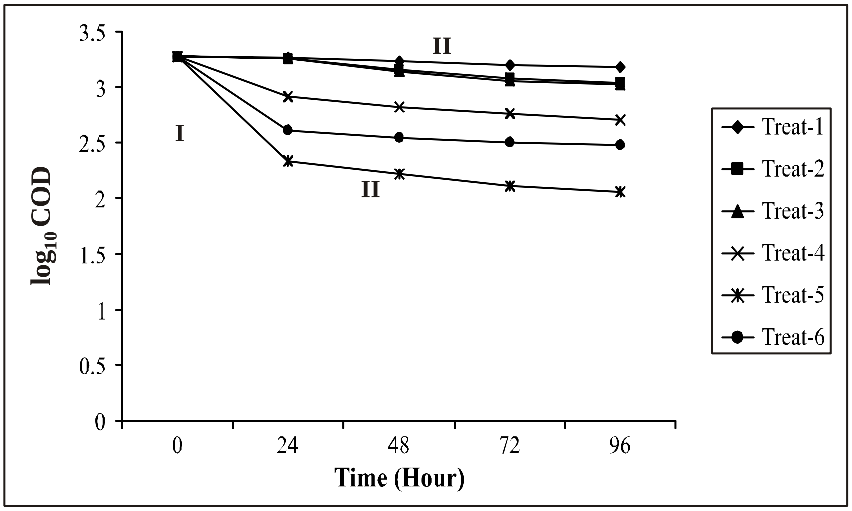


Fig. 5: $\log_{10}$ COD vs time (Sample-A)

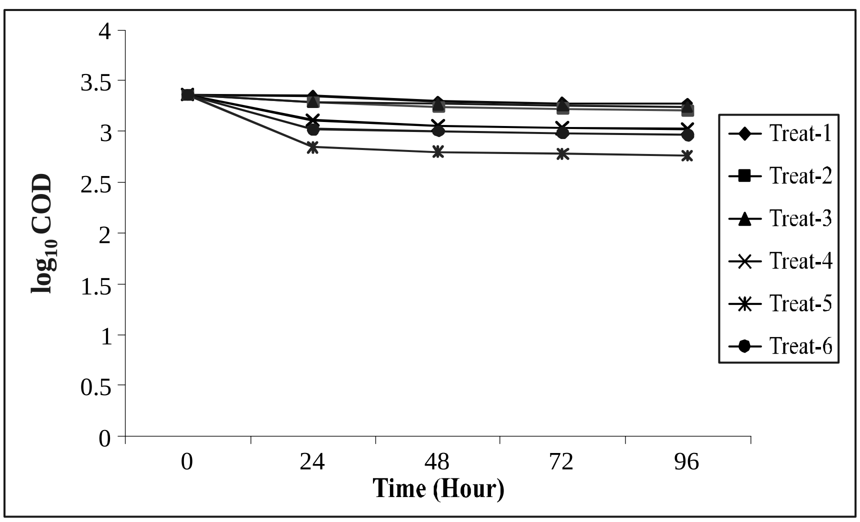


Fig. 6: $\log_{10}$ TDS vs time (Sample-A)

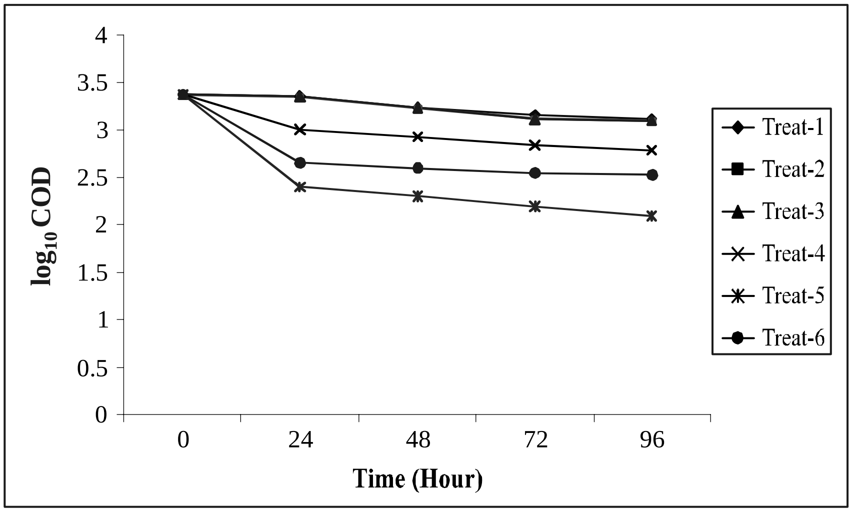


Fig. 7: log_{10} COD vs time (Sample-B)

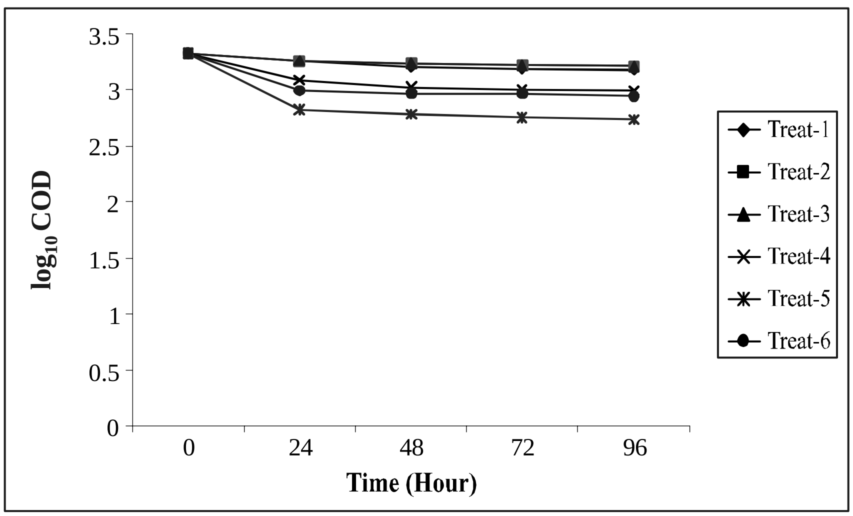


Fig. 8: log_{10} TDS vs time (Sample-B)

CONCLUSIONS

The following inferences can be drawn from this study -

(a) COD or TDS removal from rice mill waste water can be affected by slow chemical treatment with single additive(s) like bleaching powder, ferric alum or lime, or more effectively by multiple additives like a mixture of the above three or by (activated/rice husk) charcoal followed by a mixture of the above three.

(b) While the single additive chemical treatments follow a slow and first order decrease of COD or TDS, the multiple additive treatments exhibit bi-phasic kinetics of an initial first order decrease of the parameters due to nucleation/sol formation followed by a slower first order decrease of the parameters most probably due to precipitation/growth.

(c) Use of charcoal is found to encourage the initial step of nucleation/sol formation through surface adsorption.

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