Mitigation of Cyanide From Coke Plant Wastewater Using Chemical Oxidation Process

Amit Mondal (amit.mondal@tatasteel.com)
Tata Steel Ltd Jamshedpur https://orcid.org/0000-0002-2505-9776
Priyanka Saha
Tata Steel Ltd Jamshedpur
Supriya Sarkar
Tata Steel Ltd Jamshedpur
Udayabhanu G Nair
Indian Institute of Technology

Research Article

Keywords: Biological treatment, Chemical oxidation, Coking wastewater, Free cyanide, Cyanide treatment, Hypochlorite.

Posted Date: October 20th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-727204/v1

Abstract

Biological treatment with a stable activated sludge process, followed by chemical treatment is one of the potential and accepted cyanide treatment process for coke plant waste water treatment. Biologically treated coke plant wastewater contains free cyanide above permissible limit. Presently chemical treatment with NaOCl is being used to attenuate free cyanide below permissible limit in biologically treated water. This process increases the TDS and colour content in discharge water. $Ca(OCl)_2$ can be used as an alternative to NaOCl for cyanide remediation in biologically treated coke plant waste water without increasing TDS. In the present work, cyanide removal efficiency of NaOCl and $Ca(OCl)_2$ for real coke plant waste water after biological treatment has been studied. Optimisation of chemical dosage, treatment time and pH has been done for $Ca(OCl)_2$ and NaOCl treatment. It was found that up to 90% of free cyanide removal could be achieved through $Ca(OCl)_2$ treatment without increasing the TDS value. In addition, more than 50% colour of the waste water has been removed. pH elevation step required in NaOCl treatment can be eliminated in $Ca(OCl)_2$ treatment, thereby reducing caustic consumption. In conclusion, use of $Ca(OCl)_2$ is economically more viable than that of NaOCl in cyanide treatment.

Introduction

Integrated Steel Plant is a water intensive industry, where almost every process consumes a huge amount of water. Waste water from steel industry operation transport various organic, inorganic pollutants and toxic substances that have adverse effects on the environment (Park et al. 2008). Due to the toxic effects, discharge of this polluted water without detoxification cause severe damage to the environment. Coke plant is one of the major contributors for generation of waste water in an integrated steel plant. Nearly 4 m^3 of water is used to produce 1 ton of coke and the process generates a large volume of heavily polluted wastewater (Pal and kumar 2014). Coke plant waste water is generated during quenching, cleaning and recovery of valuable by-product of coke oven gas produced during carbonisation of coal in the coke oven batteries. The waste water generated during these processes contains various organic and inorganic toxic compounds like ammonia, thiocyanate, cyanides, sulphides, pyridine, phenols and other poly aromatic hydrocarbons (PAH) (Mondal et al. 2021; Dhoble et al. 2019). Cyanide is the most toxic chemical present in the coke plant discharge water among those pollutants (Ozyonar and Karagozogly 2015; Maranon et al. 2008). The wastewater from the coke plant and blast furnace blow down have been identified as the major contributors of aqueous cyanide emissions in the iron and steel industries (Saha et al. 2018; Singha et al. 2018). Thus, steel industry is coming under increasing scrutiny of environmental regulators to meet more stringent water discharge limits.

Metal-complexed cyanides are classified according to the strength of the metal cyanide bond. Cyanide in waste water are classified into three types; a. free cyanide (CN_F), which include CN- and HCN, b. weak-acid dissociable (CN_{WAD}) indicate weak cyanide complexes with metals such as copper, nickel, cadmium and zinc, c. strong-acid dissociable (CN_{SAD}) refer to strong cyanide-complexes with metals such as gold, cobalt, iron and silver. Toxicity of these cyanides are in the order of $CN_F > CN_{WAD} > CN_{SAD}$ (Johnson

2015). All cyanides are classified as hazardous to the characteristics of acute and chronic toxicity (Deveci et al. 2006). But the legislation of the Government for the cyanide discharge deals with only CN_F as it is the most toxic to living elements and sometimes is deadly in nature. The discharge limit of CN_F to the environment is up to 0.2 ppm (Mondal et al. 2019) as guided by Central Pollution Control Board.

Because of the environmental concerns and potential hazards due to the toxic effects, control and remediation of cyanide containing industrial waste water is essential. There are several physical, chemical, and biological treatment methodologies available for cyanide removal in coke plant wastewater. But, all the processes have some limitations for implementation in the plant scale. Table 1 presents some of the commonly adopted cyanide treatment technologies and their limitations. It also shows the fate of cyanide after the treatment and the reagents used in each process.

Table 1
Cyanide treatment technologies and their limitations.

Treatment method	Fate of cyanide	Reagent/ Chemical	Limitations
Ozonation. Chegini et al. 2020, Pueyo et al. 2016, Chang et al. 2008.	Oxidation to CO_3^{2-} and N_2 with O_3	O_3	Costly process. Adds ammonia to discharge water
Photocatalytic oxidation. Biswas et al. 2020, Chegini et al. 2020, Saravi et al. 2015, Dash et al. 2009.	Oxidation to CNO^-	Nano particle, UV source, TiO2	Energy intensive and costly process.
Biological oxidation/biodegradation. Das et al. 2020, Dwivedi et al. 2011, Kumar et al.2011, Dash et al. 2009, Woo et al. 2009, Kim et al. 2007.	Oxidation to $CO_3^{2-}$and NH_4^+ and then NO_3^-using microorganisms.	Na_2CO_3, H_3PO_4	Treatment of high concentrations create problem. Cannot reach the discharge standards of cyanide.
Alkaline chlorination by Hypochlorite/Perchlorate. Das et al. 2020, Khodadad et al. 2008, Dash et al. 2009, Reed et al. 2013.	Oxidation to CNO^- and then N_2 and CO_3^{2-}.	Cl_2, NaOCl, NaOH	Increase in TDS content. Requires high caustic to maintain pH
SO_2/Air (INCO) process. Dash et al. 2009, Kumar et al.2011.	Oxidation to CNO^- with SO_2 & air and soluble Cu catalyst.	SO_2, air, Cu catalyst	Partial removal of cyanide. Process adds sulphate to the treated water.
Hydrogen peroxide. Singh et al. 2018, Pueyo et al. 2016, Dash et al. 2009	Oxidation to CNO^- with H_2O_2 & Cu catalyst: Degussa process	H_2O_2	Reagent is costly, accurate measurement of chemical dose is required.
Caro's acid. Cesar et al. 2013, Pueyo et al. 2016, Dash et al. 2009,	Oxidation to CNO^- with H_2SO_5	H_2SO_5	Increase in TDS content. Difficult to handle due to decomposition to oxygen and sulfuric acid.
Iron cyanide precipitation. Arbabi et al. 2015, Dash et al. 2009,	Precipitated as $Fe(CN)_6$	$FeSO_4$	Works only with low concentration of cyanide. Maintaining pH and disposal of precipitate is difficult.

Treatment method	Fate of cyanide	Reagent/ Chemical	Limitations
AVR process. Munive et al. 2015, Yilmaz et al. 2017, Dash et al. 2009	Acidification to HCN and neutralisation.	H_2SO_4, NaOH	High acid consumption. Complex process.
Activated carbon. Adhoum et al. 2002, Dash et al. 2009	Oxidation to $CNO^-$and partially to CO_3^{2-} and $NH4^+$	Activated carbon, air/O_2, Cu catalyst	Expensive method. Used only for low concentration of CN
Catalytic oxidation. Kumar et al. 2011, Dash et al. 2009, Chiang et al. 2002. Larry et al. 1982.	Oxidation to CO_2, N_2 & $NH_4^+$with air and catalyst.	Catalyst	Restriction in treating very low concentration. Costly process.
Anodic oxidation. Pillai et al. 2016, Dash et al. 2009	Oxidation to $CNO^-$and then CO_2 and N_2	NaCl	Partial removal of cyanide.
Reverse osmosis. Pal et al. 2014, Dash et al. 2009, Gude 2012.	Uses a partially permeable membrane to separate ions.	-	Energy intensive and costly process.

To overcome these limitations, different combined treatment methodologies are being used for the remediation of cyanide in coke plant waste water. Combined treatment of biological, followed by chemical treatment is one of the potential and accepted cyanide treatment process for coke plant waste water (Pal and Kumar 2014).

Present process, uses the biological treatment through a stable activated sludge process followed by chemical treatment with sodium hypochlorite. The treatment process is schematically represented in Fig. 1.

After biological treatment, the discharge water contains high amount of CN_F which is taken care of by sodium hypochlorite (NaOCl) treatment. In this chemical treatment, oxidation transforms CN_F to cyanate (CNO^-), which has an environmental hazard 1,000 times lower than cyanide (Mosher and Figueroa 1996). But this popular treatment method has the major disadvantage of increasing TDS content in the discharge water (Ghosh et al. 2020 and Das et al. 2019) and is also expensive due to the extraneous dosing of sodium hydroxide (Tyagi et al. 2018). Moreover, biologically treated water gets more intense dark brown color than the untreated water due to the presence of degraded phenolic compounds (Mijangos et al. 2006). This acute colour could not be taken care by NaOCl treatment. Calcium hypochlorite [$Ca(OCl)_2$] can be used as an alternative chemical for reduction of cyanide in biologically treated coke plant wastewater (BTCPW), which decrease TDS and colour along with CN_F content.

$Ca(OCl)_2$ is more stable and potentially more efficient for cyanide removal as compared to the NaOCl due to having higher available chlorine (Hasab et al. 2013). Powdered $Ca(OCl)_2$ has the highest oxidation power among other chemicals used for chlorination (Parekh and Ban 2018). Moreover, removal of cyanide through $Ca(OCl)_2$ treatment is more effective considering the dosage and cost (Sinbuathong et al. 2000). However, very few studies have been reported on the application of this method to biologically treated coke plant effluent.

Present research aims to develop a continuous, effective and economical process with the use of $Ca(OCl)_2$ in cyanide treatment process of BTCPW. Comparative study of cyanide removal efficiency in BTCPW has been carried out with $Ca(OCl)_2$ and NaOCl. TDS and colour of the treated solution were also compared in both the treatments. In addition to this, optimisation of $Ca(OCl)_2$ treatment process by changing chemical dosage, treatment time and pH of the treatment solution has been carried out. Lab scale trial of $Ca(OCl)_2$ treatment in BTCPW was also performed in optimum conditions and the results are presented.

Materials & Methods

Collection of water samples

For the present study, water samples were collected from Biological Oxygen Treatment (BOT) plant of the coke plant in an integrated steel plant situated in the eastern part of India. This plant produces approximately 9 MT of coke per day and about 200 m^3 of waste water is generated daily by the process of coke making.

Characterisation of coke plant wastewater

The water samples collected from coke plant after biological treatment has the characteristics as shown in Table 2.

Table 2: General characteristics of Coke plant waste water after biological treatment

Parameter	Coke plant waste water after biological treatment
pH	7.5-8.5
TDS, ppm	2450-3350
Colour, (PtCo)	2550-2950
BOD, ppm	50-110
COD, ppm	220-550
Thiocyanate, ppm	10-30
Free cyanide, ppm	1.5-4.5
Ammonia, ppm	30-100
TKN, ppm	150-350

Experimental Set up and Procedure

The experiment for optimisation study has been carried out in 1L biologically treated water from coke plant in a glass beaker. Water samples were taken in a beaker and the pH was adjusted with sodium hydroxide and dilute hydrochloric acid. For lab scale trial, 5 L of BTCPW was taken and treated with $Ca(OCl)_2$ at its optimised condition. After maintaining the pH, 4% $Ca(OCl)_2$ was added drop wise from the burette. The samples were kept in continuous stirring condition up to the end of the treatment. Cyanide content has been tested at every 10-min time interval after filtration through Whatman 1 paper. Each experiment was performed in duplicate and the average of the results have been reported. All parameters including CN_F were tested in triplicate throughout the study and average value has been reported.

Analysis of pH

pH of the water samples was measured using the pH meter (Systronics, India, digital pH meter, model no: 335).

Analysis of TDS

TDS is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular suspended form (Hussain, 2019). During the study, TDS of the water samples has been measured by using TDS meter (Systronics, India, model no: 308).

Determination of free cyanide concentration by ion selective method

Free cyanide has been determined by filtering water sample through Whatman No. 1 filter paper and taking 10 mL of the filtered water for analysis. It was analysed potentiometrically using ion selective cyanide electrode (Thermo Scientific) according to the procedure given by manufacturer. Many tests can be done at a time through this method, due to the low analysis time (about 5 min).

Determination of ammonia concentration using ion selective electrode

Ammonia has been measured potentiometrically with ammonia ion selective electrode (Thermo Scientific) according to the procedure given by manufacturer.

Determination of thiocyanate concentration spectrophotometrically

Thiocyanate concentration in ppm was measured using spectrophotometer (Thermo Scientific, Genesys 10S UV-VIS spectrophotometer). The wavelength used was 460 nm. This was performed after a blood red colour was developed by using ferric nitrate [$Fe(NO3)_3$. $9H_20$ solution according to the standard procedure (APHA 2017).

Measurement of colour

Coke plant water gets more intense brown colour after biological treatment due to the presence of aromatic coloured compounds such as ortho- and para-benzoquinone, which form through the degradation of phenol (Mijangos et al. 2006). The color of the wastewater was measured by the color measuring instrument (Make: Lovibond) and expressed in PtCo unit.

Results And Discussion

$Ca(OCl)_2$ and NaOCl react to form hypochlorite and hydroxide ion when added to water

$$NaOCl + H_2O \rightarrow OCl^- + OH^- + Na^+ \quad (1)$$

$$Ca(ClO)_2 + 2\ H_2O \rightarrow 2\ OCl^- + 2\ OH^- + Ca^{+2} \quad (2)$$

Hypochlorite ion (OCl^-) oxidises CN^- in BTCPW to cyanogen chloride (CNCl). More the addition of $Ca(OCl)_2$, the greater the cyanide reacts to form CNCl, therefore the CN_F content in the liquid waste is reduced. Further CNCl is oxidized into CNO and finally into CO_2 and N_2 (Johnson 2015).

The oxidation reaction of cyanide and hypochlorite can be shown as follows

$$CN^- + HOCl \rightarrow CNCl + OH^- \quad (3)$$

$$CNCl + OH \rightarrow CNO^- + Cl + H_2O \quad (4)$$

$$CNO^- + OCl^- + H_2O \rightarrow N_2 + Cl^- + HCO_3 \quad (5)$$

In the present study, cyanide treatment by 4% NaOCl and 4% $Ca(OCl)_2$ solution was carried out in one litre BTCPW for 120 minutes. The residual CN_F content was checked in every 10 minutes by ion selective electrode. No significant changes were observed in CN_F concentration at the beginning of the treatment.

But, significant decrease in CN_F started after 20 minutes of NaOCl treatment and 30 minutes of $Ca(OCl)_2$ treatment Fig. 2.

Up to 80 % of CN_F was removed in 50 minutes of NaOCl treatment. Whereas $Ca(OCl)_2$ treatment took 60 minutes for the removal of 80% of CN_F. This result is in line with that reported by Muntasir et al. 2016. In addition to CN_F, significant changes were observed in TDS and colour (Fig. 3) of the treated water. It was found that TDS content was increased in NaOCl treatment and decreased in the case of $Ca(OCl)_2$ treatment. Similar trend has been observed in case of colour, where more than 55% colour was removed in $Ca(OCl)_2$ treatment against the increase in colour for NaOCl treatment. This is in accordance with the research work reported by Khandaker et al. 2020 and Massoudinejad et al. (2015).

The colour removal and TDS decrease along with the CN_F reduction shows scope of enhancement in $Ca(OCl)_2$ treatment efficiency by optimising treatment parameters like pH, treatment time and dosing rate, to get maximum efficiency compared to NaOCl treatment of BTCPW.

Optimisation study

Optimum condition of pH

For optimisation study, BTCPW containing CN_F 4.08 ppm, TDS 2970 ppm and colour 2780 PtCo was considered. Treatment of $Ca(OCl)_2$ and NaOCl were carried out in 1 L of BOT water at a constant treatment time of 60 minute. The experiment was done for three different dosing rates (20ml, 30ml and 50 ml) with 4% of NaOCl and 4% $Ca(OCl)_2$ solutions. pH of the solution was varied from 7.5 to 12. Colour and TDS of the solution at different pH were also checked before and after the treatment along with CN_F.

It has been found that cyanide removal efficiency of $Ca(OCl)_2$ increases with pH and reaches the maximum at pH 8.5. Further increase in pH has not shown any increase in removal efficiency of CN_F with 50ml, 30ml and 20 ml of $Ca(OCl)_2$ solution as shown in Fig. 4a. However, for NaOCl, maximum CN_F removal was achieved at pH 10.5 as shown in Fig. 4b.

Maintaining proper pH allows calcium hypochlorite to react perfectly with CN_F in wastewater (Cidu et al. 2011 and Muntasir et al. 2016). At optimum pH decrease in the levels of CN_F ismaximum. This is in line with the research work reported by Lee and Tiwary (2009). Optimum pH for NaOCl and $Ca(OCl)_2$ treatment in BTCPW has been found as 10.5 and 8.5 respectively through this experiment. As the pH of the BTCPW lies around 7.5 to 8.5, elevation of solution pH up to 10.5 is required in NaOCl treatment to get maximum efficiency. Whereas $Ca(OCl)_2$ treatment does not require such elevation of pH.

It was also found that during $Ca(OCl)_2$ treatment, colour and TDS content of the treated water were in lower range at pH 8.5 as shown in Fig. 5a and Fig. 5b. For NaOCl treatment colour (Fig. 5a) and TDS (Fig.

5b) content of the treated water varies throughout the pH range. This has again confirmed the optimum pH of $Ca(OCl)_2$ treatment at 8.5.

Optimum condition of dosage and time

Considering the oxidation reaction of CN^- by chlorine compound, during which CN^- has been changed to CNO^-, hypochlorite ion (OCl^-) is the active chlorine group in the oxidation process. This reaction can be slow, from 30 minutes to 2 hours. The $Ca(OCl)_2$ has 2 groups of OCl^-, hence more effective in oxidation than NaOCl. The optimum condition is achieved by the equilibrium between the volume of $Ca(OCl)_2$ solution added and the cyanide content in the waste water (Teixeira et al. 2013).

To attain the best condition for maximum treatment efficiency with removal of CN_F to its MPL and simultaneous removal of colour from BTCPW, different experiments were carried with NaOCl and $Ca(OCl)_2$ solutions. Condition was assumed to be optimum when the residual CN_F concentration of the solution reached its MPL (0.2ppm) with minimum time and minimum doses of the hypochlorite solution.

Treatment of NaOCl and $Ca(OCl)_2$ was done at their optimum pH (10.5 and 8.5 respectively) for 60-minute reaction time to find out the dosage at which both methods are at their maximum efficiency level. The results are as shown in Fig. 6.

From the above experiment, it was found that cyanide removal efficiency increases as the volume of NaOCl and $Ca(OCl)_2$ solution is increased. The removal rate was faster up to addition of 30 ml of hypochlorite solution and then gets slower. No significant changes were observed after the addition of 40 ml of the solution. This may be due to the faster reaction of CN_F with OCl^- to form CNCl and thereby reducing the CN^- at higher concentration of OCl^- in the initial stage of the treatment. The reaction gets slower as the concentration of hypochlorite ion is decreased for both (NaOCl and $Ca(OCl)_2$) treatment (Teixeira et al. 2013).

From the above treatment, it was clear that the maximum removal efficiency of CN_F lies in between 30 and 40 ml of the NaOCl or $Ca(OCl)_2$ solution. To find out the exact dose and more precise condition, experiment has been carried out at 2 minutes interval with five different volume of doses between 20 ml and 40 ml (20ml, 25ml, 30ml, 35ml and 40 ml). pH was kept constant at 10.5 and 8.5 respectively for NaOCl and $Ca(OCl)_2$.

Result shows that, addition of 35 ml of $Ca(OCl)_2$ up to 62 minutes treatment reduces the residual CN_F concentration to 0.2 ppm as shown in Fig. 7a. Which is the optimum condition for $Ca(OCl)_2$ treatment of BTCPW. Whereas, optimum condition for NaOCl reached at 58 minutes of treatment time and 35ml of NaOCl addition as in Fig. 7b.

Lab scale trial

After the completion of the optimisation study, 5 litre BTCPW water was treated with 4% $Ca(OCl)_2$ solution at its optimum dose of (35 ml or 1.4 gm per litre) and treatment time (62 min). Physico chemical parameters like pH, TDS, thiocyanate, ammonia and colour have been analysed along with CN_F (Table 3), to know the changes in water characteristics before and after the treatment.

Table 3: Characteristics of BOT wastewater before and after $Ca(OCl)_2$ treatment

Parameters	Before Treatment	Mean ± SE*	After Treatment	Mean ± SE
pH	8.26 ± 0.03		8.25 ± 0.03	
TDS, ppm	2812 ± 15.4		2345 ± 11.8	
Free cyanide, ppm	2.75 ± 0.04		0.22 ± 0.01	
Thiocyanate, ppm	12.6 ± 0.08		3.34 ± 0.02	
Ammonia, ppm	66 ± 1.3		56 ± 1.3	
Colour, (PtCo)	2610 ± 3.0		1240 ± 3.4	

*SE: In the table SE stands for standard error.

In the table, data represents mean ±SE (Standard error) of n = 5.

The results presented in Table 3 show 92% CN_F removal by calcium hypochlorite with removal of more than 50% of colour and no increase in TDS content. In addition to this, no negative impact was observed in other important parameter like thiocyanate and ammonia content.

Economic aspect of $Ca(OCl)_2$ use over NaOCl

From the economic aspect of cyanide remediation from coke plant waste water, the cost can be calculated for optimum dose of the two treatment processes. Using the price of 1 gm NaOCl (Rs 0.55) and 1 gm $Ca(OCl)_2$ (Rs 0.27), the cost of cyanide removal for one litre of waste water can be computed as Rs 0.77 and Rs 0.38 for NaOCl and $Ca(OCl)_2$ respectively. In addition to this, cost of pH elevation step is required in NaOCl treatment where as it is not required in $Ca(OCl)_2$ treatment. Therefore, use of $Ca(OCl)_2$ of cyanide removal from coke plant waste water is economically more viable than that of NaOCl.

Conclusion

The removal of cyanide from steel industrial wastewater using either NaOCl or $Ca(OCl)_2$ can be achieved. The optimum condition for cyanide remediation in BTCPW with NaOCl or $Ca(OCl)_2$ treatment has been reported. $Ca(OCl)_2$ could be more effective than NaOCl considering the cost, TDS and colour removal from the coke plant wastewater. There is no requirement of pH adjustment in case of $Ca(OCl)_2$ treatment as the optimum condition is close to the original pH of the feed water, thereby reducing expensive caustic

consumption. The experiment showed that more than 90% removal of CN_F could be achieved along with more than 50% reduction of colour by optimising calcium hypochlorite treatment. Therefore, $Ca(OCl)_2$ can be one of the promising chemical treatment method for reduction of cyanide treatment without increasing the TDS value of the Coke plant water after biological treatment.

Declarations

Ethical Approval:

Hereby, I /Amit Mondal/ consciously assure that for the manuscript / Mitigation of cyanide from coke plant wastewater using chemical oxidation process / the following is fulfilled:

1) This material is the authors' own original work, which has not been previously published elsewhere.

2) The paper is not currently being considered for publication elsewhere.

3) The paper reflects the authors' own research and analysis in a truthful and complete manner.

4) The paper properly credits the meaningful contributions of co-authors and co-researchers.

5) The results are appropriately placed in the context of prior and existing research.

6) All sources used are properly disclosed (correct citation). Literally copying of text must be indicated as such by using quotation marks and giving proper reference.

7) All authors have been personally and actively involved in substantial work leading to the paper, and will take responsibility for its content.

Consent to Publish: The authors have been declared consent to publish this article in Environmental Science and Pollution Research.

Authors Contributions: All authors have been actively involved in research work leading to the manuscript as follows:

U. G. Nair and S. Sarkar designed and directed the project. U. G. Nair and S. Sarkar helped supervise the project. A. Mondal, P. Saha and S. Sarkar were involved in planning of experimental work. A. Mondal and P. Saha contributed to sample collection and sample preparation. A. Mondal, U. G. Nair and S. Sarkar verified the analytical methods. A. Mondal and P. Saha performed the measurements, A. Mondal and P. Saha compiled all data. A. Mondal and S. Sarkar verified the compiled data. A. Mondal, P. Saha and S. Sarkar contributed analysis of data. A. Mondal, U. G. Nair and S. Sarkar contributed in literature review. A. Mondal and P. Saha wrote the manuscript. All authors contributed to the interpretation of the results. All authors discussed the results and contributed to the final manuscript. All authors provided critical feedback and helped shape the research, analysis and manuscript.

Conflicts of interest: The authors declare that they have no conflict of interest.

Availability of data and material: The data that support the findings of this study are available with the corresponding author, upon reasonable request.

Funding: There are no specific funding received by the authors for this work.

Acknowledgement

Authors are thankful to Research and Development department of Tata Steel Limited for providing necessary laboratory facilities in completing the research work.

References

1. Adams M D (1994) Removal of cyanide from solution using activated carbon. Miner Eng 7(9):1165–1177.
2. Adhoum N, Monser L. (2002) Removal of cyanide from aqueous solution using impregnated activated carbon. Chem Eng Process. 41(1): 17-21.
3. American Public Health Association (APHA) (2017) Renowned 'Standard Methods' water manual updated, 23rd edition, Washington, D.C.
4. Arbabi M, Masoudipour N, Amiri M 2015. Negative effects of cyanide on health and its removal options from industrial wastewater. International Journal of Epidemiologic Research, 2015; 2(1): 44-49.
5. Biswas P, Bhunia P, Saha P, Sarkar S, Chandel H, De S (2020) In situ photodecyanation of steel industry wastewater in a pilot scale, Environmental Science and Pollution Research, Environ Sci Pollut Res Int 27(26) : 33226-33233.
6. Chang, E. E., Hsing, H. J., Chiang, P. C., Chen, M. Y. & Shyng, J. Y. (2008) The chemical and biological characteristics of cokeoven wastewater by ozonation. Journal of Hazardous Materials 156 (1–3), 560–567.
7. Chegini ZG, Hassani AH, Torabian A, Borghei SM, (2020) Comparing the efficacy of catalytic ozonation and photocatalytical degradation of cyanide in industrial wastewater using ACF-TiO2 : catalyst characterisation, degradation kinetics, and degradation mechanism , International Journal of Environmental Analytical Chemistry, 10.1080/03067319.2020.1762874.
8. Chiang K, Amal R, Tran T. (2002) Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide. Adv Environ Res. 6(4): 471-85.
9. Cidu R, Pelo DS, Frau (2011) Impact of gold mining on the aquatic system: a case study at Furtei (Sardinia, Italy). Mine Water – Managing the Challenges. IMWA, 575-580.
10. Das S, Biswas P, Sarkar S (2020) Tertiary treatment of coke plant effluent by indigenous material from an integrated steel plant: a sustainable approach. Environmental Science and Pollution Research International 27(7):7379-7387.

11. Dash RR, Gaur A, Balomajumder C (2009) Cyanide in industrial wastewaters and its removal: A review on biotreatment Journal of Hazardous Materials 163: 1–11.
12. Deveci H, Yazici EY, Alp I, Uslu T (2006) Removal of cyanide from aqueous solutions by plain and metal-impregnated granular activated carbons. Int J Miner Process 79(3):198–208.
13. Dwivedi N, Majumder CB, Mondal P and Dwivedi Shubha (2011) Biological Treatment of Cyanide Containing Wastewater. Res.J.Chem.Sci 1(7):1-21.
14. Ghosh T K, Ghosh R, Chakraborty S, Saha P, Sarkar S, Ghosh P (2020) Journal of Water Process Engineering 37:01364. DOI: 10.1016/j.jwpe.2020.101364.
15. Dhoble YN and Ahmed S (2019) Treatment of wastewater generated from coke oven by adsorption on steelmaking slag and its effect on cementitious properties. Current Science 116(8): 1346-1355.
16. Gude VG (2012) Energy consumption and recovery in reverse osmosis. Desalination and water treatment 36(1):239-260.
17. Hasab MG, Rashchi F, Raygan S (2013) Chloride–Hypochlorite Oxidation and Leaching of Refractory Sulphide Gold Concentrate. Physicochem. Probl. Miner Process 49(1):61–70.
18. Hussain MS 2019 Total Dissolved Salts.
19. Johnson CA (2015) The fate of cyanide in leach wastes at gold mines: An environmental perspective. Applied Geochemistry 57:194-205. https://doi.org/10.1016/j.apgeochem.2014.05.023
20. Khandaker NR, Afreen I, Diba DS, Huq FB, Akter T (2020) Treatment of textile wastewater using calcium hypochlorite oxidation followed by waste iron rust aided rapid filtration for colour and COD removal for application in resources challenged Bangladesh. Groundwater for Sustainable Development 10:100342, https://doi.org/10.1016/j.gsd.2020.100342.
21. Khodadad A, Teimoury P, Abdolahi M, Samiee A (2008) Detoxification of Cyanide in a Gold Processing Plant Tailings Water Using Calcium and Sodium Hypochlorite. Mine Water Environ 27(127):52–55.
22. Kim YM, Park D, Lee DS, Park JM (2007) Instability of biological nitrogen removal in a cokes wastewater treatment facility during summer. J Hazard Mater 141(1):27–32.
23. Kim YM, Park D, Lee DS, Jung K, Park JM (2009) Sudden failure of biological nitrogen and carbon removal in the full-scale pre-denitrification process treating cokes wastewater. Biores Technol 100: 4340–4347.
24. Kumar R, Bhakta P, Chakraborty S, and Pal P (2011) Separating Cyanide from Coke Wastewater by Cross Flow Nanofiltration. Separation Science and Technology, 46: 2119–2127
25. Larry DB, Joseph F, Judkins Jr., Barron LW (1982) Process Chemistry for Water and Wastewater Treatment. Prentice-Hall INC, Englewood Cliffs, New Jersey 510.
26. Lee SM, Tiwari D (2009) Application of Ferrate (VI) in the treatment of industrial wastes containing metal complexed cyanides: A green treatment. Journal Environmental Sciences 21: 1347-1352.
27. Ma J, Dasgupta PK (2010) Recent developments in cyanide detection. Analytica Chimica Acta 673(2):117–125.

28. Maranon E, Vazquez I, Rodriguez J, Castrillon L, Fernandez Y, Lopez H (2008) Treatment of coke wastewater in a sequential batch reactor (SBR) at pilot plant scale. Bioresource Technology 99:4192-4198. DOI:10.1016/j.biortech.2007.08.081.
29. Massoudinejad M, Ghaderpoori M, Azari MR (2015) The Removal of COD and Color from Textile Industry by Chlorine Hypochlorite. International Journal of Advanced Science and Technology 76:35-42. http://dx.doi.org/10.14257/ijast.2015.76.05.
30. Mijangos F, Varona F, Villota N (2006) Changes in solution color during phenol oxidation by fenton reagent. Environ Sci Technol 40(17):5538–5543.
31. Mondal A, Sarkar S, Nair UG (2021) Comparative characterization of cyanide-containing steel
32. industrial wastewater. Water Science & Technology 83(2):322-330.
33. Mondal M, Mukherjee R, Sinha A, Sarkar S, De S (2019) Removal of cyanide from steel plant effluent using coke breeze, a waste product of steel industry. Journal of Water Process Engineering 28:135–143. DOI: 10.1016/j.jwpe.2019.01.013.
34. Mosher JB, Figueroa L (1996) Biological oxidation of cyanide: A viable treatment option for the minerals processing industry. Miner Eng 9(5):573-581.
35. Munive GT, Coronado H, Encinas RM, Vazquez VV, Parga JR, (2015) Leaching of Sludge from the AVR Process with Ammonium Thiosulfate: Alternative Technology to the Cyanidation, Journal of Multidisciplinary Engineering Science and Technology (JMEST). 2(5): 1221-1225.
36. Muntasir, Sjahrul M, Zakir M, Raya I (2016) Elimination Cyanide with Hydrogen Peroxide (H2O2) and Calcium Hypochlorite (Ca(OCl)2 on Gold Mine Waste from North Luwu, South Sulawesi. American Journal of Environmental Protection 5(4):97-102.
37. Ozyonar F, Karagozogly B (2015) Treatment of pre-treated coke wastewater by electrocoagulation and electrochemical peroxidation processes. Sep Pur Tech 150:268-277. DOI:10.1016/j.seppur.2015.07.011.
38. Pal P, Kumar R (2014) Treatment of coke wastewater: a critical review for developing sustainable management strategies. Sep Purif Rev 43(2):89–123.
39. Pal P, Pamela Bhakta P, Kumar R (2014) Cyanide Removal from Industrial Wastewater by Cross-Flow Nanofiltration: Transport Modeling and Economic Evaluation. 86(6):698-706.
40. Parekh F, Ban GH (2018) Reduction of COD from Secondary Effluent of CETP by Chlorination. International Journal of Latest Technology in Engineering, Management & Applied Science 7(2):155-157.
41. Park D, Kim YM, Lee DS, Park, JM (2008) Chemical treatment for treating cyanides-containing effluent from biological cokes wastewater treatment process. Chem Eng J 143:141–146.
42. Pillai IMS, Gupta AK (2016) Anodic oxidation of coke oven wastewater: Multiparameter optimization for simultaneous removal of cyanide, COD and phenol. Journal of Environmental Management 176: 45-53.

43. Pueyo N, Miguel N, Ovelleiro JL and Ormad MP 2016 Limitations of the removal of cyanide from coking wastewater by ozonation and by the hydrogen peroxideozone process. Water Science & Technology 74(2):482-490.
44. Reed BE, Islam AA, Bendick J (2013) Ferrate and Alkaline Chlorination Treatment of Cyanide-Heavy Metal Maritime Wastewater. Journal of Environmental Engineering 139(5): 661-666.
45. Saha P, Mondal A, Sarkar S (2018) Phytoremediation of cyanide containing steel industrial wastewater by Eichhornia crassipes. International Journal of Phytoremediation 20(4):407–416.
46. Sinbuathong N, Kongseri B, Plungklang P, Khun-anake R (2000) Cyanide Removal from Laboratory Wastewater Using Sodium Hypochlorite and Calcium Hypochlorite. Kasetsart J. (Nat. Sci.) 34:74-78.
47. Saravi HI, Dehestaniathar S, Darban AK, Zolfaghari M & Saeedzadeh S (2015) Photocatalytic decomposition of cyanide in pure water by biphasic titanium dioxide nanoparticles. Desalination and Water Treatment 57(43): 20503-20510.
48. Singh H and Mishra BK (2018) Degradation of cyanide, aniline and phenol in pre-treated
49. coke oven wastewater by peroxide assisted electrooxidation process. Water Science & Technology 78(10) : 2214-2227.
50. Singha U, Arora NK, Sachan P (2018) Simultaneous biodegradation of phenol and cyanide present in coke-oven effluent using immobilized Pseudomonas putida and Pseudomonas stutzeri. Brazilian Journal of Microbiology 49:38-44. https://doi.org/10.1016/j.bjm.2016.12.013.
51. Teixeira LAC, Arellano MTC, Sarmiento CM, Yokoyama, L., Araujo, F. V da F. (2013) Oxidation of cyanide in water by singlet oxygen generated by the reaction between hydrogen peroxide and hypochlorite, Minerals Engineering, 50–51, 57-63.
52. Tyagi M, Rana A, Kumari S, Jagadevan S (2018) Adsorptive removal of cyanide from coke oven wastewater onto zero-valent iron: Optimization through response surface methodology, isotherm and kinetic studies, Journal of Cleaner Production, 178, 398-407.
53. Woo SH, Jeon CO, Yua YS, Choi CH, Lee CS, Lee DS (2009) On-line estimation of key process variables based on kernel partial least squares in an industrial coke wastewater treatment plant. J. Hazard Mater. 161(1):538-544.
54. Yilmaz E, Ahlatci F, Yazici EY, Celep O, Deveci H (2017) Recovery of cyanide from effluents using carbon dioxide. Mugla Journal of Science and Technology, 3(2): 171-177.

Figures

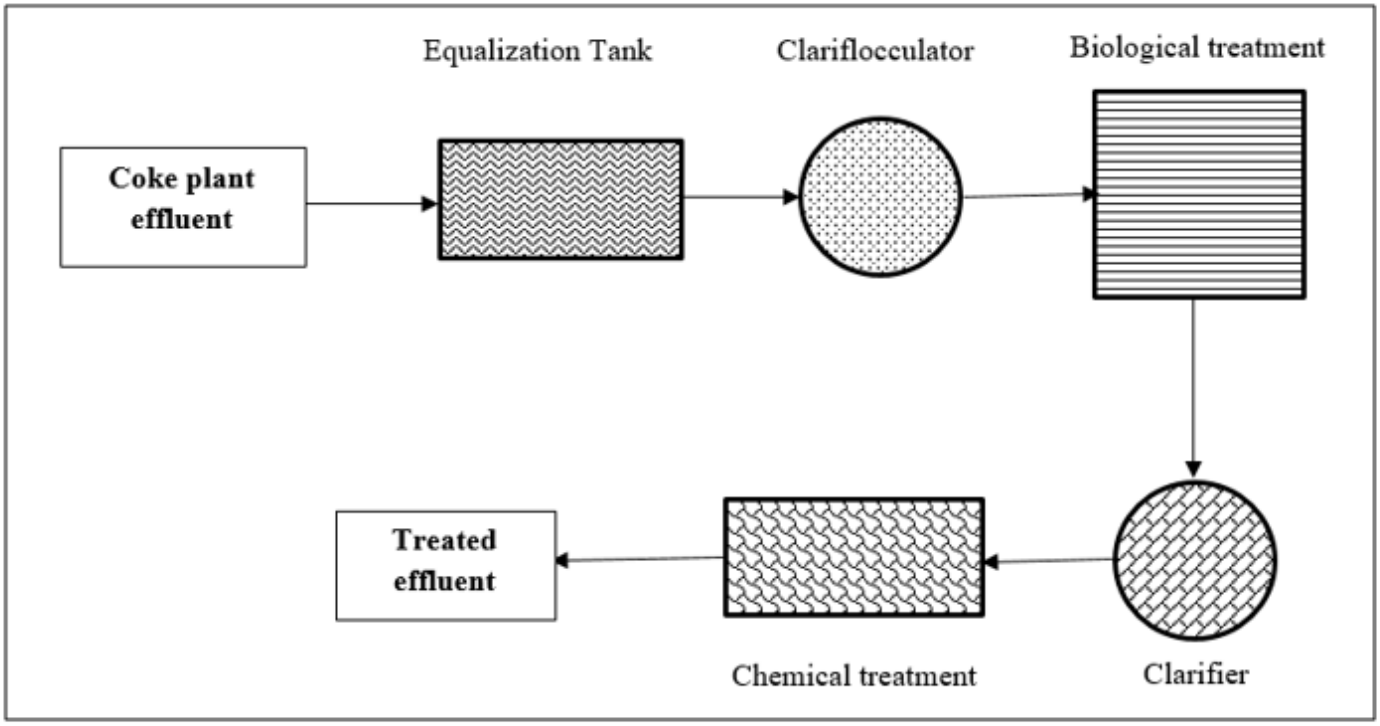

Fig. 1

Figure 1

Schematic diagram of coke plant effluent treatment through biological process

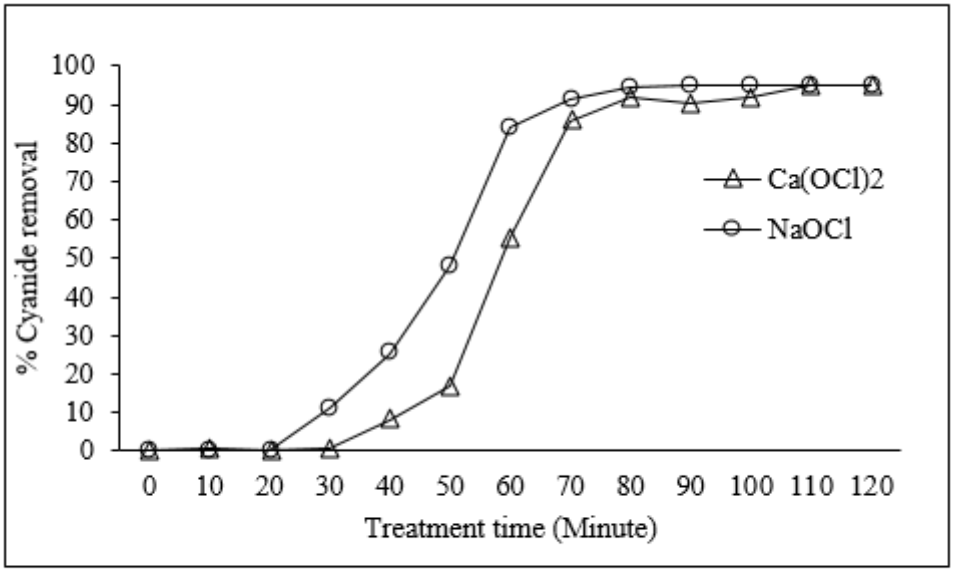

Fig. 2

Figure 2

Removal of cyanide by NaOCl and Ca(OCl)2

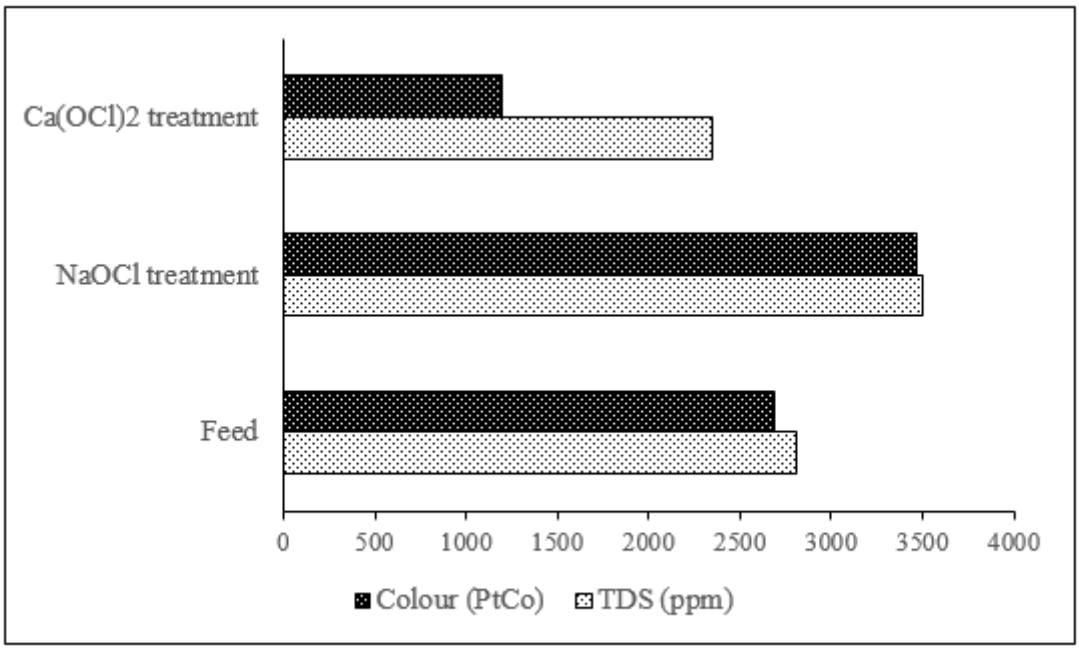

Fig. 3

Figure 3

Removal of colour and TDS by NaOCl and Ca(OCl)

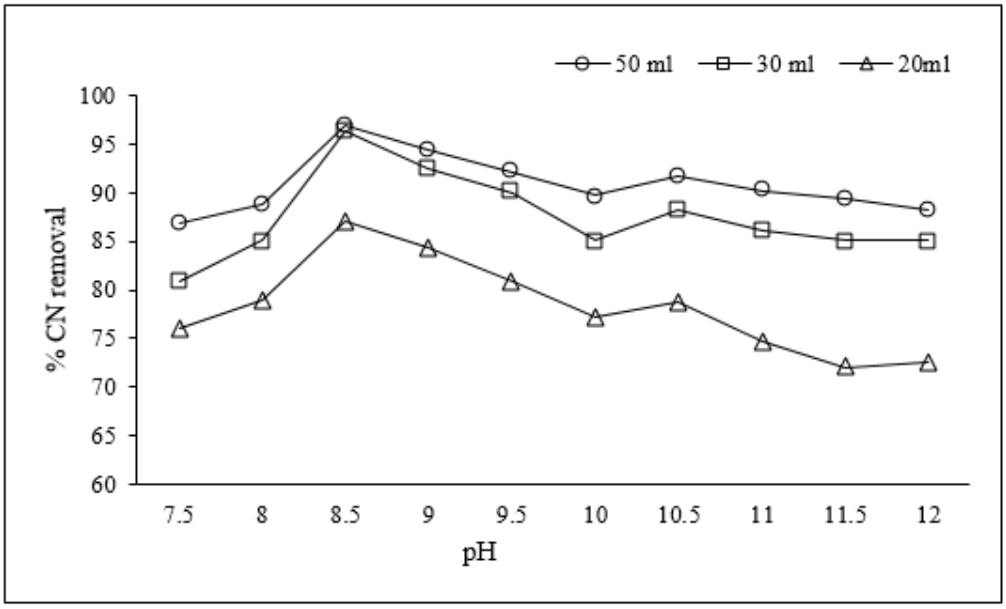

Fig. 4a

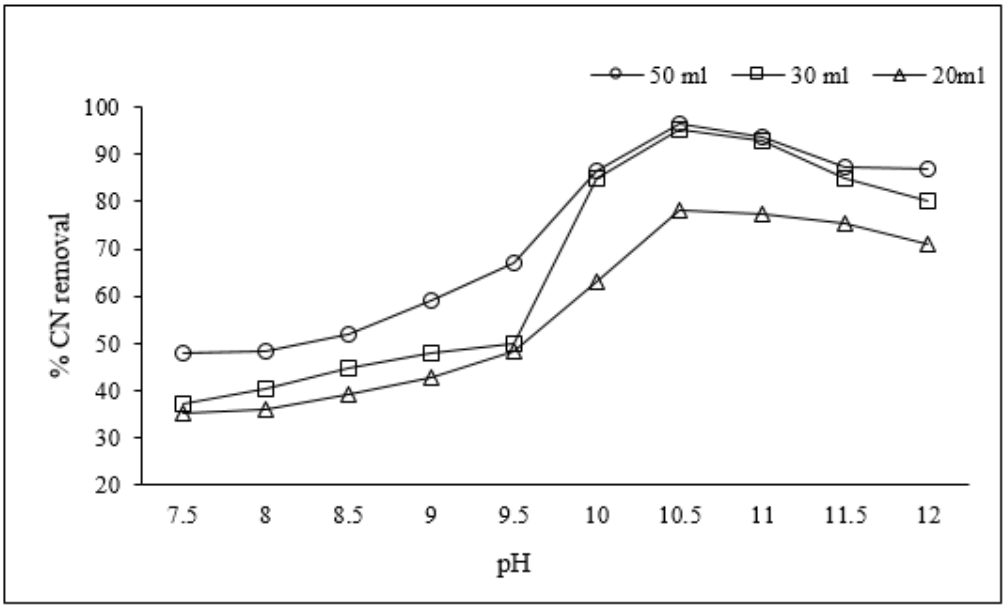

Fig. 4b

Figure 4

a Effect of pH on cyanide removal by using different concentration of Ca(OCl)2 b Effect of pH on cyanide removal by using different concentration of NaOCl

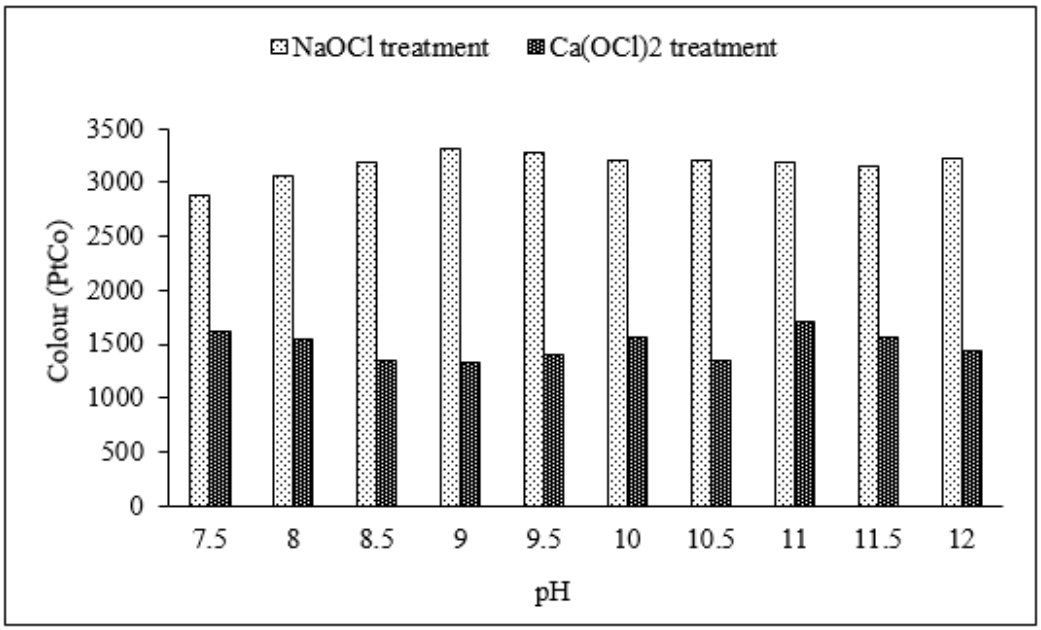

Fig. 5a

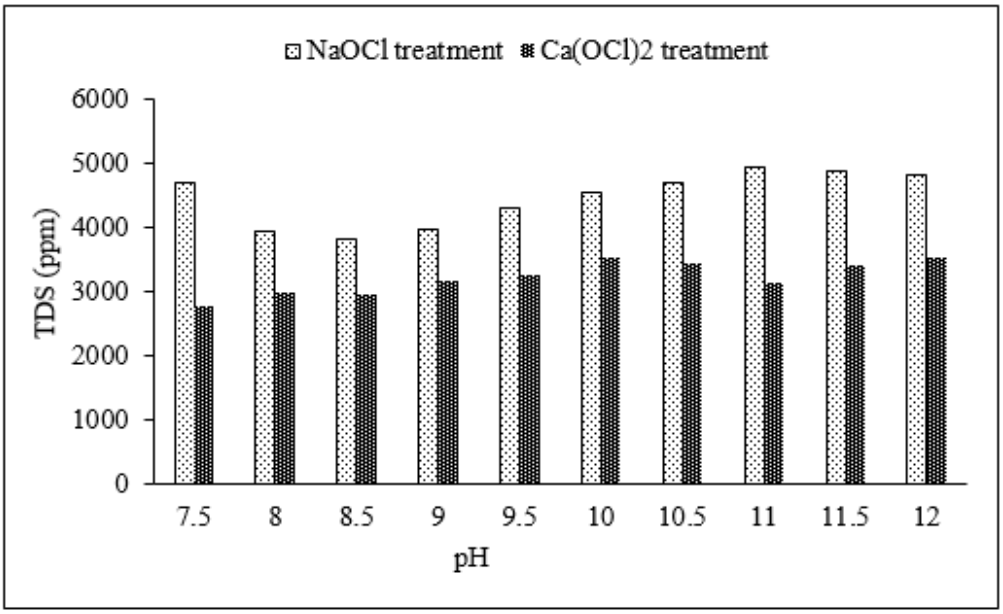

Fig. 5b

Figure 5

a Changes of colour at different pH during NaOCl and Ca(OCl)2 treatment b Changes of TDS at different pH during NaOCl and Ca(OCl)2 treatment

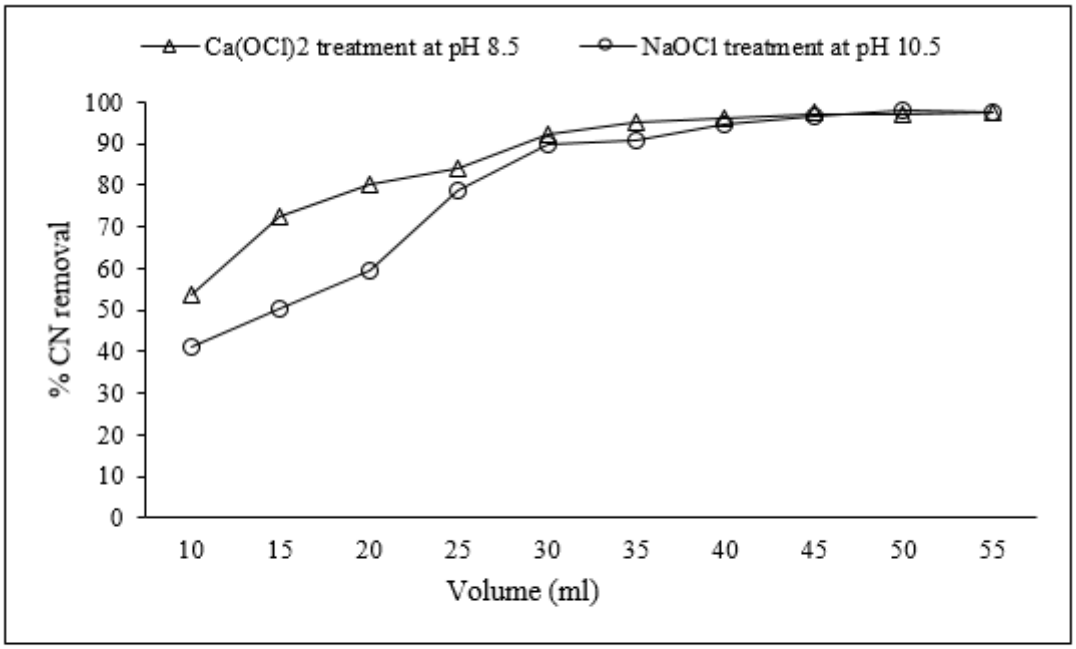

Fig. 6

Figure 6

Cyanide removal efficiency by different volume of NaOCl and Ca(OCl)2 at optimum pH

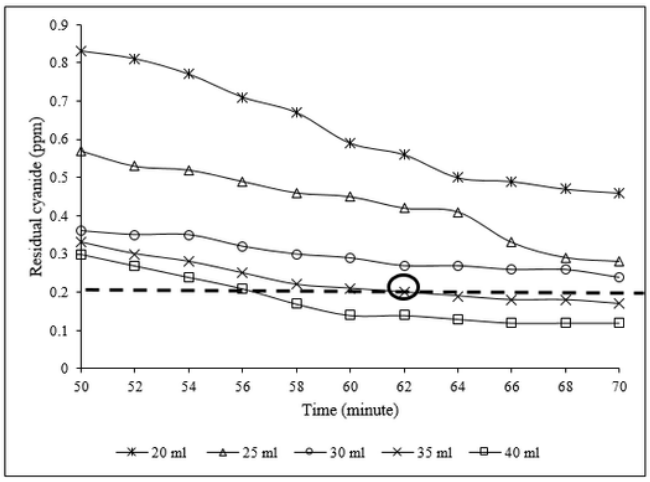

Fig. 7a

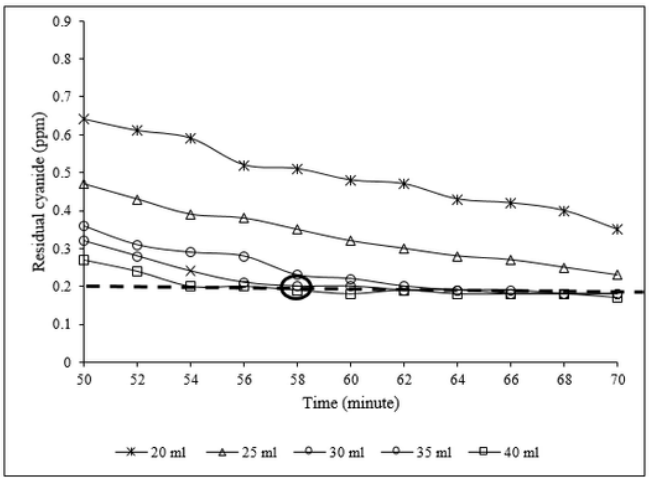

Fig. 7b

Figure 7

a Optimum condition for Ca(OCl)2 treatment b Optimum condition for NaOCl treatment