GAVIN PUBLISHERS

Archives of Petroleum & Environmental Biotechnology

ElMorsi AK, Arch Pet Environ Biotechnol 2017: APEB -117.

DOI: 10.29011/2574-7614. 100117

Research Article

Treatment of Industrial Wastewater Contaminated by Nitro Compounds

Akila K El Morsi[1*], SA Shokry[2], AA Ismail[3]

[1]Department of Process Development, Egyptian Petroleum Research Institute, Egypt

[2]Science and Technology, Centre of Excellence, Elsalem City, Cairo, Egypt

[3]Abu Zaabal Company for Speciality Chemicals, Cairo, Egypt

[*]**Corresponding author:** Akila K El Morsi, Department of Process Development, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt. Tel: +20222745902; Fax +20222747433; Email: drakilakamel158@yahoo.co.uk

Citation: ElMorsi AK, Shokry SA, Ismail AA (2017) Treatment of Industrial Wastewater Contaminated by Nitro Compounds. Arch Pet Environ Biotechnol: APEB -117. DOI: 10.29011/2574-7614. 100117

Received Date: : 27 June, 2017; **Accepted Date:** 5 August, 2017; **Published Date:** 14 August, 2017

Abstract

Disposal of wastewater (red water) produced during the Production of Trinitrotoluene (TNT) causes serious environmental problems. Using adsorption followed by Advanced Oxidation Processes (AOPs) are the most feasible technologies for red water treatment. In the present work two types of carbon are used for treatment separately and simultaneously which are Bone Charcoal (BC) and Activated Carbon (AC). Operational parameters in each step are tested and optimized. The adsorption isotherms of TNT red water at a wavelength of 200 nm by (BC), (AC) have been evaluated. Then, treatment of red water by mixing (BC) and (AC) are assessed, followed by advanced oxidation with ultraviolet and hydrogen peroxide. As a measure of extent of treatment, we use the % removal at wavelength 200 nm, also we measure the Total Organic Carbon (TOC), and Chemical Oxygen Demand (COD) before and after treatment. The removal was favoured at low pH, with maximum removal 90 % at pH =2 for BC while for AC the maximum removal 95 % at pH=12. After the treatment of red water by adsorption on mixing carbons (BC+AC) followed by AOPs, the removal is 95 %, total organic carbon is 95 % & chemical oxygen demand is 97 %.

Keywords: Activated Charcoal; Advanced Oxygen Processes; Adsorption; Oxidation-Bone Charcoal; Wastewater- Nitro Compounds

Abbreviations:

BC	:	Bone Charcoal
AC	:	Activated Charcoal
TOC	:	Total Organic Carbon
COD	:	Chemical Oxygen Demand
AOPs	:	Advanced Oxidation Process
% R	:	Percent Removal

Introduction

The symmetrical 2,4,6-trinitrotoluene (α-TNT) is one of the most important and widely used explosives. The manufacture of TNT consists of main processes: nitration of toluene to crude TNT and TNT purification to remove any asymmetric TNT isomers (for example, 2,3,5-TNT, 2,4,5-TNT).

During the purification stage, sodium sulphiteis added to react with the asymmetric TNTs, resulting in the formation of Dinitrotoluene(DNT) sulphonated compounds (for example 2,4-DNT-5-SO3Na). These sulfonates are water soluble and are easily separated from α-TNT. The wastewater resulting from the purification process exhibits an intense "Red"colour and is commonly referred to as TNT Red Water. In addition to the sulfonated compounds, red water also contains products of complete nitration (for example, priority pollutants 2,4-DNT and 2,6-DNT) and complex by products formed during the nitration and purification stages. Currently, red water is classified by US Environmental Protection Agency (EPA) as a Resource Conservation and Recovery Act (RCRA)-regulated hazardous waste (K047) based on its reactivity. Furthermore, TNT and red water are toxic to aquatic life[1-3]. Consequently, the treatment and disposal of red water presents a significant environmental problem for the public and private sectors involved in the manufacturing of TNT.

Because of the complicated nature of red water, conventional biological treatment, carbon adsorption, chemical precipitation fractional distillation, Ozonation are ineffective for red water-treatment.The treatment of wastewater or ground water from military ammunition plants or other such facilities contaminated with various nitro-compounds such as trinitrotoluene dinitrotoluene, RDX, HMX and tetryl etc. has been well studied using different types of activated carbons [4-9]. As a whole, adsorption is a simple-to-operate process and relatively cost- effective, due to (or no) energy requirements. Adsorption parameters can be simply established by using an appropriate isotherm equation. The last decade has witnessed Advanced Oxidation Processes (AOPs) emerging as promising alternatives to tertiary treatment, owing to their high potency to render partial and ultimate destruction of many refractory compounds including dyestuff-halogenated and aromatic organics [10-14]. These processes involve the formation of highly reactive free radical species, which are far more powerful as oxidizing agents than commonly known strong oxidants like molecular oxygen and ozone. The chemistry, kinetics and quantum yields in free radical reactions have been widely investigated and reviewed in the paste [15-18].These processes have two unique advantages over other advanced treatment processes; (i) they are non-selective to a very broad range of chemicals, and (ii) they involve no sludge production due to the character of their removal mechanism, which is based on the oxidative destruction of organic carbon by conversion to higher oxidation states. It is our interest to make use of the coupling techniques (Adsorption and AOPs) in treatment of TNT manufacturing red water. In this concern, two types of carbons were tested separately and simultaneously. The optimal conditions were obtained and the non-adsorbed pollutants remaining in bulk after filtration was further treated using UV/H_2O_2.

Experimental

Instrumentation

A Hewlett Packard Diode array spectrophotometer (Model 8451 A) was used to measure UV-Vis absorbance for raw and treated water samples. A microprocessor pH meter HANNA model HI-9321 was used for pH measurement. A water bath shaker of American optical corporation (Buffalo, New York) was used for all the adsorption experiments. Dohraman, model DC-190 was used for TOC measurement. COD was determined according to standard methods 1985 [19]. Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) Perkin Elmer optima 3000 was used to detect the trace metals and cations. The laboratory-scale thermostated Pyrex glass-columnPhotoxidation reactor is used (Figure 1). The procedure was carried out batch wise under illumination of a single 400 WHQL high pressure mercury vapour lamp (Phillips) whose protective cover was removed. The reactor was water-jacketed to keep solution temperature at 25ºC for all runs.

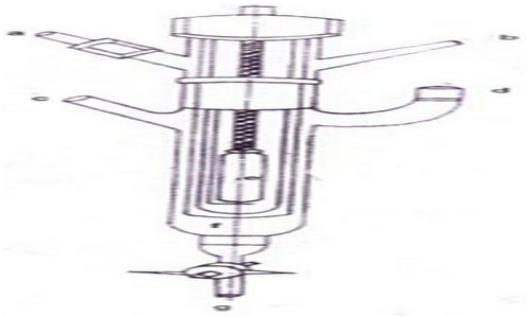

Figure 1: Photo reactor a. cooling water inlet; b. cooling water outlet; c. gas inlet (nitrogen); d. gas outlet (Nitrogen); e. UV lap; f. sample solution; g. sampling stopcock.

Materials

Adsorbents: two types were used:

(i) Discard bone char (BC) residue from Pakin Co., Egypt, was tested. This local biomass derived material of animal origin. The (BC) residue is the resultant of pyrolysis process occurred according to the following conditions:

Animal bones $\xrightarrow[\text{Inert atmosphere}]{800ºC/5\ hr}$ (BC) residue + steams + oils + ammonia liquor

The residue content was varied according to the type of animal (e.g. camel, buffalo, or cattle) and its food. The (BC) residue is left in an inert atmosphere to avoid any oxidation. Then, it is crushed and sieved to give constant particle sizes used for different purposes. The remaining size from sieving (30 mesh) is considered as carbidge i.e. waste of no use. This waste is used as an adsorbent in our study. A characterization of (BC) is presented elsewhere [20].

(ii) The Rice Husk (Rh), with properties in Table 2, was pyrolyzed in 20 cm I.D. bench-scale, fluidized-bed reactor Shown in (Figure 2), Abu Zaabal Company for specialty chemicals) at temperature 673 K and a retention time of 60 min., the fluidizing gas was nitrogen. The gas flow rate is so chosen as to operate the reactor between 1 and 2 times the minimum fluidization velocity. 300 g of (Rh) was subjected to pyrolysis in presence of constant flow of nitrogen gas. The steam was introduced into the reactor from boiler (3 kilo steam/hr) when the temperature in the reactor was 300ºC.

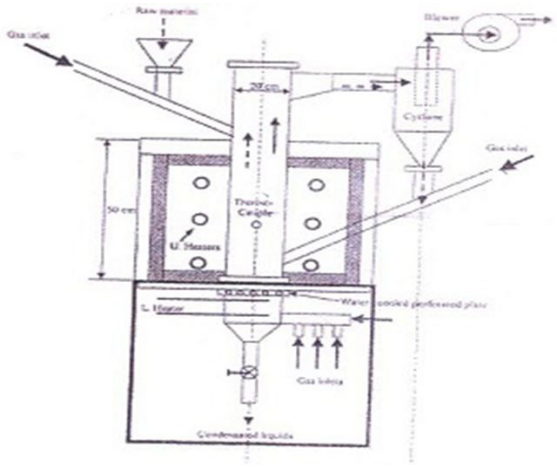

Figure 2: Circulated Fluidized-Bed.

The reactor was heated at constant rate (3ºC/min) up to 400ºC. Then, hold for 60 min. at this temperature. After that period, the electrical heater was switched off and sample is left to cool down. This led to the virgin carbon (MC-0). This carbon was subsequently treated chemically with HNO3 (100 ml) and heated slowly on hot plate in a fuming cupboard till boiling near dryness, then left to cool. After the treatment, the sample was washed with distilled water several times to remove the excess reagent used and the pH of the filtrate was measured. Then, the sample was dried at 105ºC in a dryer

Adsorbate:

The red water was obtained from TNT manufacturing plant in September 2001, from Abu Zaabal Company for Speciality Chemicals. The red water was filtered through cotton, placed in dark bottle and stored in a refrigerator at 4ºC. The prolonged refrigeration, however, produced crystalline flakes. The samples were kept at room temperature and thoroughly mixed using a magnetic stirrer to re dissolve the crystals before each experiment. A typical red water composition is shown in (Table 1). Only diluted raw red water (1:100) was used in all of the adsorption experiments, and (AOPs), primarily for safety reasons.

Parameters	Value
pH units	7.6
sp. Gravity	1
solids	
Total	2840
Volatile	1020
Fixed	1820
Organics	36
Inorganic salts	
[$NaNO_2$]	209
[$NaNO_3$]	0
[Na_2SO_3]	55
[Na_2SO_4]	514
[Na_2SO_3+ Na_2SO_4]	569
Alkalinity	
as [CaCO3]	43
Organic content	
COD	685
TOC	
Nitro bodies	
α-TNT	2.27
2,4-DNT	0.21
2,6-DNT	0.03
1,3,5-TNB	3.1
DNTS[b]	
2,4-DNT-3-SO3Na	272
2,4-DNT-5-SO_3Na	228

Table1: All concentration was in mg/L for diluted red water (1:100).

Methods:

Factors affecting adsorption using BC or AC

In this concern, the equilibrium time, pH and adsorbent mass were determined. In all these experiments, accurately weighed masses of (BC) or (AC) were placed in 100-ml glass bottles. Fifteen and fifty milliliters of the Adsorbate solution were mixed with (BC) and (AC) respectively then equilibrated the solutions to a desired pH values with dilute HCl or dilute NaOH solutions. Contents of the bottles were then shaken at 120 rpm, for predetermined time intervals in a thermostatic shaker. The first 5 ml of the filtered samples were discarded before samples were taken for analysis in order to minimize the effect of any adsorption of the Adsorbate that may occur on the filter paper. The absorbances of the samples before and after adsorption were measured spectrophotometrically using an HP 8451A diode array at a wavelength 200 nm (representing an abundance of aromatic compounds content of the TNT red water) [21].

Isotherm experiments

50 ml of stock Adsorbate solution of initial concentration 355.42 mg/L was mixed with various amounts of each sorbent separately (200-2000 mg in case of BC and 20-250 mg in case of AC). The solutions were equilibrated to a desired pH value and shaken to achieve equilibration. Each mixture was filtered. The ultraviolet absorbance of the filtrate was measured at λ_{max} 200 nm.

Photo oxidation using UV/H_2O_2

In general, the procedures were performed by mixing (BC) and (AC) simultaneously in a ratio (4:1) with 50 ml of red water and shaken for 12h at pH 2. Then, the filtrate was used to study the parameters affecting the photoxidation (e.g. exposure time and hydrogen peroxide amount). All samples before and after photoxidation were analyzed for TOC, COD as well as UV light absorbance at λ^{max} 200 nm.

Results and Discussion

Table 2 shows some data on BC and AC which are used as adsorbents in this study.

BC		AC	
Constituent	**(w/w%)**	**Constituent**	**(w/w%)**
C	10.3	C	37
H	1.3	H	5.1
N	3.6	N	0.4
Cl	1.9	O*	37
$Ca_3(PO4)_2$	78	Ash	20.5
$CaCO_3$	3.5		
Others (Mg, Fe, SiO_2, etc.)	<1.0		
SBET	73 m^2/g	SBET	100 m^2/g
pH	8.2	pH	2.15

Table 2: By differencesome data on (BC) and (AC).

Equilibrium Time

Figure 3 reveals that the percent removal (%R) of aromatic compounds was 81 % and 65 % after 1/2 h using AC and BC, respectively. A plateau is reached after 6 hrs indicating that both BC and AC are saturated at this level.

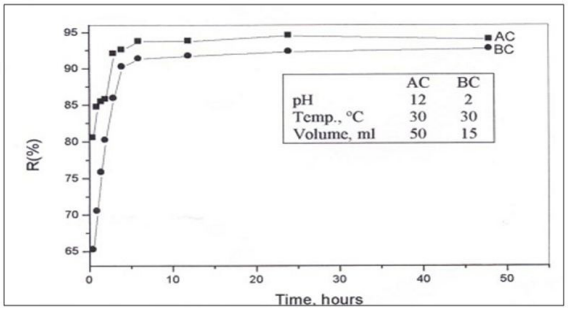

Figure 3: Effect of Equilibrium time on percent removal of TNT red water.

Effect of adsorbent mass

Figure 4 illustrates as the adsorbent amount increases, the % R increases. However, a steady state condition is apparent indicating that 1.4 gm of BC and 0.15 gm of AC was enough to achieve maximum removal of pollutants for 15 ml and 50 ml respectively of TNT red water. Excess of BC or AC will inhibit good mixing and in turn prevent the pollutants to reach all the BC or AC particles i.e., of no use.

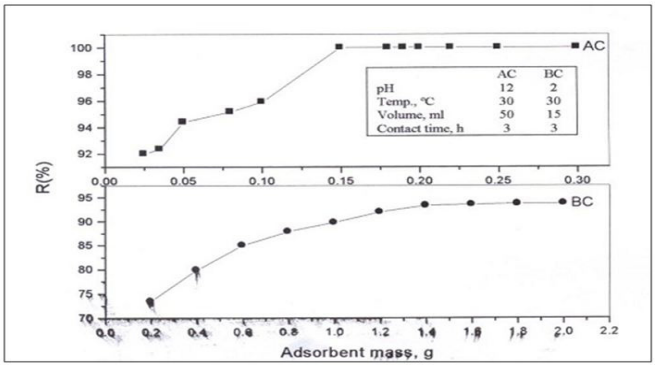

Figure 4: Effect of adsorbent mass on percent removal of TNT red water.

Effect of pH

Figure 5 illustrates the maximum % R was obtained at pH=12 and reaches 98 % using AC and this will help for treatment of known and unknown pollutants contained in red water in alkaline range.

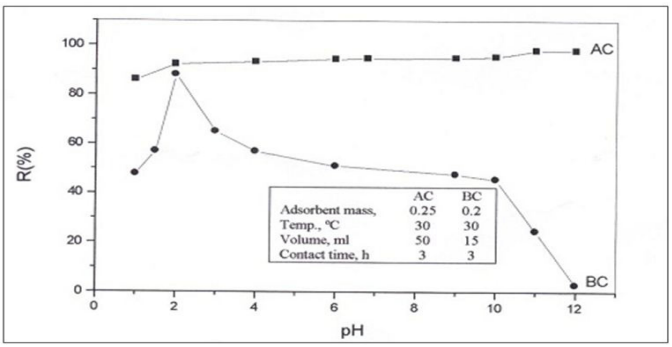

Figure 5: Effect of pH on percent removal of TNT red water adsorption isotherms.

Also, the maximum % R was observed at pH=2 and reaches 90 % using BC and this will help for treatment of some other pollutants in acidic ranges. In conclusion, it is worth to mention that mixed adsorbents (BC and AC) will be effective in removal of many pollutants contained in TNT red water whether pH adjusted in ranges acidic or basic.

Adsorption data for wide range of Adsorbate concentrations are most conveniently described by adsorption isotherms which correlate adsorption density (q_e Adsorbate uptake per unit weight of adsorbent) to equilibrium Adsorbate concentration in the bulk fluid phase, Ce(Figure 6)

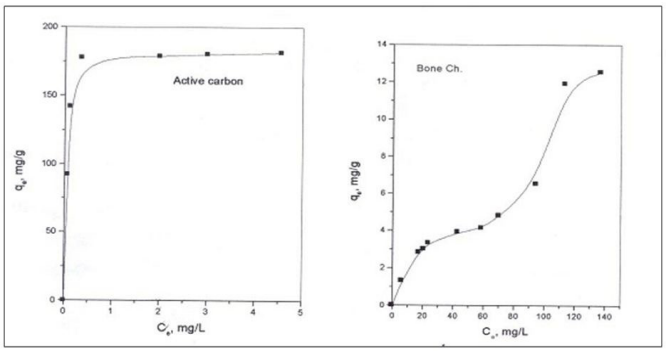

Figure 6: Adsorption isotherms of red water on AC and BC, (equilibrium Adsorbate uptake q_e and equilibrium Adsorbate concentration in the bulk fluid phase C_e).

Isotherm data are analyzed in term of Langmuir adsorption isotherm model. Langmuir plot was obtained, (Figure 7) using the well-known equation

$$\frac{1}{q_e} = \frac{1}{q} + \left[\frac{1}{bq_o}\right]\frac{1}{C_e}$$

or

$$\frac{C_e}{q_e} = \frac{1}{q^o b} + \frac{1}{q^o}C_e$$

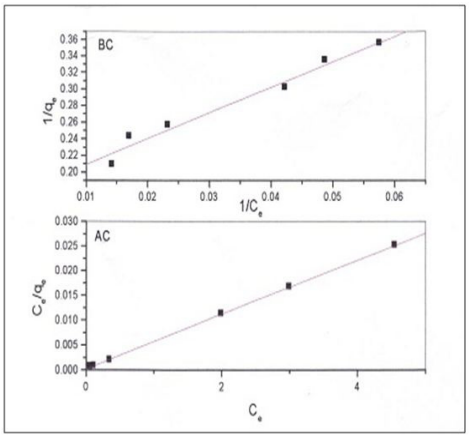

Figure 7: Langmuir adsorption isotherms of TNT red water on BC and AC.

Where qe is the amount of solute adsorbed per unit mass adsorbent, Ce is equilibrium concentration of solute and qo, b are constants, were evaluated and their values are listed in (Table 3).

Carbon type	Surface area m^2/g	Correlation coefficient	Dimensionless separation factor	Langmuir constants	
				q^omg/g	b
AC	100	0.999	0.000102	181.812	27.5
BC	73	0.9721	0.046607	5.614	0.057

Table 3: Langmuir constants for TNT manufacturing red water on AC and BC.

Effect of isotherm shape:

Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (r) which is defined by the following relationship given by

$$r = \frac{1}{\left[1 + b\,C_o\right]}$$

Where b is Langmuir constant and Co is the initial concentration of solute concentration in mg/L

As shown from theTable 3 the values of "r" are less than one indicating that the adsorption of red water by (BC), (AC) are favorable. The applicability of the Langmuir model suggests monolayer coverage of the Adsorbate at the outer surface of the (BC), (AC) are significant as shown from Table 3. The qo values have the following sequence AC > BC. It is worth to mention that the adsorption technique using (BC+AC) will affect the removal of metal ions as well as organic content (Table 4).

Metal	Concentration (mgl^{-1})		Removal (%)
	Before treatment	After treatment	
Cd^{++}	0.001	0.0001	90 %
Ba^{++}	ND	ND	
Co^{++}	ND	ND	
Cr^{+++}	0.041	0.006	85 %
Cu^{++}	0.043	0.002	95 %
Fe^{+++}	0.059	0.059	
Mn^{++}	ND	ND	
Ni^{++}	ND	ND	
Pb^{++}	0.05	0.014	72 %
Sb^{+++}	0.03	0.03	
Se^{++++}	ND	ND	
Ti^{++++}	ND	ND	
V^{+++++}	ND	ND	
Zn++	0.049	0.016	67 %
Hg^{++}	ND	ND	
As^{+++}	ND	ND	

Table 4: Concentration of metals in raw red water (1:100) before and after treatment using adsorption technique (pH=2; contact time = 12 h; 1 g BC + 0.25 g AC).

Second-stage operation

Effect of H_2O_2 amounts

The presence of H_2O_2 has a great influence for the reduction of organic chemical concentration in water. Moreover, it was necessary to decide the amount of H_2O_2 to fulfill the lowest possible value of TOC and COD. This is due to the much higher H_2O_2 concentration will be 1) economically undesirable [22] and 2) scaven-

gers for hydroxyl radicals [23]. The residual H_2O_2 in solution was determined by the KI titration method[24]. As can be seen from Figure 8, the ratio between H_2O_2/sample, (v/v) to achieve the maximum (%R) was ~ 1:8 and no accumulation of H_2O_2 was found.

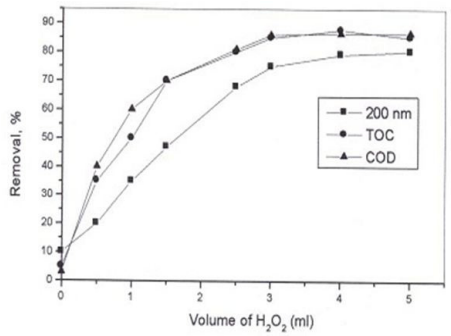

Figure 8: Effect of H_2O_2 dosage on the percent removal.

Effect of UV exposure time:

In the presence of the H_2O_2 Photo catalyst and radiation with $\lambda > 300$ nm, the reaction follows as:

$$H_2O_2 + \lambda\nu \longrightarrow 2OH^-$$

The destruction of red water was rapid (Figure 9). After a 2 hr reaction there was an 81.4 % reduction in TOC, 83.8 % reduction in COD and 88.1 % at 200 nm by UV-spectrophotometer. The solution pH after the AOP is altered, pH decreased from 2.15 to approximately 1.2. The red water has little buffer capacity and the reduction in pH indirectly infers that SO_3 groups were rapidly detached from the DNTs, resulting in the formation of H_2SO_4. (I.e. acidity increases). Also, the formation of new components due to AOP may also cause a reduction in pH,

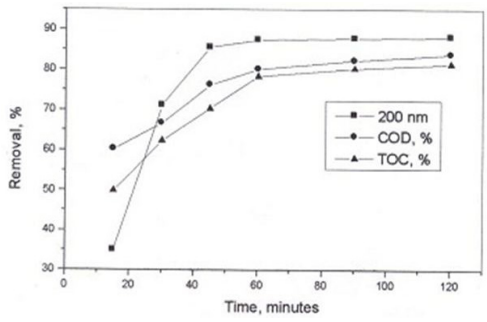

Figure 9: Effect of exposure time on percent removal of TNT red water.

Recommended procedures:

Based on the results of experiments, the amounts of (BC) and (AC) are 20, 5 g/L respectively, to achieve permissible level of nitro body concentration in a treated effluent. In case of 2nd step (photooxidation using UV/ H_2O_2), the ratio of H_2O_2 to the contaminant is 1:8 and the exposure time required for complete degradation is 2 hours. On the basis of adsorption and advanced oxidation process (AOPs) studies, a pilot plant for the treatment of effluent wastewaters from a TNT production plant was designed and construct and now in operation in our factory.

Conclusion

The maximum removal of red water was obtained at pH=12 reached 98% using AC i.e. treatment can be done in alkaline range. At pH=2 maximum removal reached 90% using BC and thus treatment of some pollutants could be done in acidic ranges.The adsorption technique using BC+AC willaffect the removal of metal ions as well as organic content. It was obtained that q_e values using AC higher than BC.

The ratio between H_2O_2/ sample was 1.8 to achieve the maximum % removal with no accumulation of H_2O_2.After 2h reaction, a reduction of 81.4%in TOC, 83.8% in COD and 88.1%at 200 nm by UV- spectrophotometerTreatment of red water from TNT manufacture using adsorption & AOPs prove its efficiency in the removal of organic matters as well as heavy metals. Hence the treated water can pass safely into river without any risks health.

References

1. Burrows EP, David HR,Wayne RM, David LP (1989) Organic explosives and related compounds; Environmental and Health Considerations. Technical Report 8901, U.S Army biomedical Research Development Laboratory Fort Detrick Md.
2. Nay MW, Clifford WR, Paul HK (1974) Biological treat ability of trinitrotoluene manufacturing wastewater. J Water pollutes Control Fed 46: 485.
3. Smock LA, Stone burner DL, Clark JR (1976) The toxic effects of trinitrotoluene (TNT) and its primary degradation products on two species of Algae and the fathead minnow. Water Res (GB) 10: 537-543.
4. Burrows WD (1982) Tertiary treatment of effluent from Holston, Army Ammunition plant, US Army Armanent R & D command, Dover, NJ Report No 8207.
5. Jerome Heberman (1983) Competitive adsorption of 2,4,6 TNT and RDX, Report No. AR LCD-TR-8303-AD-6401033.
6. Pennington JC (1988) Adsorption and desorption of 2,4,6-TNT by soil, Report No. AD-A18971918.
7. HOPC & DAWCS (1988) Environmental Technol 22: 919.
8. Hinshow GD (1987) Granular activated carbon (GAC) system performance capabilities and optimization, US Army Toxic and Hazardous Materials Agency (USATHAMA) Report No. AMXTHTE CR 8711.
9. Wujcik WJ, Lowe WL, Marks PJ, Sisk WE (1992) Environ Prog 11:1178.
10. Bauman LC,Stenstrom MK (1990) Removal of organohalogens and organohalogens precursors in reclaimed waste water Wat. Res 24:949.
11. Kusakab K, Aso S, Wada T, Hayashi J, Moroka S, et l. (1991) Destruction rate of volatile organ chloride compounds in water by ozonization with ultraviolet radiation. Water Res 25: 1199.
12. Ince NH, Stephen MI,Bolton JR (1997) UV/H_2O_2 degradation and toxicity reduction of textile azodyes. J Adv OxidTechnol2: 442-448.

13. Ince NH (1998) Light enhanced chemical oxidation for tertiary treatment of municipal landfill leachate. Water Env Res 70: 1161-1168.

14. Ince NH, Tezcanli G (1999) Treatability of textile dyebath effluents by advanced oxidation: Preparation for reuse. Wat Sci Tech40:183-190.

15. Glaze WH, Kang JW,Chapin DH (1987) The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Sci Eng9: 335-352.

16. Stachelin J,Hoigne J (1985) Decomposition of ozone in water in the presence of organic solutes acting as promotors and inhibitors of radical chin reactions. Env Sci of Technol19: 1206-1213.

17. Guittonneau S, De Laat J, Duguet JP, Bonnel C, Dore B (1990) Oxidation of PCNM in dilute aqueous solutions by O_3 + UV and H_2O_2 + UV; a comparative study. Ozone Sci Eng12: 73-94.

18. Gŭral MD, Vatista SR (1987) Oxidation of Phenolic compounds by ozone and ozone/UV radiation: a comparative study. Water Res 21: 895-900.

19. APHA (1985) Standard methods for the examination of water and waste water, 16th edition, American Public Health Association. Washington DC.

20. Dainfullah AAM, El Reefy SA,Gad HMH (1997) Ads Sci&Technol 15: 845.

21. Hao OJ, Phull KK, Davis AP, Chen JH, Maloncy SW (1992) Evaluation of wet air oxidation of TNT red water, Proce 24th Mid-Atlanitic Ind. Waste Conf. Morgantown WV. TechnomicLancaster PA: 110-119.

22. Jerome O, Niragu,Milagross Simmons (1994) Environmental oxidants, John Wiley & Sons Inc, USA, 534.

23. Yung-Shuen Shen, Young Ku,Kuen-Chyrlee (1996)Decomposition of chlorophenols in aqueous solution by UV/H_2O_2 process.Toxicol Environ Chem 54: 51-67.

24. Snell FD, Ettre LS (1987) Encyclopedia of industrial chemical analysis. John Wiley & Sons Inc, New York, 24: 427.