

Complete Reduction of Hazardous Cr(VI) in Chromium Ore Processing Residue Dump Site

VANITHA MURUGAIYAN, T. SEHAR, S. SELVARAJ^{*} and P. KAMATCHI SELVARAJ

PG & Research Department of Chemistry, Government Arts College for Men (Autonomous), Nandanam, Chennai-600 035, India

*Corresponding author: E-mail: pethkams64@gmail.com

Received:	23	September 2017	:
necerren.	20	September 2017	•

Accepted: 9 November 2017; Published online: 31 January 2018;

AJC-18755

This paper discusses the remediation of hexavalent chromium in the contaminated groundwater at laboratory scale. For simulated chromium water, different concentrations of sodium dithionite have been used to optimize the pH, dosage and time. Trials have been extended to chromium contaminated groundwater. The results are compared. An optimum condition for removal of hexavalent chromium is proposed. The treated groundwater is examined for various discharge standards of regulatory level. Reduction in concentration of hexavalent chromium, total chromium, chloride, sulphate, BOD, COD load and metals have been taken as the benchmark for efficacy of the process adopted. Direct application of sodium dithionite in this treatment indicates that the concentration of Cr(VI) can be successfully reduced to zero level concentration within 30 min, at pH 2.5 and its reduced form Cr(III) can be precipitated at pH 9. It is suggested to adopt, pump and treat method for restoration of groundwater.

Keywords: Contaminated groundwater, Hexavalent chromium, Total chromium, Sodium dithionite, Chromium ore.

INTRODUCTION

Disposal of any hazardous waste on open land may threaten species, population or endangered ecological communities, or their habitats, known on the site or likely to occur in the locality of the site [1]. Typically for aquifers to get contaminated, overlying soils tend to be contaminated first. Therefore, soil and groundwater contamination often occur simultaneously and are therefore assessed at the same time. As per the notification given by the Ministry of Environment, Forest and Climate Change, Government of India, if the concentration of chromium and/or trivalent chromium compounds present in any waste is equal or more than 5 mg/L it is classified as hazardous waste [2]. Total chromium level in drinking water has been given as 0.05 mg/L by National Drinking Water Regulation [3].

As per the USEPA regulatory norms, maximum contaminant level for total Cr is 0.1 mg/L [4]. Chromium ore processing residue (COPR) dump site at M/s Tamilnadu Chromates and Chemicals Ltd (TCCL), Ranipet, Vellore Dt., Tamilnadu, India contains about 2.2 lakh tonnes of untreated chromium ore processing residue. The ground water in and around the site is highly contaminated with hexavalent chromium. The run-off and leachate from the TCCL dump site affects the nearby residential neighbourhood. In our previous study, solidification and stabilization of chromium ore processing residue waste at TCCL site has been proposed as phase-I clean up activity [5]. Present work, a phase-II clean up activity deals solely with the investigation on remediation of contaminated Cr(VI) groundwater.

Though number of methodologies like adsorption, RO membrane and phyto-remediation have been developed for remediation of ground water contamination, chemical precipitation processes offer significant potential to remove soluble ionic species from solution particularly containing heavy metals [6-9]. Pump-and-treat method is commonly used for aquifer remediation [10]. Sodium dithionite $(Na_2S_2O_4)$ has the potential to reduce through dissolution and reduction of indigenous amorphous or crystalline Fe(III) which occurs naturally in minerals as oxides within the aquifer sediments [11]. Chou et al. [12] have used sodium dithionite for the recovery of copper. Ludwig et al. [13] carried out a field investi-gation on in situ Cr(VI) reduction using combination of sodium dithionite and ferrous sulphate. The solid or powder form of dithionite is classified as spontaneously combustible material [14]. The liquid form of sodium dithionite, a powerful reducing agent, is classified as non-combustible according to Material Safety Data Sheet.

The main objective of the present work is to investigate and demonstrate the performance of $Na_2S_2O_4$ for complete removal of Cr(VI) from the contaminated groundwater collected at chromium ore processing residue dump site. The second objective is to find out a statistical methodology for the removal of reduced Cr(VI) as Cr(III) using Ca(OH)₂, NaOH and MgO. **Study area:** About 2.2 lakh tonnes of waste containing chromium has been dumped in the northern side of the TCCL factory. The nearby area of the dump site is used for residential, commercial and industrial purposes. The leaching of Cr(VI) is polluting the groundwater in and around the factory and adjoining residential colonies, as the groundwater flow direction is from chromium ore processing residue dump site towards the Puliankannu, Karai Lake and Palar River in southern direction. Several hundred single and multi-family residential buildings, commercial buildings and industrial facilities are located within two km radius of the site. The presence of Cr(VI) in the ground water at various places in and around the site was analyzed and the concentration of Cr(VI) is found to be in the range of 0.01 mg/L to 1983 mg/L.

The chromium contaminated sites, which require remediation existing in various parts of the World are discussed briefly in the earlier works [15-19].

EXPERIMENTAL

All the chemicals used in this study were of analytical grade and procured from E-Merck India Ltd. The important chemicals used were sodium dithionite (Na₂S₂O₄), sodium hydroxide, calcium hydroxide, magnesium oxide and sulphuric acid. Distilled water of highest purity was used for optimization. The lower pH was adjusted with H₂SO₄ and higher pH was adjusted with NaOH. The pH was determined using pH meter 240 (Elico L1614). The concentration of Cr(VI) was determined by recording the absorbance at 540 nm using UVvisible spectrophotometer (UV-3200, Lab India). Jar apparatus was used for stirring at 100 rpm and reduction of Cr(VI) was performed using Na₂S₂O₄. After reduction, the reduced samples were stirred and the supernatant was analyzed to measure Cr(VI) and total chromium. The total chromium and arsenic concentrations were determined on an atomic absorption spectrometer (Shimadzu 6800). APHA method was adopted to analyse other parameters [20].

Chromium contaminated groundwater: The samples of chromium contaminated groundwater were collected in the month of May 2016, from a monitoring well of 7 cm diameter and 25 m depth in the chromium ore processing residue dump site. The seasonal variation influences the concentration of chromium in the groundwater. The samples were collected in polypropylene containers. The Cr(VI) concentration varied with depth and was in the range of 1,111 to 1,983 mg/L. The filtered samples were used for analysis. The parameters such as turbidity, total dissolved solid and electrical conductivity were analyzed for the sample containing 1360 mg/L of Cr(VI) and were found to be 175 NTU, 4920 mg/L and 7580 µs/cm, respectively. The presence of heavy metals and other parameters were also analyzed.

Preparation of simulated chromium water: An average level of Cr(VI) and total chromium present in the contaminated groundwater was estimated as 1591 and 1672 mg/L, respectively. Hence, simulated chromium water (SCW) was prepared by dissolving 5.25 g of potassium dichromate in 1000 mL distilled water such that it was in congruence with that of the contaminated groundwater. The reaction time, optimum dosage at various pH for reduction of Cr(VI) to Cr(III) and precipi-

tation were recorded. From the data observed, the influence of various parameters in the contaminated groundwater was worked out.

RESULTS AND DISCUSSION

Effect of pH, dosage and contact time for the simulated chromium water: The pH of the aqueous solution is one of the most important parameters in Cr(VI) removal [21]. To 100 mL of simulated chromium water, 0.02 g, 0.03 g, 0.04 g and 0.05 g of $Na_2S_2O_4$ were added. The pH of the solutions was found to be 5.8, 6.5, 7.1 and 7.6, respectively without adjusting the pH level externally. This is in agreement with the earlier report [22]. The samples were stirred continuously and analyzed for Cr(VI) after 15, 30, 45 and 60 min. Maximum amount of Cr(VI) was reduced to Cr(III) within first 15 to 30 min. No significant change of reduction was observed after 30 min. Maximum reduction was observed for 0.04 g dosage of $Na_2S_2O_4$. All these observations are presented in Fig. 1.



Fig. 1. Reduction of Cr(VI) in simulated chromium water using Na₂S₂O₄ without pH adjustment

Effect of pH and dosage on the reduction of Cr(VI): In precipitation method, the removal of Cr(VI) is carried out by reducing Cr(VI) to Cr(III) at lower pH range and precipitation of Cr(III) at higher pH value [23]. To 1000 mL of simulated chromium water 0.40 g of Na₂S₂O₄ is added with continuous stirring and the pH of the solution is brought to 2, 2.5 and 3 using pure 1 N H₂SO₄. The concentration of Cr(VI) is measured after 30 min. For effective precipitation, required amount of 1 N NaOH is added with stirring and the mixture is filtered after 30 min. The pH of the filtrate is found to be around 7.5. The amount of Cr(VI) and total chromium are also estimated for the filtrate. Similar experiments were carried out for 0.45 g, 0.50 g and 0.55 g of Na₂S₂O₄ and the level of Cr(VI) after reduction and precipitation, at various pH was depicted in Fig. 2a and Fig. 2b, respectively.

The filtrates obtained do not contain Cr(VI). Complete removal of Cr(VI) has not been reported earlier in any precipitation techniques adopted so far without tertiary treatment like RO plant [24-26]. The pH of the filtrate (discharge water) is also within the discharge limit. The report revealed that pH 2.5 is the optimum pH for reduction of Cr(VI). This is in agreement with the previous report [27,28].



Study on contaminated groundwater

Optimization of reduction pH and dosage of reducing agent: An attempt was made to ascertain the requirement of $Na_2S_2O_4$ dosage for a contaminated groundwater sample containing 1800 mg/L of Cr(VI) and 2166 mg/L of total chromium. The amount of Cr(VI) and total Cr value present in the treated water were estimated. The results show that the 100 % reduction and total chromium level within discharge limit (< 2 mg/L) starts from the dosage of 5.0 g/L at reduction pH 2, 4.5 g/L at reduction pH 2.5, 5.5 g/L at reduction pH 3 and 5.5 g/L at reduction pH 4.

As an example, the effect of reduction at pH-2.5 and precipitation at pH 8, 9 and 10 are presented in Table-1.

It is concluded that pH 2.5 is optimum for complete reduction of Cr(VI) and pH 9 is optimum for Cr(III) precipitation and the amount of total chromium is found to be less than the disposal standard (< 2 mg/L). Further the amount of $Na_2S_2O_4$ consumed at this condition for 100 % reduction of Cr(VI) is the lowest value.

Another study was carried out with Cr(VI) concentration of 1617 mg/L with $Na_2S_2O_4$ dosage of 4.0 to 5.5 g/L. The results are given in Table-2.

Fixing the suitability of precipitation agent: Attempts are made to find out the best suitable precipitation agent among NaOH, MgO and Ca(OH)₂. The efficacy of NaOH on precipitation of reduced Cr(VI) is represented in Fig. 3a.

Earlier report suggested that precipitation of treated Cr(VI) using Ca(OH)₂ and MgO reduces the precipitation pH to neutral pH value [28]. An attempt is made to explore the role of Ca(OH)₂ and MgO along with Na₂S₂O₄ as reducing agent. The results obtained for Ca(OH)₂ and MgO are presented in Figs. 3b and 3c, respectively.

For the addition of 0.2 g of Ca(OH)₂, at the pH of 2.5 with 4.5 g Na₂S₂O₄/L, the percentage of Cr(VI) reduction is 99.99 %. The total chromium value obtained (0.2342 mg/L) for the above condition is too much lower than the recommended

EFFECT OF pH AND DOSAGE OF Na ₂ S ₂ O ₄ ON THE REDUCTION OF Cr(VI) IN CONTAMINATED GROUNDWATER CONTAINING 1800 mg/L OF Cr(VI) AND 2166 mg/L OF TOTAL CHROMIUM									
Weight of	Reduction at pH 2.5 and precipitation at pH 8			Reduction at pH 2.5 and precipitation at pH 9			Reduction at pH 2.5 and precipitation at pH 10		
(g/L)	Cr(VI) (mg/L)	Total chromium (mg/L)	Reduction (%)	Cr(VI) (mg/L)	Total chromium (mg/L)	Reduction (%)	Cr(VI) (mg/L)	Total chromium (mg/L)	Reduction (%)
2.0	694.00	929.75	61.44	735.6	873.35	59.13	767.60	746.75	57.36
2.5	443.20	563.75	75.38	296.34	472.80	73.77	264.46	513.20	71.49
3.0	250.00	315.82	86.11	172.37	285.80	84.12	297.20	406.73	83.48
3.5	43.68	96.60	94.63	10.44	50.17	99.42	136.07	143.00	92.05
4.0	0.2076	24.85	99.99	0.00	13.22	100	0.0376	12.30	99.99
4.5	0.0146	0.8311	99.90	0.00	0.6026	100	0.00	0.6026	100
5.0	0.00	0.9683	100	0.00	0.2946	100	0.00	0.1616	100
5.5	0.00	0.6967	100	0.00	0.3041	100	0.00	0.2826	100
6.0	0.00	0.5864	100	0.00	0.5246	100	0.00	0.4386	100
Observation: 100 % reduction and total chromium level within discharge limit (< 2 mg/L) starts from the dosage of 4.5 g/L.									

TADLE 1

TABLE-2

EFFECT OF PH AND DOSAGE OF Na ₂ S ₂ O ₄ ON THE REDUCTION OF CI(VI) IN CONTAMINATED
GROUNDWATER CONTAINING 1617 mg/L OF Cr(VI) AND 1771 mg/L OF TOTAL CHROMIUM

Weight of	Reduction at pH 2 and precipitation at pH 9			Reduction at pH 2.5 and precipitation at pH 9			Reduction at pH 3 and precipitation at pH 9		
(g/L)	Cr(VI)	Total chromium	Reduction	Cr(VI)	Total chromium	Reduction	Cr(VI)	Total chromium	Reduction
(5/2)	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)
4.0	0.2920	0.6564	99.98	0.1266	0.1156	99.99	0.197	0.3796	99.99
4.5	0.1840	0.4735	99.98	0.00	0.2772	100	0.00	0.8661	100
5.0	0.00	0.0782	100	0.0061	0.1797	99.99	0.00	0.8096	100
5.5	0.00	0.4412	100	0.00	0.0016	100	0.00	0.0433	100



Fig. 3a. Reduction of Cr(VI) in contaminated groundwater-precipitating agent NaOH



Fig. 3b. Reduction of Cr(VI) in contaminated groundwater-precipitating agent Ca(OH)₂



Fig. 3c. Reduction of Cr(VI) in contaminated groundwater-precipitating agent MgO

total chromium value of 1.0 mg/L in the discharge water [29]. The pH of the filtrate (discharge water) observed is 7.2 only. It can be used safely without further treatment. The amount of

NaOH required for 4.5 g Na₂S₂O₄/L at pH 2.5 is 0.528 g. Further the amount of total chromium and pH in the filtrate are 0.1186 and 8.5 mg/L, respectively. Though the total chromium value obtained for NaOH is less than the value obtained for Ca(OH)₂, the pH of the filtrate obtained for NaOH is higher but within discharge level.

Data obtained for MgO shows that 0.2 to 0.3 g of MgO per litre is required for the reduction of Cr(VI) completely. Total chromium value in the filtrate obtained is higher than the value obtained for NaOH and Ca(OH)₂ treatment. pH of the filtrate is also higher than that observed for Ca(OH)₂ treatment. The cost of MgO per Kg is 5 times greater than the cost of Ca(OH)₂.

As an overview, comparison on the efficacy of NaOH, $Ca(OH)_2$ and MgO is presented in Table-3. The results in Table-3 revealed that $Ca(OH)_2$ appears to be a better co-reactant for the removal of hazardous Cr(VI). But at the same time the weight of the dried sludge obtained for $Ca(OH)_2$ is considerably higher than that obtained for NaOH and MgO. Though the weight of dried sludge and pH of the filtrate obtained on using MgO as co-reactant are lower than that observed for NaOH, the cost of MgO and the total chromium recorded in the filtrate are high. Further the ease of solubility of NaOH is very high compared to Ca(OH)_2 and MgO. On considering all these factors, we suggested that NaOH is a better co-reactant for the removal of Cr(VI).

Bench scale treatment of contaminated groundwater: The contaminated groundwater containing 1617 mg/L of Cr(VI) is analyzed for the various parameters before and after treatment. 5 L of the contaminated groundwater is subjected to the treatment at pH 2.5. Addition of NaOH effected the precipitation of reduced Cr(III) at pH-9. The results revealed that the parameters such as arsenic, mercury, selenium, cyanide, sulphide and total residual chlorine were under detectable limit and other parameters observed are given in Table-4.

Conclusion

Previous reports on the removal of Cr(VI) by precipitation method dealt with diluted contaminated water. In the present work we have used the contaminated ground water directly without dilution. The complete removal of hazardous Cr(VI) within 30 min is reported in treatment process. Precipitation of reduced chromium using NaOH, Ca(OH)₂ and MgO poses much ambiguity about the best suitability. Cost of MgO compared to other precursors, excess amount of total chromium in the filtrate and solubility of MgO in water grant third position as precipitating agent, even though the amount of sludge produced is comparatively low. Cost of Ca(OH)₂ and PH of the filtrate seems to raise the suitability of Ca(OH)₂. But the amount of sludge produced and solubility of Ca(OH)₂ placed it in the second position as precipitating agent. Though more amountof NaOH is required for precipitation, the total chromium after

TABLE-3								
EFFECT OF PRECIPITATING AGENTS ON THE REMOVAL OF Cr(VI)								
Reagent	Dosage of	pH for	Amount of preci-	Cr(VI)	Total chromium	Reduction	pH of the	Weight of the
	$Na_{2}S_{2}O_{4}(g/L)$	reduction	pitation reagent (g)	(mg/L)	(mg/L)	(%)	filtrate	dried sludge (g)
NaOH	4.5	2.5	0.528	0.0180	0.1186	99.99	8.5	0.9617
$Ca(OH)_2$	4.5	2.5	0.200	0.0164	0.2342	99.99	7.2	1.1506
MgO	4.5	2.5	0.200	0.0124	1.4523	99.99	7.5	0.8951

Parameters	CGW	Treated CGW	Disposal standard				
Cr(VI) (mg/L)	1617	0.00	0.05				
Total chromium (mg/L)	1771	0.2100	2.00				
Chloride (mg/L)	528.8	120	1000				
Sulphate (mg/L)	2344.5	281.5	1000				
BOD (mg/L)	42	11.2	30				
COD (mg/L)	113.2	30.2	250				
Cadmium (mg/L)	0.0510	0.0139	2.0				
Nickel (mg/L)	0.2092	0.00	3.0				
Copper (mg/L)	0.1139	0.0370	3.0				
Lead (mg/L)	0.5568	0.0445	0.1				
Zinc (mg/L)	2.4419	0.036	1.0				
Fluoride (mg/L)	0.3	BDL	2.0				
NH₄N (mg/L)	1.2	BDL	50				
TKN (mg/L)	100	BDL	100				
Dissolved phosphate (mg/L)	2.38	0.03	5.0				
Total dissolved solids (mg/L)	4085	8347	2100				
BDL = Below detectable limit: CGW = contaminated groundwater							

treatment and sludge produced is less. Solubility of NaOH placed it in the first position as precipitating agent. The results obtained highlighted that sodium dithionite can reduce the hazardous Cr(VI) to zero level within 30 min. The analysis report reveals that all the parameters are within the limit except TDS. Since the contaminated groundwater itself contains TDS as 4085 mg/L and further add up of chemicals increased the TDS level, which could be removed through reverse osmosis process.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge M/s Tamilnadu Waste Management Limited, certified by National Accreditation Board for Testing and Calibration Laboratory, SIPCOT Industrial Estate, Gummudipoondi, India for their kind permission to carry out all the analytical studies at free of cost.

REFERENCES

- M.A. Hossain, M. Alam and D.R. Yonge, *Water Res.*, **39**, 3342 (2005); https://doi.org/10.1016/j.watres.2005.05.033.
- Hazardous and Other Wastes (Management and Transboundary Movement) Rules, GOI, MoEF & CC. Notification dated: 04.04.2016 (2016).
- World Health Organization (WHO), Guidelines for Drinking Water Quality, edn 3 (2008).
- U.S. Environmental Protection Agency (USEPA), Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human health, EPA/822/B-00/004 (2000).
- T. Sehar, V. Murugaiyan and S. Selvaraj, *Indian J. Sci. Technol.*, 9, 0974 (2016);
- https://doi.org/10.17485/ijst/2016/v9i20/88164.
- K.M.S. Sumathi, S. Mahimairaja and R. Naidu, *Bioresour. Technol.*, 96, 309 (2005); <u>https://doi.org/10.1016/j.biortech.2004.04.015</u>.

- 7. A. Hafez and S. El-Mariharawy, *Desalination*, **165**, 141 (2004); https://doi.org/10.1016/j.desal.2004.06.016.
- 8. D. Marbaniang and S.S. Chaturvedi, *Int. Res. J. Environ. Sci.*, **3**, 25 (2014).
- A. Velasco, M. Ramírez, S. Hernandez, W. Schmidt and S. Revah, J. Hazard. Mater., 207-208, 97 (2012);
- https://doi.org/10.1016/j.jhazmat.2011.04.012. 10. E.A. Voudrias, *Global Nest: Int. J.*, **3**, 1 (2001).
- U.S. Protection Agency (USEPA), Treatability Study of *in situ* Technologies for Remediation of Hexavalent Chromium in Groundwater at the Puchack Well Field Superfund Site, New Jersey (2006). https://www.pnl.gov.
- Y.-H. Chou, J.-H. Yu, Y.-M. Liang, P.-J. Wang, C.-W. Li and S.-S. Chen, *Chemosphere*, 141, 183 (2015); <u>https://doi.org/10.1016/j.chemosphere.2015.07.016</u>.
- R.D. Ludwig, C. Su, T.R. Lee, R.T. Wilkin, S.D. Acree, R.R. Ross and A. Keeley, *Environ. Sci. Technol.*, 41, 5299 (2007); <u>https://doi.org/10.1021/es070025z</u>.
- S. Irwin, A Comparison of the Use of Sodium Metabisulfite and Sodium Dithionite for Removing Rust Stains from Paper, The Book and Paper Group Annual, 30, 37, (2011).
- 15. K. Freese, R. Miller, T. Cutright and J. Senko, *Curr. Environ. Eng.*, **1**, 82 (2014);
 - https://doi.org/10.2174/221271780102141117101551.
- V. Estaún, A. Cortés, K. Velianos, A. Camprubí and C. Calvet, *Span. J. Agric. Res.*, 8(S1), 109 (2010); https://doi.org/10.5424/sjar/201008S1-1229.
- D.C. Adriano, W.W. Wenzel, J. Vangronsveld and N.S. Bolan, *Geoderma*, 122, 121 (2004);
- https://doi.org/10.1016/j.geoderma.2004.01.003.
- S. Loyaux-Lawniczak, P. Lecomte and J.-J. Ehrhardt, *Environ. Sci. Technol.*, 35, 1350 (2001); https://doi.org/10.1021/es0010731.
- D.J. Lapworth, D.C.W. Nkhuwa, J. Okotto-Okotto, S. Pedley, M.E. Stuart, M.N. Tijani and J. Wright, *Hydrogeol. J.*, **25**, 1093 (2017); <u>https://doi.org/10.1007/s10040-016-1516-6</u>.
- APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, The American Water Works Association (AWWA) and the Water Environment Federation (WEF) Publication (2006).
- G. Wang, Q. Chang, M. Zhang and X. Han, *React. Funct. Polym.*, 73, 1439 (2013);

https://doi.org/10.1016/j.reactfunctpolym.2013.07.009. 22. W. Wayman and W. Lem, *Can. J. Chem.*, **48**, 782 (1970);

- 22. w. wayman and w. Leni, *Car. J. Chem.*, **46**, 762 (1970), https://doi.org/10.1139/v70-127.
- P.V.V. Prasad, C. Das and A.K. Golder, *Can. J. Chem. Eng.*, **89**, 1575 (2011); https://doi.org/10.1002/cjce.20590.
- L.-Y. Chang, Chrome Reduction and Heavy Metals Removal from Wastewater-A Pollution Prevention Approach, WM'01 Conference, February 25-March 1, Tucson, AZ, USA (2001).
- C.R. Ramakrishnaiah and B. Prathima, *Int. J. Eng. Res. Appl.*, 2, 599 (2012).
- 26. T.P. Sowmya, Int. J. Innov. Res. Dev., 5, 2278 (2013).
- 27. R.S. Karale, V. Wadkar and P.B. Nangare, *J. Environ. Res. Dev.*, **2**, 209 (2007).
- C.E. Barrera-Díaz, V. Lugo-Lugo and B. Bilyeu, J. Hazard. Mater., 223-224, 1 (2012);
- https://doi.org/10.1016/j.jhazmat.2012.04.054.
- The National Environment (Standards for Discharge of Effluent into Water or on Land) Regulations, S.I. No. 5 (1999).