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Comparative evaluation of various chelators for removal of pollutants and heavy metals from distillery effluents

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Abstract

Chelating efficiency of three different chelators (EDTA, DTPA and NTA) has been observed and compared for the removal of various pollutants and heavy metals from distillery effluent. The experiment was brought about at polyhouse conditions and the changes in physico-chemical characteristics i.e. pH, colour, COD, TS, TDS, TSS, Ca, Mg, Na, K, and heavy metals (Cu, Zn, Fe) of distillery effluent using various chelators has been examined. EDTA was found to be best chelating agent in comparison to DTPA and NTA.

Keywords: *Chelation* | *Distillery effluent* | *EDTA* | *DTPA*

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Introduction

Water pollution due to discharge of industrial waste water has become a serious problem in most of areas in our country (Sheth and Soni, 2004). Waste generated from various industries includes the effluent from textile, chemical fertilizers, pulp & paper, petrochemical, food processing, pharmaceuticals, dairies, distilleries, and breweries, metal processing, automobile manufacturing, power plants, tannery industries etc (Cox and Kamprath, 1972). Improper disposal methods and inadequate treatment of toxic constituents from different industries have led to widespread contamination of surface and ground water and have made the water resources unfit for usage (Odum, 1967). Hence, there is an urgent need for waste water treatment. The utilization of industrial effluent for irrigation of agricultural crops is one of the highly beneficial propositions of waste water disposal (Chauhan and Tewari, 2009).

Distilleries are one of the major agro-based polluting industries, with about 88% of raw material ending up as wastes (Jain *et al.*, 2000). These industries discharge large volumes of waste water carrying huge pollution load (Odum, 1967). The waste released from distillery is a complex, caramelized and recalcitrant in nature and contain high percentage of organic matter and heavy metal ions (Nemade and Shrivastava, 1998; Norvell and Lindsay, 1969), which affects the ground water, soil properties and vegetable plants grown in the area (Shrivastava *et al*., 1990; Shrivastava *et al*., 1995). This warrants adoption of safe and effective means of effluent treatment to fulfill both a practical necessity and a social responsibility (Vaidhyanthan *et al*., 1995). Keeping this in view, the present study therefore is planned to investigate the pollutants removal efficiency of various chelators against distillery effluent.

Materials and Method

The study was conducted with the distillery effluent collected from the Kesar Enterprises, Baheri, Uttar Pradesh State of India. For experiment, three chelators i.e. EDTA (Ethylenediamine Tetra Acetic Acid), DTPA (Diethylene Triamine Penta Acetic Acid) and NTA (Nitrilo Triacetic Acid) were taken. Seven sets of 2 kg plastic pots were filled with equal amount of soil. Wheat (*Triticum aestivum* L. var. UP - 2329) was grown in the pots. After 10 days of growth, 5 gm of various chelators i.e. EDTA, DTPA, and NTA were added separately to 6 sets of pots and irrigated with two different concentrations (50% & 100%) of the effluent. One set of pot was maintained as control in which no chelator was added. On each irrigation date one liter of effluent was poured in each pot. After 6 hours of irrigation the leachate was collected and all the selected parameters i.e. pH, colour, COD, TS, TDS, TSS, Ca, Mg, Na, K and heavy metals (Fe, Cu, Zn) were analyzed to find out the best chelator, which resulted into maximum reduction in pollution load of distillery effluent. Various physico-chemical parameters viz. pH, colour, COD, TS, TDS, TSS, Ca, Mg, Na, K and heavy metals (Fe, Cu, Zn) were analyzed as per standard method (APHA, 1995).

Statistical analysis

Data were analyzed through two-way ANOVA using SPSS software (SPSS Inc., version 10.0) for assessing the significance of quantitative changes in different parameters due to chelators.

Results and Discussion

Experimental results showed that the distillery effluent was acidic pH - 4.38, colour - 1466.66 CU, COD - 7883.33 ppm, TS - 42166.66 ppm, TDS - 28233.33 ppm, TSS - 13933.33 ppm, Ca - 111.66 ppm, Mg - 20.66 ppm, Na - 110.66 ppm, K - 79.33 ppm, Cu - 1.60ppm, Zn - 1.38ppm, Fe - 6.43 ppm, which is very high than their MINAS values.

Reduction in all physico-chemical parameter (i.e. colour, COD, TS, TDS, TSS, Ca, Mg, Na, K, Cu, Zn, & Fe) was considerably more when effluent was treated with EDTA at 50% effluent concentration followed by DTPA and NTA (Table 1-2, Fig: 1-4).

Values of colour, COD, TS, TDS, TSS was found minimum 228.66 CU, 1406.33, 4686.33, 2843.33 and 1843.33 ppm, respectively, after treated with EDTA at 40th day of irrigation with 50% spent wash (Table 2, Fig 3) and maximum 984.66 CU, 7223.33, 19586.66, 17163.33, and 2423.33 ppm, respectively, after treated with DTPA at 20th day of irrigation with 100% spent wash (Tables 1, Fig 1).

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Parameters	Untreated Effluent	EDTA			DTPA			NTA		
		20 days	30 days	40 days	20 days	30 days	40 days	20 days	30 days	40 days
pH	4.38 ±0.10	6.50 ±0.07***	6.60 ±0.11***	6.43 ±0.12***	6.50 ±0.12***	6.73 ±0.10***	6.80 ±0.22***	6.60 ±0.19***	6.70 ±0.20***	6.80 ±1.20***
Colour (CU)	1466.66 ±17.20	833.33 ±8.34***	626.66 ±6.20***	428.66 ±5.40***	984.66 ±11.80***	742.33 ±9.22***	563.33 ±6.12***	886.66 ±9.98***	706.66 ±8.89***	516.66 ±5.84***
COD (ppm)	7883.33 ±33.60	6600.00 ±22.20*	5883.33 ±19.16*	3606.66 ±12.64	7223.33 ±14.52*	6283.33 ±13.06*	4436.66 ±11.08*	6443.33 ±13.88*	5943.33 ±10.78*	4166.66 ±11.06*
TS (ppm)	42166.66 ±164.20	19103.33 ±113.60***	12663.33 ±111.18***	7883.33 ±39.47***	19586.66 ±111.64***	13896.66 ±121.26***	9643.33 ±41.66***	25726.66 ±121.36***	15663.33 ±122.24***	9643.33 ±41.14***
TDS (ppm)	28233.33 ±157.30	16566.66 ±102.40***	8866.66 ±28.40***	4866.66 ±21.13***	17163.33 ±112.48***	9643.33 ±31.54***	5566.66 ±19.48***	17330.00 ±109.36***	9236.66 ±29.53***	5566.66 ±30.06***
TSS (ppm)	13933.33 ±144.06	2536.67 ±12.10***	3796.60 ±17.31***	3016.67 ±14.02***	2423.33 ±8.96***	4253.33 ±18.08***	4076.67 ±17.82***	8376.66 ±25.26***	6426.64 ±22.12***	4076.67 ±13.32***
Ca (ppm)	111.66 ±8.12	92.66 ±6.60***	84.60 ±5.40***	78.33 ±5.80***	95.66 ±2.04***	88.33 ±6.87***	82.66 ±9.54***	94.33 ±10.45***	87.66 ±8.94***	80.33 ±12.12***
Mg (ppm)	20.66 ±0.46	16.66 ±2.20**	12.33 ±1.80**	9.66 ±1.67**	17.66 ±3.30**	14.66 ±4.60**	10.33 ±5.62**	17.33 ±3.30**	14.33 ±1.49**	10.66 ±0.94**
Na (ppm)	110.66 ±8.11	107.33 ±8.33	102.66 ±4.24*	96.66 ±8.70*	109.33 ±10.03*	105.66 ±11.22*	98.66 ±10.25*	108.66 ±12.20*	106.33 ±11.84*	98.33 ±12.29*
K (ppm)	79.33 ±5.12	68.33 ±4.41***	63.66 ±1.60***	61.33 ±6.32***	74.33 ±0.06***	73.66 ±11.04***	71.33 ±8.96***	74.33 ±8.96***	73.66 ±3.30***	70.66 ±4.69***
Cu (ppm)	1.60 ±1.29	1.42 ±0.06**	1.28 ±0.03**	1.16 ±1.60**	1.56 ±0.03**	1.52 ±0.09**	1.42 ±0.22**	1.52 ±0.66**	1.48 ±0.49**	1.42 ±0.22**
Zn (ppm)	1.38 ±1.60	1.25 ±0.04^{ns}	1.20 ±0.02^{ns}	1.18 ±2.20^{ns}	1.36 ±1.40^{ns}	1.30 ±0.08^{ns}	1.28 ±0.33^{ns}	1.35 ±0.21^{ns}	1.28 ±0.47^{ns}	1.26 ±0.09^{ns}
Fe (ppm)	6.43 ±1.40	5.44 ±0.03**	5.02 ±1.14**	4.68 ±0.14**	6.12 ±3.30**	5.96 ±0.67**	5.24 ±1.22**	6.02 ±0.25**	5.82 ±1.41**	5.25 ±0.52**

Significant at: *$p < 0.05$, **$p<0.01$, ***$p<0.001$, ns = non significant, EDTA = Ethylenediamine Tetra Acetic Acid, DTPA = Diethylene Triamine Penta Acetic Acid, NTA = Nitrilo Triacetic Acid.

Table 1: Physico-chemical characteristics of 100% distillery spent wash treated with different chelators at varied irrigation period irrigation period

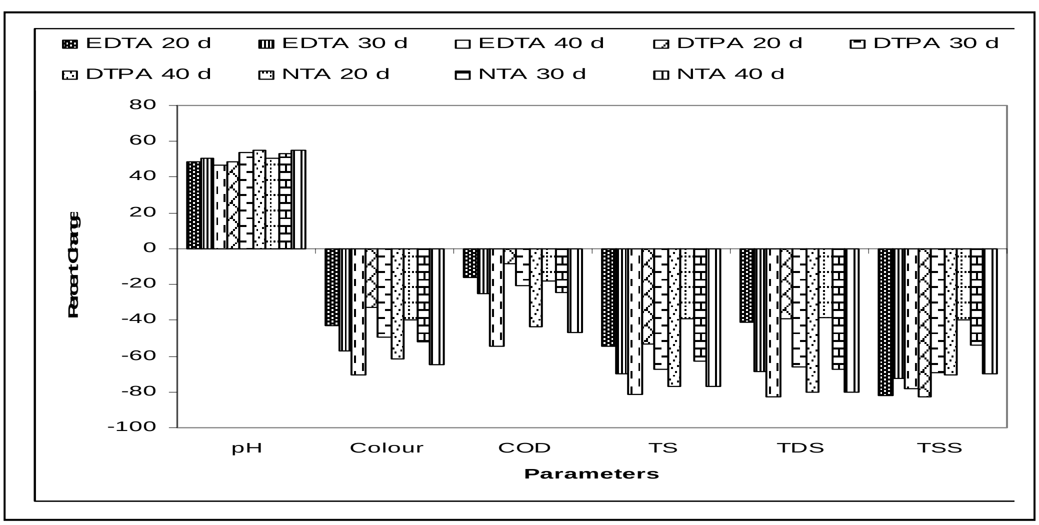

Fig 1: Percent change (+ increase, - decrease) over control in physico–chemical characteristics of 100% diluted spent wash treated with different chelators at varied irrigation

Amount of calcium, magnesium, sodium, and potassium was found minimum 68.33, 8.33, 92.66, and 53.66 ppm respectively after treated with EDTA at 40th day of irrigation with 50 % spent wash (Table 2, Fig. 4) and maximum 95.66, 17.66, 109.33, and 74.33 ppm respectively after treated with DTPA at 20th day of irrigation with 100% spent wash (Table 1, Fig 2).

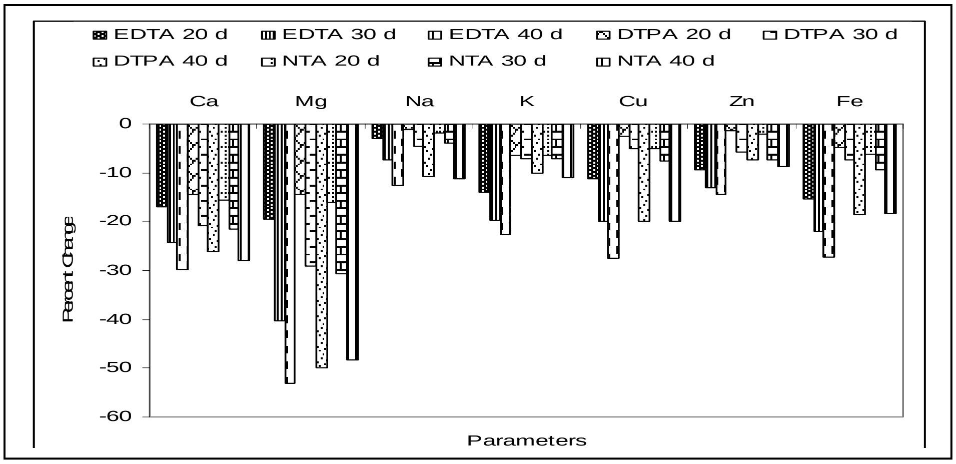

Fig 2: Percent change (+ increase, - decrease) over control in physico–chemical characteristics of 100% diluted spent wash treated with different chelators at varied irrigation.

Heavy metals i.e. Cu, Zn, and Fe was found minimum 1.02, 1.04, and 2.6 ppm respectively in EDTA at 40th day of irrigation with 50% spent wash (Table 2, Fig.3) and maximum 1.56, 1.36 and 6.12 ppm, respectively, in DTPA at 20th day of irrigation with 100% spent wash (Table 2, Fig 4).

Parameters	Untreated Effluent	EDTA			DTPA			NTA		
		20 days	30 days	40 days	20 days	30 days	40 days	20 days	30 days	40 days
pH	4.38 ±0.10	6.60 ±0.25***	6.40 ±0.12***	6.80 ±0.13***	6.50 ±0.14***	6.30 ±0.11***	6.40 ±0.24***	6.60 ±0.21***	6.80 ±0.25***	6.70 ±1.01***
Colour (CU)	1466.66 ±17.20	456.66 ±8.34***	326.33 ±11.02***	228.66 ±9.06***	492.33 ±10.05**	386.66 ±10.23***	256.66 ±10.16***	466.33 ±12.02***	353.33 ±8.95***	268.66 ±7.89***
COD (ppm)	7883.33 ±33.60	3486.66 ±22.38***	2663.33 ±18.96***	1406.33 ±13.43***	3963.33 ±19.54***	3146.33 ±20.14***	2236.33 ±14.59***	4866.66 ±22.36***	3266.66 ±20.92***	2453.33 ±20.26***
TS (ppm)	42166.66 ±164.20	12900.00 ±29.14***	8606.66 ±21.55***	4686.66 ±20.13***	13663.33 ±31.28***	9443.66 ±22.36***	5643.33 ±19.65***	13966.66 ±33.36***	9886.33 ±22.03***	5886.66 ±12.89***
TDS (ppm)	28233.33 ±157.30	5776.33 ±14.22***	4200.00 ±13.14***	2843.33 ±10.56***	6196.33 ±13.66***	5886.33 ±10.11***	3666.66 ±8.99***	7996.66 ±10.56***	5568.33 ±13.36***	4253.33 ±14.06***
TSS (ppm)	13933.33 ±144.06	7123.67 ±18.10***	4406.66 ±15.18***	1843.33 ±10.66***	7467.00 ±23.36***	3557.33 ±20.12***	1976.67 ±15.82***	5970.00 ±22.23***	4378.00 ±22.24***	1633.33 ±12.47***
Ca (ppm)	111.66 ±8.12	88.99 ±9.69***	78.33 ±8.87***	68.33 ±6.39***	90.33 ±9.04***	82.33 ±12.87***	76.66 ±9.74***	91.33 ±11.25***	85.33 ±8.94***	76.66 ±1.80***
Mg (ppm)	20.66 ±0.46	14.66 ±2.10**	11.66 ±2.37**	8.33 ±2.67**	15.66 ±2.30**	12.33 2.60**	8.66 ±0.62**	16.33 ±3.30**	12.66 ±1.89**	8.66 ±0.94**
Na (ppm)	110.66 ±8.11	106.33 ±8.73*	98.66 ±9.24*	92.66 ±9.24*	108.33 ±11.24*	101.66 ±9.44*	96.33 ±10.33*	106.66 ±11.20*	99.66 ±9.20*	96.33 ±8.55*
K (ppm)	79.33 ±5.12	73.33 ±6.41*	64.66 ±8.60*	53.66 ±5.32*	75.66 ±1.80*	65.66 ±1.98*	58.33 ±3.20*	76.66 ±1.18*	65.66 ±3.30*	55.33 ±3.29*
Cu (ppm)	1.60 ±1.29	1.30 ±0.08**	1.26 ±0.02**	1.02 ±0.05**	1.42 ±0.09**	1.36 ±0.08**	1.30 ±0.04**	1.42 ±0.07**	1.35 ±0.08**	1.28 ±0.09**
Zn (ppm)	1.38 ±1.60	1.18 ±0.06 ns	1.12 ±0.08 ns	1.04 ±2.20 ns	1.24 ±0.06 ns	1.22 ±0.08 ns	1.20 ±1.14 ns	1.30 ±0.23 ns	1.28 ±0.14 ns	1.26 ±0.09 ns
Fe (ppm)	6.43 ±1.40	4.23 ±0.33***	3.30 ±1.14***	2.60 ±0.19***	5.62 ±0.30***	4.80 ±0.67***	4.20 ±0.32***	5.62 ±0.45***	4.90 ±0.39***	3.30 ±0.52***

Significant at: $*p < 0.05$, $**p<0.01$, $***p<0.001$, ns = non significant, EDTA = Ethylenediamine Tetra Acetic Acid, DTPA = Diethylene Triamine Penta Acetic Acid, NTA = Nitrilo Triacetic Acid.

Table 2: Physico-chemical characteristics of 50% distillery spent wash treated with different chelators at varied irrigation period irrigation period

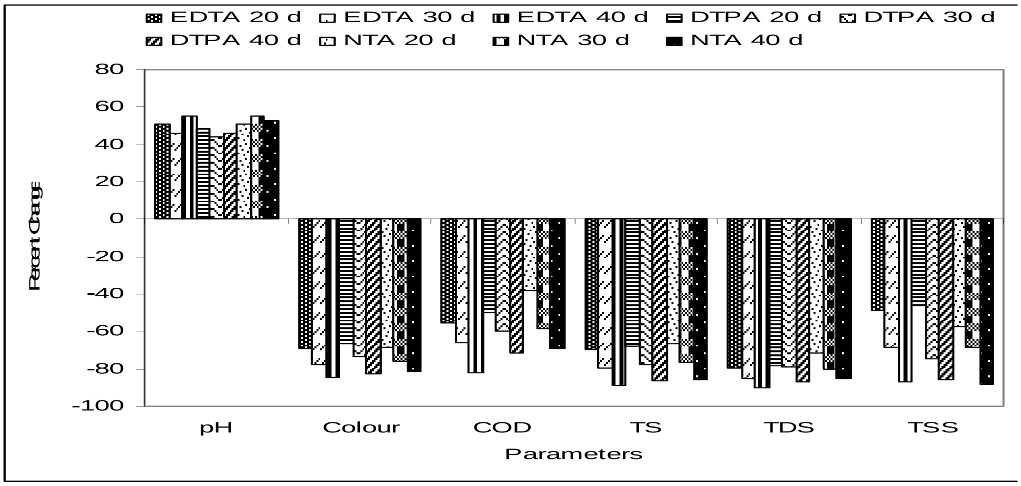

Fig 3: Percent change (+ increase, - decrease) over control in physico–chemical characteristics of 50% diluted spent wash treated with different chelators at varied irrigation

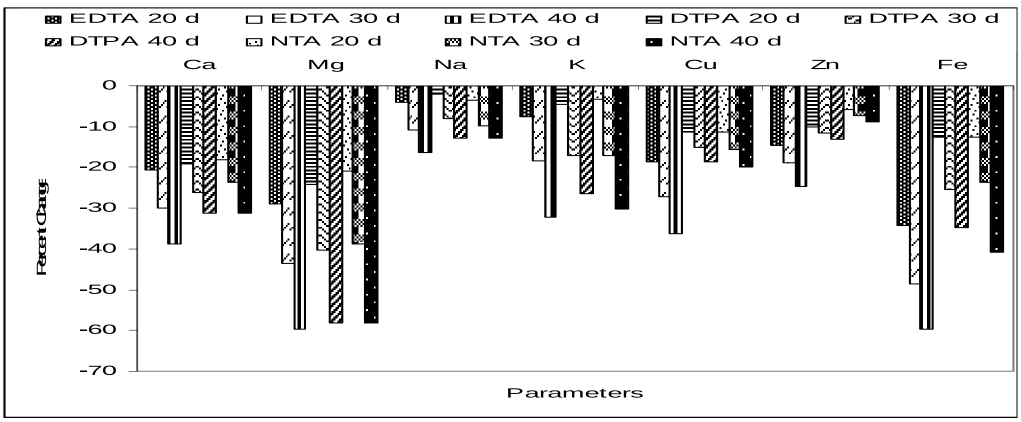

Fig 4: Percent change (+ increase, - decrease) over control in physico-chemical characteristics of 50% diluted spent wash treated with different chelators at varied irrigation

In the present study, among all the three chelators, EDTA was most effective chelating agent removes pollutants and trace metals with less impact on soil properties (Hodgson *et al*., 1966; Elliott *et al*., 1989).It is a powerful complexing agent of metals and a highly stable molecules. This is due to the fact that EDTA is organic in nature and has ability to keep metals in soluble form under many conditions in which they would otherwise be precipitated. EDTA solution is far superior for soil washing than either water or an anionic surfactant solution (Davis and Singh, 1995). This chelating agent removes trace metals with less impact on soil properties than decontamination systems using acids as the flushing agents and is only slowly degradable by microorganisms (Hodgson *et al*., 1966).

Attachment of EDTA–like chelators to carbon coated metal nanomagnets results in magnetic reagent for the rapid removal of heavy metals from solution or contaminated water (Koehler *et al*., 2009). Chelation is a chemical reaction. It occurs when more than one bond is formed between a cation and the functional group of the complexing agent. It results in the formation of a ring structure incorporating the metal ion. DTPA and NTA are also used as chelating agent but their pollutant removal efficiency is less in comparison to EDTA. DTPA is a good chelate for Fe in acidic soils because of the relatively high solubility of soil Fe at low pH and the high stability of Fe-DTPA chelate (Norvell and Lindsay, 1972; Morere *et al.*, 2001; Cox and Kamprath, 1972; Hill and Lloyd, 1957). Polyamine-polyacetate chelates are organic compounds which have the ability to keep metals in a soluble form (Zing *et al.*, 2005; Norvell and Lindsay, 1969; Xu and Xu, 2008).

Conclusion

EDTA has been observed best chelating agent in comparison to DTPA and NTA to remove organic pollutants and heavy metals from distillery spent wash.

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